18.4.5 Chemical/Tracer Yield

Issue: Some methods require that radionuclides should be separated chemically from their sample matrix and purified before measurement. During chemical processing, some of the analyte radionuclide will be lost due to sample spillage, evaporation, incomplete chemical reactions (i.e., precipitation or extraction), etc., as discussed in Chapter 12. While these losses may correlate with a group of samples of similar chemical composition or from the same sampling area, they can be sample specific. For quantitative analysis, it is necessary to correct observed instrument responses for these losses for each analytical sample. Corrections are made using compounds that are stable (carriers) or radioactive (tracers). An inappropriate method for determining chemical yield may result in an analytical bias.

Discussion: Most alpha- and beta-emitting radionuclides require chemical separation prior to measurement, in part because of the short effective range of the radiation.

CARRIERS. Since it is impossible to determine exactly how much of the analyte is lost during processing, and because the physical mass of the radionuclide is too small to measure gravi-metrically, a compound is added to the sample at the start of the chemical processing, and is carried through the analytical process and assayed. The added compound typically is stable and exhibits the same chemical properties as the analyte and therefore "carries" the analyte radionuc-lide—for example, stable barium that carries radium isotopes, or stable yttrium that carries ^{90}Y. These added compounds are called "carriers" and are added in sufficient quantity to allow gravimetric assay upon completion of the analysis. The ratio of the carrier recovered to the amount added is the chemical recovery, or yield. Because the carrier and analyte exhibit similar chemical behavior, the chemical yield of both should be equal, i.e., if 85 percent of the stable barium is recovered, then it follows that the observed instrument response represents 85 percent of the radium present in the sample.

TRACERS. For radionuclides above atomic number 83, stable isotopes do not exist, and a different approach often is taken to determine the analyte's yield. For these radionuclides, an isotope other that those being measured is added to the sample in the same manner as described above, e.g., ^{232}U used as a tracer for isotopic uranium (^{234}U, ^{235}U, and ^{238}U), ^{236}Pu, or ^{242}Pu used as a tracer for isotopic plutonium (^{238}Pu, ^{239}Pu, and ^{240}Pu).

This approach to chemical yield determination is based on the following assumptions regarding the carrier/tracer:

• It exhibits similar chemical behavior as the analyte under the protocol's conditions.

• The energy emission of the tracer and progeny should not interfere with the resolution of the analytes of interest.
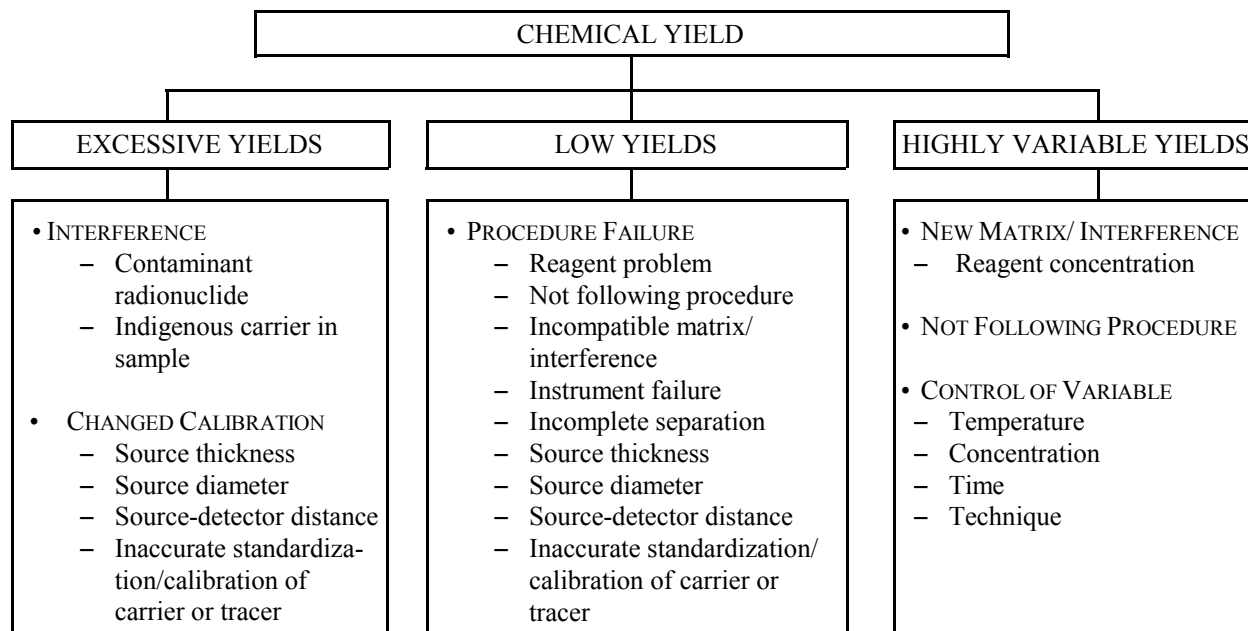
• It is chemically and physically equilibrated with the sample before losses of either occur.

• Indigenous concentrations of carrier or tracer are insignificant, or are well known and can be quantified and corrected for during subsequent data analysis.

• The chemical form of carrier or tracer precipitates are consistent with what was used during the material's preparation and standardization.

Care should be taken during the analytical procedure to ensure that these assumptions are valid. Different conditions, such as a lack of equilibrium between the tracer and sample analyte, can result in inaccurate data. If there is indigenous tracer or carrier in the sample, this quantity should be known so that the appropriate correction can be made for its contribution to the chemical yield. In some cases, this will prevent the procedure's use, as described below. As stated previously, the quantity of tracer or carrier added to the sample should overwhelm its indigenous concentration, which cannot be determined for samples with unknown tracer or carrier content. A separate analysis for trace elements or interfering radionuclides could provide information to estimate the uncertainty contributed by the sample's indigenous tracer or carrier.

It should be noted that some analytical methods exclude direct assessment of the procedure's chemical yield for each sample analysis. In such cases, chemical yield typically recovery is addressed by analyzing a group of prepared standards by the same protocol and the results are analyzed statistically to derive a chemical yield factor. The recovery factor is applied to routine samples based on the assumption that the standards used for its derivation are representative of routine samples. This approach precludes the empirical assessment of a sample specific chemical yield, and would probably require scrutiny and periodic verification.

Acceptance limits for chemical/tracer yields should be specified in the laboratory's quality manual. While it is customary to establish lower limits for chemical yield, upper limits may also be necessary since excessive yields indicate a loss of analytical control. All limits developed by the laboratory should be either statistically based or based on historical data, and should include warning and control limits. The inherent differences among sample matrices generally require the use of matrix specific criteria, i.e., finished drinking water limits may differ from limits for high solid content waters, sandy soils or heterogeneous media. Irrespective of medium, where practical, the chemical yield and its uncertainty should be determined, recorded and tracked for each radiochemical measurement.

Excursions: There are several possible reasons for the yield to be outside of the acceptance limits. These are summarized in Figure 18.5 and discussed below.

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┌─────────────────────────────────────────────────────────────────┐
│                        CHEMICAL YIELD                             │
└─────────────────────────────────────────────────────────────────┘
        │                        │                        │
┌──────────────────┐   ┌──────────────────┐   ┌──────────────────────────┐
│ EXCESSIVE YIELDS │   │   LOW YIELDS     │   │ HIGHLY VARIABLE YIELDS   │
└──────────────────┘   └──────────────────┘   └──────────────────────────┘
        │                        │                        │
```

EXCESSIVE YIELDS	LOW YIELDS	HIGHLY VARIABLE YIELDS

• INTERFERENCE
  – Contaminant radionuclide
  – Indigenous carrier in sample
 	
• CHANGED CALIBRATION
  – Source thickness
  – Source diameter
  – Source-detector distance
  – Inaccurate standardization/calibration of carrier or tracer
	• PROCEDURE FAILURE
	  – Reagent problem
	  – Not following procedure
	  – Incompatible matrix/interference
	  – Instrument failure
	  – Incomplete separation
	  – Source thickness
	  – Source diameter
	  – Source-detector distance
	  – Inaccurate standardization/calibration of carrier or tracer
		• NEW MATRIX/ INTERFERENCE
		  – Reagent concentration
		
		• NOT FOLLOWING PROCEDURE
		
		• CONTROL OF VARIABLE
		  – Temperature
		  – Concentration
		  – Time
		  – Technique

FIGURE 18.5 — Failed performance indicator: chemical yield

EXCESSIVE YIELDS: A chemical yield significantly greater than 100 percent indicates a problem. Typical causes of excessive chemical yields are provided below:

• Interference. The sample may contain an interfering radionuclide that cannot be distinguished from the tracer and therefore biases the tracer response; the sample may contain an indigenous concentration of the tracer or carrier used; or large amounts of another stable element are present.

• Counting. Changes in instrument calibration factor or other factors that affect counting, e.g., source thickness, diameter, source-detector distance or change in chemical form of final sample precipitate.

• Instrument failure.

LOW YIELDS: A very low yield usually indicates a procedural failure caused by incomplete or unsuccessful chemical separation, matrix interference, missing reagents, or the exclusion of a key element in the sample processing. A significantly lower yield will increase the overall measurement uncertainty and degrade the procedure's effective detection capability unless the counting time is appropriately extended, which may be impractical or even ineffective in many cases. Furthermore, measurement of the recovered carrier or tracer becomes increasingly more adversely affected by background, stable element, water absorption, and other corrections as the yield decreases. Fixed lower limits for yields often are established and

should be specific to analytical procedures and sample matrices. Setting an upper limit is recommended for the acceptable relative uncertainty in a yield measurement.

HIGHLY VARIABLE YIELDS: High variability in procedural temperature, concentration, time, reagent concentration, or laboratory technique can have dramatic effects on yield. Highly variable yields indicate a lack of procedural control and should be investigated and corrected. A simple step such as heating samples on a hotplate can lead to variability in yield because the hotplate surface is thermally uneven. Samples can be dried and reconstituted several times during the course of the preparation protocol, and samples may require different amounts of heat or water, which introduces additional variability. When highly variable chemical yields are observed, a careful examination of the analytical procedure's application is recommended to determine critical variables and the controls needed to re-establish adequate management over yields.

18.5 Instrumentation Performance Indicators

Radiometric and non-radiometric instruments are used currently to quantify radionuclides in a variety of environmental matrices, and quality control measures are necessary to ensure proper instrument performance. This section presents radiometric instrument performance measures that indicate a measurement system is in control. For detailed information on instrument concepts and specific techniques, see Chapter 15 as well as ASTM standard practices (e.g., D3648, for the Measurement of Radioactivity). The specific quality control procedures to be followed depend on the measurement equipment. Sufficient checks are needed to demonstrate that the measurement equipment is properly calibrated, the appropriate background has been recorded, and that all system components are functioning properly. QC measures for instrumentation should include at a minimum: (1) instrument background measurements, (2) instrument calibration with reference standards, and (3) periodic instrument performance checks subsequent to the calibration. Acceptable control limits should be specified in appropriate laboratory documents.

18.5.1 Instrument Background Measurements

Issue: In general, radionuclide detection covers more than 17 orders of magnitude of sample activity, from irradiated material that produces high radiation fields to environmental samples. All radiation detection instruments have a background response even in the absence of a sample or radionuclide source. To determine the instrument's response to the radioactivity contributed by the sample alone (net), the instrument background response is subtracted from the sample-plus-background response (gross). Background corrections become more critical when the instrument net response is small relative to the background. Careful control of contamination and routine monitoring of instrument background are therefore integral parts of a control program. Inappropriate background correction results in analytical error and will increase the uncertainty of data interpretation.

Discussion: Every radionuclide detector produces a signal response in the absence of a sample or radionuclide source. These signals are produced by electronic dark current, cosmic radiation, impurities in the instrument construction materials, crosstalk between the detector's alpha and beta channels, sources in the general vicinity of the detector, and residual contamination from previous counting episodes. The majority of these contributors (i.e., dark current, cosmic radiation, construction material impurities) to instrument background produce a fairly constant count rate, given sufficient measurement time. For other sources, instrument backgrounds vary as a function of time (i.e., from decay or ingrowth of residual contamination or as radon levels fluctuate throughout the day and season). For low-level measurements, it is imperative that the background be maintained as low as feasible. Active or passive detector shielding, removing or adequately shielding radioactive sources in the vicinity of the detector, and good laboratory practices to prevent residual contamination are necessary to maintain low instrument background.

The instrument's background should be determined in the absence of a radionuclide source. The instrument background should be well characterized. The instrument background is an important factor in determining the ability to achieve a specific minimum detectable concentration (MDC). Control limits for the background should be specified in appropriate laboratory documents. The background population considered in the statistical calculations should cover a sufficient period of time to detect gradual shifts in the measurement system's background contamination or detector instability. Additionally, backgrounds should be determined in such a way that they mimic actual sample measurement conditions as closely as possible, i.e., using appropriate sample containers, geometries, and counting times.

Background measurements should be made on a regular basis and monitored using control charts. For instruments with well established background performance records and a low probability of detector contamination, this frequency may be modified by the laboratory. For mass spectrometry and kinetic phosphorimetry analysis, background measurements should be performed on a real time basis. See ASTM E181, ANSI N42.12, and NELAC (2002) *Quality Systems Appendix D* for more information on the suggested frequency of background measurement.

Excursions: Variations in instrument backgrounds may indicate instrument malfunction. Variations may take the form of rapid increase or decrease in background, slow increase or decrease in backgrounds, and highly variable or erratic backgrounds. These variations can result in the measurement system's reduced precision and decreased detection capability. Rapid or significant increases in background measurements may be due to instrument or blank contamination, insufficient shielding with relocation of nearby radionuclide sources, or large scale equipment malfunction (e.g., a broken window on a gas proportional system).

Instrument background data should be evaluated for trends, which is facilitated by regular inspection of control charts. A slowly changing background could alert laboratory personnel to a potentially serious instrument failure. A sufficient number of data points (Chapter 15) taken over

time should be included in any trend analysis. Slowly changing instrument backgrounds could be caused by low counting-gas flow rates, small incremental instrument contamination, or electronic drift or noise.

When the instrument background is more variable than expected, the reliability of measurements becomes questionable, resulting in loss of confidence and increased uncertainty. This indicates a loss of control over the measurement environment, or limitations of the data handling software. The root cause of the variability should be identified and corrected to re-establish statistical control over the instrument background. Table 18.2 presents reasons for changing backgrounds.

TABLE 18.2 — Instrument background evaluation

Instrument Background Failed Performance Indicator		
Rapid Change in Background	**Slow Change in Background**	**Excessively Variable Background**
Electronic failure Detector failure Loss of coolant/vacuum Instrument contamination Counting gas changes Temperature/humidity fluctuation Laboratory contamination External sources Insufficient shielding Personnel with nuclear medicine dose	Instrument contamination Electronic drift Low counting gas flow rate	Sources being moved Radon fluctuation Insufficient shielding Insufficient counting statistics Interfering radionuclides Poor peak deconvolution Intermittent electrical grounding problems Failing electronics

18.5.2 Efficiency Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in-depth, technical discussion is provided in Chapter 16. The number of events (counts) recorded by a detector is converted to activity (actual radionuclide transformations) by empirically determining this relationship with NIST-traceable radionuclide sources when available. This relationship is expressed in the system's efficiency calibration. A separate efficiency is determined for each detector-source combination and is typically energy or radionuclide specific.

Detector efficiency is critical for converting the detector's response to activity. As discussed above, routine performance checks can evaluate several aspects simultaneously (sample geometry, matrix, etc.) and provide a means to demonstrate that the system's operational parameters are within acceptable limits. These are typically included in the assessment of the analytical method's bias and are specified in terms of percent recovery based on the source's known disintegration rate. Performance checks for measurement efficiency are usually determined statistically from repeated measurements with a specific check source. Detection of a shift in measurement efficiency should be investigated.

The frequency of performance checks for efficiency calibrations is instrument specific. The frequency of these checks is often based on a standardized time scale or a percentage of the total number of analyses performed using that method.

Performance checks for instrument efficiency typically are performed on a day-of-use basis. The level of activity in the check source should be sufficient to allow the accumulation of enough counts in a short time so that daily performance checks do not impose an unnecessary burden on the laboratory. However, the source strength for spectrometry systems should be such that instrument dead time is not significant and gain shifts do not occur (ANSI 42.23). For detectors that are used infrequently, it may be necessary to perform a check before and after each set of measurements.

Control charts provide a useful tool for documenting and evaluating performance checks for efficiency calibrations, and should be established and maintained for the intrinsic efficiency of each detector. There are several methods available for evaluating performance using control charts (see Attachment 18A).

Discussion: Most radiation detectors do not record all of the nuclear transformations that occur in samples undergoing measurement, i.e., they are not one hundred percent efficient. This occurs for several reasons, and the prominent reasons are discussed briefly below.

- Intrinsic or absolute efficiency[2] – In the absence of all other factors, a detector will only record a fraction of the emissions to which it is exposed due to its composition and other material-related aspects. Intrinsic efficiency is a measure of the probability that a count will be recorded when a particle or photon of ionizing radiation is incident on a detector (ANSI N1.1).

- Geometry – The spatial arrangement of source, shielding, and detection equipment, including the solid angle subtended by the detector and sample configuration, largely determines what fraction of the emissions from the source actually reach the detector (ANSI N15.37). Geometry includes the source's distance from the detector and its spatial distribution within the counting container relative to the detector and shielding components.

- Absorption – Radiation emitted by the source can be absorbed by the source itself (self-absorption), as well as other materials placed between the source and the detector, i.e., source container, detector housing, and shielding (NCRP 58).

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[2] Efficiency measures the fraction of emitted photons or particles that are actually detected. It is affected by the shape, size, and composition of the detector as well as by the sample-to-detector geometry. There are two ways that efficiency can be expressed: "Absolute efficiency" is the fraction of all the photons or particles emitted by the source that are actually detected, and "intrinsic efficiency" is the ratio of photons or particles detected to the number that actually fall on the detector.

- Backscatter – Radiation emitted by the source can hit the source container or detector shielding and scatter into the detector.

The detector response is a composite of these factors.

Each radiation detector should be calibrated to determine the relationship between the observed count rate of the detector and the emission rate of the source being assayed. This relationship is called the efficiency calibration—typically expressed in counts per second/emissions per second, or cps/dps—and is an integral part of the measurement protocol. For alpha spectrometry systems, the efficiency of detection is energy-independent. Efficiencies for gamma spectrometry are energy dependent, and an efficiency calibration typically covers a range for a specific counting geometry, e.g., 50 to 1,800 keV.

Once this relationship is established, it should be checked at regular intervals using what is called a performance or calibration check. The performance check does not seek to reestablish the detector's efficiency but simply demonstrates that the relationship is within acceptance limits. When designed properly, an efficiency performance check evaluates the intrinsic efficiency, geometry and absorption in a single measurement. Accordingly, it takes the form of a single value that incorporates all effects for a target radionuclide and a specific detector-sample configuration. Detectors that are energy dependent and measure radionuclides with multiple energies, such as photon or alpha spectrometers, should have performance checks at several energies throughout the measurement range. For these detectors, the performance check can simultaneously address the system's efficiency, energy calibration and resolution using a single source. An internal pulser can be used to check the electronics.

Because the performance check's purpose is to demonstrate that the system's efficiency remains constant, the source's absolute disintegration rate need not be known, provided its purity can be established, its half-life is known, and its activity is sufficient to provide adequate precision. Accordingly, it is not necessary to use a NIST-traceable check source for this purpose. Check sources that are non-NIST-traceable can meet the precision objectives of the performance check and they are less expensive.

Excursions: Changes in the efficiency of a detector can only be corrected by determining the root cause of the problem and repeating the efficiency calibration. Gradual changes in geometry usually indicate a problem with the technique of sample mounting or preparation. A visual inspection of the prepared source is often helpful in eliminating sample geometry as a cause of the problem. For example, a precipitated sample counted on a gas proportional counter has an expected appearance, i.e., a circle of precipitate centered on the planchet and often covered with thin plastic film. If the prepared source does not have the correct appearance, there could be a problem with the geometry, self-absorption, and backscatter. This can sometimes be corrected by

preparing the source a second time, inspecting it and presenting it for counting a second time. Re-training personnel responsible for the error may also be indicated. Because sources that have been improperly prepared for counting can result in contamination of or physical damage to the detector, it is strongly recommended that every source be visually inspected prior to counting. Significant changes in geometry caused by modifications to the source preparation method can only be corrected by recalibrating the detector. Examples of modifications to source preparation methods are (1) using a new filter so that the geometry of the test source is different than the geometry used for calibration, and (2) replacing the containers used for gamma spectrometry with containers that have a different wall thickness or are made from different materials.

Changes in intrinsic efficiency generally result from a physical change to the detector and often result in rapid changes in efficiency. In many cases, changes that affect the intrinsic efficiency of a detector render it inoperable. These are specific to a detector type and are listed below:

- HPGe, Ge(Li), and surface barrier detectors – Real or apparent changes in intrinsic efficiency may be caused by vacuum leaks or failure of field effect transistor.

- Thin window detectors (gas proportional counters, low-energy photon) – Changes in measurement efficiency are typically associated with damage to the detector window.

- Gas proportional systems – Problems may be related to the quality or flow of counting gas.

- Anti-coincidence systems with guard detectors – Electrical problems with the anti-coincidence circuits may produce apparent changes in efficiency.

- Scintillation detectors – Gradual changes in efficiency are associated with the scintillator or the photomultiplier tube. For example, NaI(Tl) crystals may gradually turn yellow over time resulting in a lower intrinsic efficiency, and liquid scintillation counters may have residue gradually build up on the surface of the photomultiplier tube affecting the detection of photons by the tube.

18.5.3 Spectrometry Systems

18.5.3.1   Energy Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in depth, technical discussion of instrument calibration is provided in Chapter 15 (*Quantification of Radionuclides*). All radiation measurements are energy dependent to a certain extent. However, spectrometric techniques such as gamma and alpha spectrometry identify radionuclides based on the energy of the detected radiations. For these techniques a correct energy calibration is critical to accurately identify radionuclides. Problems

with energy calibration may result in misidentification of peaks.

Discussion: Spectrometry systems should be calibrated so that each channel number is correlated with a specific energy. To identify radionuclides correctly, this energy calibration needs to be established initially and verified at regular intervals. The energy calibration is established by determining the channel number of the centroid of several peaks of known energy over the applicable energy range. Typically, a minimum of three peaks is used, and commercially available sources contain nine or ten photopeaks. The relationship between energy and channel number can be determined by a least squares fit. To account for non-linearity, a second or third order fit may be used. However, these require more points to define the curve. For example, a first order calibration requires at least two points, while a second order calibration requires a minimum of three points. The end points of the curve define a range of applicability over which the calibration is valid, and peaks identified outside the curve's range should be used carefully. The uncertainty associated with the curve should be available at any point along the calibration curve.

Quality control checks for energy calibration may be combined with checks for efficiency calibration and resolution. Radiations emitted over the range of energy of interest are measured, and two or more peaks are used to demonstrate that the energy calibration falls within acceptable limits. Check sources may consist of a single radionuclide or a mixture of radionuclides (e.g., mixed gamma). Because only the location of the peak is of concern, there is no requirement that the check source be calibrated or certified, except for ensuring that it does contain the radionuclide(s) of interest at a specified level of purity.

The energy calibration is determined when the system is initially set up by adjusting the gain of the amplifier, analog-to-digital conversion (ADC) gain, and zero. Criteria that indicate when readjustment is required because of gradual and abrupt changes in the energy versus channel calibration should be established as an integral part of the system's operating procedure. These changes usually are monitored by the measurement system's software, and the user specifies the allowable difference between that the system's response and the radionuclide's known energy. The tolerable difference often relates to the instrument's resolution. For example, a high resolution instrument such as an intrinsic germanium detector typically will have acceptable limits on the order of a few keV, while a low resolution instrument such as a NaI(Tl) detector typically will have acceptable limits on the order of several tens of keV.

Spectra also can be analyzed by identifying each peak manually. With manual identification, the acceptable limits for the energy calibration are determined for each spectrum based on the professional judgment of the person analyzing the spectrum.

The frequency of QC checks for energy calibrations can be related to the expected resolution of the instrument, the electronic stability of the equipment, or the frequency needs of QC

measurements for efficiency calibration or resolution. These are specified typically in the laboratory's quality manual or other typical project-related documentation. Examples for three detector types are provided below and in Tables 18.5 through 18.8.

- HPGe and Ge(Li) Photon Detectors. Energy calibrations are typically verified using a check source on a day of use basis. Every source spectrum should include verification of the energy calibration as part of the data review process, when possible. Under extreme conditions (e.g., *in situ* measurements in bad weather), it may be necessary to perform checks at the beginning and end of each measurement period or day the instrument is used.

- Surface Barrier Alpha Spectrometry Detectors. The energy calibration is often performed using an alpha source when the instrument is setup initially and when a detector has been serviced or replaced. Electronic pulsers can be used for daily checks on energy calibration. Most alpha spectra include a chemical yield tracer with a peak of known energy that can be used to verify the energy calibration during data review. Alpha spectrometers have a lower resolution than germanium detectors, and newer spectrometers are sufficiently stable to allow weekly or monthly performance checks. The frequency of performance checks should be based on the number and frequency of measurements and historical information on the stability of the instrument.

- Low-Resolution NaI(Tl) Detectors. These typically are less stable than HPGe detectors and may require more frequent quality control checks, depending on the conditions under which they are used.

For all detectors where energy calibrations are performed daily, plotting the channel numbers of peak centroids can be useful for identifying trends and determining the need for adjusting the system. Changes in peak location may result in mis-identification of radionuclides. When this is observed, all spectra obtained since the last acceptable energy calibration check should be reviewed. If there is sufficient information within the spectrum to determine the acceptability of the energy calibration, no further action may be required for that spectrum. If the spectrum contains too few peaks of known energy, reanalysis should be initiated.

Gradual changes in peak location are not unexpected and the rate of these gradual changes can be used to establish the appropriate frequency of energy calibration checks. The acceptable limits on peak location established during the initial system setup may be used to indicate when the energy calibration needs to be readjusted.

Excursions: Changes in the energy calibration can be the result of many factors including power surges, power spikes, changes in the quality of the electrical supply, variations in ambient conditions (e.g., temperature, humidity), physical shock to the detector or associated electronics, and electronic malfunction.

Rapid changes in energy calibration are usually caused by power surges, power spikes, or physical shocks to the system. Corrective actions typically involve recalibrating the system and repeating the analysis. If changes result due to loss of cryostat vacuum, the instrument may need to be returned to the manufacturer to be refurbished or replaced.

Gradual changes in the energy calibration are usually the result of a variable or poorly conditioned power source, changes in the ambient conditions, or electronic malfunction. Corrective actions generally begin with identifying the root cause of the problem. Gradual changes that begin following relocation of the instrument are more likely to be caused by the power source or the ambient conditions. Installing a line conditioner, surge protector, and uninterrupted power supply is recommended to address problems related to the system's electrical power source. Problems with low humidity can be corrected through the use of a humidifier in dry climates or cold weather; conversely, high or variable humidity may require the use of a dehumidifier. Problems associated with fluctuations in temperature may require significant changes to the heating and cooling system for the room or building containing the instrument in order to stabilize the temperature. Gradual changes that occur following physical shocks to the system or following a rapid change in peak location with an unidentified cause are more likely to be the result of problems with the electronic equipment. In most cases the amplifier is the source of these problems, but the analog-to-digital converter, pre-amplifier, power supply voltages, and multi-channel (or single-channel) analyzer may also cause this type of problem. However, they could also be the result of crystal or detector failure. Systematic switching out of components and discussions with the instrument manufacturer will often help to identify which component may be the source of the trouble. It may be especially difficult to identify the source of problems with new instruments in a new facility.

18.5.3.2   Peak Resolution and Tailing

Issue: The shape of the full energy peak is important for identifying radionuclides and quantifying their activity with spectrometry systems. Poor peak resolution and peak tailing may result in larger measurement uncertainty. If consistent problems with peak resolution are persistent , then an analytical bias most likely exists. Many factors will affect peak resolution and these are discussed below.

Discussion: Detectors with good resolution permit the identification of peaks which are close in energy. When a monoenergetic source of radiation is measured with a semiconductor, scintillation, or proportional spectrometer, the observed pulse heights have a Gaussian distribution around the most probable value (Friedlander et al., 1981). The energy resolution is usually expressed in terms of the full width at half maximum (FWHM) or the full width at tenth maximum (FWTM).

In a semiconductor detector, fluctuations in output pulse height result from the sharing of energy

between ionization processes and lattice excitation (Friedlander et al., 1981). The number of charge pairs created by radiation of a given energy will fluctuate statistically. This fluctuation occurs because the energy causes lattice vibrations in the semiconductor as well as the formation of charge pairs. This sharing of energy causes a variation in the number of charge pairs created and gives rise to the width of a measured peak. The magnitude of the statistical fluctuation is proportional to the energy of the radiation. There is also a variation in the number of charge pairs collected by a detector.

In a scintillation detector, the statistical fluctuations in output pulse heights arise from several sources. The conversion of energy of ionizing radiation into photons in the scintillator, the electronic emission at the photocathode, and the electron multiplication at each dynode are all subject to statistical variations. Note that the distance of the source to the detector also impacts the resolution.

In a proportional counter, the spread in pulse heights for monoenergetic rays absorbed in the counter volume arises from statistical fluctuations in the number of ion pairs formed and the gas amplification factor (Friedlander et al., 1981). If the gas gain is made sufficiently large, the fluctuations in the number of ion pairs determine the resolution.

The FWHM typically is used as a measure of resolution, while the FWTM is used as a measure of tailing for the full energy peak. For Gaussian peaks with standard deviation σ, the FWHM is equal to 2.35σ. The resolution of a detector is the ratio of the FWHM (in keV) to the energy (in keV) at the most probable peak height. The sources of fluctuations that contribute to the standard deviation are dependent on the type of detector (see Chapter 15, *Quantification of Radionuclides*, for a more detailed discussion of detector resolution).

Resolution affects the ability to identify individual peaks in two ways (Gilmore and Hemingway,1995). First, it determines how close together two peaks may occur in energy and still be resolved into the two components. Second, for gamma spectrometry, when a peak of small magnitude sits on the Compton continuum of other peaks, its ability to be detected can depend on its signal-to-noise ratio. With good resolution, the available counts are distributed in fewer channels, thus those counts will be more easily identified as a peak by the spectrometry analysis software. If resolution degrades significantly the efficiency may be in error. This is especially true when the spectrum analysis involves the region of interest (ROI) concept. When the calibration is performed, the full energy peak may fit within the defined ROI limits, whereas the resolution degraded peak may have counts which fall outside them. Thus, the detector efficiency will be effectively decreased and inconsistent with the previously determined efficiency.

Tailing is another observable feature of the peak shape. Tailing is an increased number of counts in the channels on either side of the full energy peak. Tailing affects the FWTM more than the FWHM, so the ratio of FWTM to FWHM can be used as a measure of tailing. For a Gaussian distribution the ratio of FWTM to FWHM is 1.823. For most germanium detectors this ratio

should not exceed 2.0. Tailing may be caused by imperfect or incomplete charge collection in some regions of the detector, escape of secondary electrons from the active region of the detector, electronic noise in the amplification and processing circuitry, loss of vacuum and escape of bremsstrahlung from the active region of the detector. Tailing may also result from the source's self-absorption for alpha emitting radionuclides.

The resolution (FWHM) is routinely calculated for gamma and alpha spectrometry peaks by the spectrum analysis software and can be monitored by observing the FWHM calculated for the check sources routinely counted. Resolution monitoring and charting is normally an integral part of a measurement quality system. Acceptance parameters may be established for resolution and incorporated in the analysis software. For alpha spectrometry, where radionuclide tracers are used for chemical yield determination, the FWHM can be monitored for each analysis, if desired. Some projects may specify FWHM limits for internal tracer peaks on each sample run.

The shape of the peak is important for quantifying the activity, and resolution is important for identifying peaks in a spectrum. The shape of the peak is also important for monitoring the performance of a detector. Germanium detectors have very good resolution on the order of 1 percent. The FWHM at specific energies is provided by the manufacturer. The FWHM should be established at several energies throughout the range being measured because the FWHM is directly proportional to the energy. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Tolerance or ontrol limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

The resolution of an alpha spectrum is dominated typically by self-absorption in the source. This is indicated by low energy tailing and elevated FWTM and FWHM. Most surface barrier detectors are capable of resolutions on the order of 30-40 keV for monoenergetic nuclides and 80-100 keV for unresolved multiplets. Acceptance of sample resolution is usually monitored by visual inspection of individual spectra. For well-prepared samples, the FWHM of the alpha peaks may be expected to be from 30 to 80 keV.

The resolution of scintillation detectors is not as good as the resolution of semiconductor detectors, but peak shape and tailing are just as important for analyzing samples. The FWHM should be established at several energies throughout the range being measured. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Control limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

Performance checks for resolution and tailing should be performed for all instruments used as spectrometers. These measurements are usually combined with the performance checks for energy calibration and efficiency calibration. Quality control activities should include visual inspection of all spectra to evaluate peak shape and tailing.

Tolerance limits or control charts for FWHM and the ratio of FWTM to FWHM can be developed and used to monitor the performance of any detector used as a spectrometer. Because the concern is when the resolution degrades (i.e., the FWHM increases) or tailing becomes a problem (i.e., the ratio of FWTM to FWHM increases), control limits are necessary. Limits can be developed based on historical performance for a specific type of detector. Control charts offer a convenient method for monitoring the results of the performance checks. As mentioned previously, the concern is associated with an increase in the FWHM or the ratio of FWTM to FWHM. This means that only an upper control limit or tolerance limit is required for the chart.

Excursions: Changes to the FWHM are associated with malfunctioning or misadjusted electronics, excessive electronic noise or interference, or detector or source problems. Electronics problems include changes in the high voltage applied to the detector, noise (including cable noise and high voltage breakdown), and electronic drift. Electronics problems may be caused by changes in the high voltage, improper adjustment of the pole zero or baseline restorer, or drift of the amplifier gain or zero during acquisition. Source problems are usually only associated with alpha spectra and result in excessive self-absorption resulting in low-energy tailing. This can result in counts being identified with an incorrect peak. Problems that are not electronic or source related imply that the detector is malfunctioning.

Changes to the ratio of FWTM to FWHM indicate problems associated with tailing. Tailing can occur on the high- or low-energy side of the peak. High-energy tailing indicates electronics problems that may be caused by excessive activity in the sample, incorrect adjustment of the pole zero or pile-up rejector, or drift of the amplifier gain or zero while acquiring the spectrum. Low-energy tailing indicates an electronic or a source problem—a possible corrective action is to check to see if the vacuum is set properly for alpha detectors. Table 18.3 lists common problems, the implied root cause of the problem, and possible corrective actions.

TABLE 18.3 — **Root-cause analysis of performance check results for spectrometry systems**

Observed Problem	Implied Root Cause	Possible Corrective Actions
Efficiency changed	Unknown Electronics degradation Geometry changed Poor source Software application	Ensure the correct check source was used Check to ensure the efficiency was evaluated using the correct geometry Ensure high voltage is set properly Pulser check of electronics
Peak centroid moved	Gain changed	Check amplifier gain Check conversion gain Check stability of amplifier for gain shifts or drifting
	Offset shifted	Check zero offset Check digital offset Check stability of amplifier for gain shifts or drifting
FWHM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Increased source-to-detector distance (for alpha spectrometry)

Observed Problem	Implied Root Cause	Possible Corrective Actions
FWTM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Repeat test-source/sample preparation and recount Reanalyze sample Check with weightless (plated) source Increased source-to-detector distance (for alpha spectrometry)
No peak or broad peaks	Electronics problem	Ensure that high voltage is correct
Low-energy tailing	Electronics problem	Ensure that high voltage is correct Check pole zero adjustment Check baseline restorer Check stability of amplifier for gain shifts or drifting Check for loss of vacuum
	Source problem	Repeat test-source/sample preparation and recount Reanalyze the sample
High-energy tailing	Electronics problem	Check pole zero adjustment Check pile-up rejector Check stability of amplifier for gain shifts or drifting
	Source problem (too much activity)	Reduce volume of sample analyzed Increase distance between the source and detector
Spectra shifted uniformly	Offset shifted	Check zero offset Check digital offset Check amplifier for zero drift
Spectra stretched or compressed	Gain changed	Check amplifier gain Check conversion gain Check amplifier for gain shifts

18.5.4 Gas Proportional Systems

18.5.4.1   Voltage Plateaus

Issue: The accuracy of the results produced by a gas proportional system can be affected if the system is not operated with its detector high voltage properly adjusted, such that it is on a stable portion of the operating plateau.

Discussion: The operating portion of a detector plateau is determined by counting an appropriate source at increasing increments (e.g., 50 volts) of detector high voltage. For detectors which will be used to conduct analyses for both alpha- and beta-emitting radionuclides, this should be done with both an alpha and beta source. The sources used should be similar in both geometry and energy to that of the test sources to be counted in the detector.

A plot of the source count rate (ordinate) versus high voltage (abscissa) rises from the baseline to a relatively flat plateau region, and then rises rapidly into the discharge region for both the alpha

and beta determinations. From the plateau, the operating voltage is selected so that small voltage changes will only result in minor fluctuations to detector efficiency. Operation of the counter at the upper end of the plateau is not recommended and can result in the generation of spurious discharge counts. Modern high-voltage supplies, operating properly, experience little actual voltage fluctuation. The detector response should be checked after repairs and after a change of gas. The detector plateau should again be determined and plotted (voltage vs. count rate) after repairs, particularly to the detector unit.

The historical tracking of the establishment and maintenance of this operating parameter is recommended; it aids in determining the probable cause of quality control failure and the identi-fication of long-term instrument deterioration. Items to be recorded include date/time, instrument detector designation, source number, check source response at the operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha-discriminator setting, length of the plateau, operating high voltage setting, etc.

Excursions: Voltage changes of short- or long-term duration will affect reliability of a propor-tional counter. If the detector voltage is lowered sufficiently, there is a danger of operating below the plateau knee which, in effect, reduces the efficiency and would bias the results of any sample count low. Should the voltage applied to the proportional detector be driven up to a point where the slope of the plateau is sufficiently great enough to increase the efficiency of the detector, sample counts may be biased high. A transient voltage increase of great enough magnitude could introduce spurious counts.

Shifts in the operating voltage along the plateau or length of the plateau could also result from long-term detector deterioration or electronic drift or failure.

18.5.4.2   Self-Absorption, Backscatter, and Crosstalk

Issue: The accuracy of alpha and beta activity determinations in samples with discernable solids in a gas proportional system depends in large part on the determination and maintenance of self-absorption and crosstalk curves.

Discussion: Samples counted for alpha and beta activity in a gas proportional system are typi-cally prepared as inorganic salts, e.g., nitrates, carbonates, oxides, sulfates, or oxalates, and contain on the order of tens to hundreds of milligrams of solids when counted, which result in absorption and scattering of the particles in the sample material and mounting planchet (Chapter 16). Thus, for gas proportional systems, the detection efficiency for a given test source depends on the self-absorption occurring within each sample volume/mass. To establish the correction factor, a calibration curve is generated using a series of calibration sources consisting of an increasing amount of solids and known amounts of radionuclide. The relative efficiency for each calibration source is plotted against the amount of solids, and these data are used to determine a

test source's efficiency as a function of test-source mass. The diameter and the composition of the test-source planchet, not just the test-source mass, should be identical with what was used for routine samples. This allows calculation of the corrected amount of activity regardless of the test-source mass (mass/efficiency curves).

The counting of alpha and beta particles simultaneously in a proportional counter requires that an electronic discriminator be adjusted, such that pulses of heights below that represented by the discriminator are registered as betas, and those of greater heights are counted as alphas. Crosstalk occurs when alpha particles are counted in the beta channel or betas are registered as alphas. For example, the alpha-to-beta crosstalk for ^{241}Am, which also has a 59.5 keV gamma-ray emission (35.9 percent), would be greater than the alpha-to-beta crosstalk factor for a pure alpha emitter (such as ^{210}Po). However, this relationship is energy dependent, and care should be taken to identify samples that differ significantly from the sources used to establish the crosstalk ratio. For example, ^{90}Sr + ^{90}Y ($E_{\beta max}$ 2.28 MeV) is typically used as a beta source for instrument calibration. However, samples containing natural uranium in equilibrium with its progeny produce beta emissions that are considerably more energetic from the 3.28 MeV $E_{\beta max}$ betas of ^{214}Bi. The crosstalk ratio established with ^{90}Sr will be inadequate for such samples.

As the amount of solids in the test source increases, the beta crosstalk can increase due to the degradation of the alpha particle energy by interaction with test-source material. Similarly, the beta into alpha crosstalk decreases. Thus, crosstalk should be evaluated as a function of sample weight to correct the observed relative alpha and beta counts. This is normally determined in conjunction with the self-absorption curve. To check these parameters, calibration sources should be prepared at the low and high ends of the calibration curve, and the limit of their acceptability should be better than 1 percent (one sigma). These checks should be performed annually, at a minimum, and following detector replacement or significant repair. The historical tracking of the establishment and maintenance of these operating parameters is recommended. This aids in determining the probable cause of quality control failure and the identification of long-term instrument deterioration. In addition, items to be recorded include date/time, instrument detector designation, source number, operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha discriminator setting, etc.

Excursions: Any change in the detector-source geometry or adsorption characteristics between the source and detector, can affect the self-absorption and crosstalk correction factors. For example, the replacement of a detector window with one whose density thickness is different from the original window can necessitate the reestablishment of these parameters. Electronic drift of the alpha discriminator can also affect the crosstalk ratios.

18.5.5 Liquid Scintillation

Issue: The accuracy and reproducibility of radionuclide measurements by liquid scintillation are

dependent on accounting for the quench (Section 15.5.3.3) of the measured test source. Quench is one of the most significant factors to be accounted for, and can be affected by solvent-to-fluor ratio, cocktail characteristics, suspension composition, acid concentration, and chemical and radiological impurities. Care must be taken to assure radionuclide purity and chemical-composition equivalence to calibration and test sources. An additional factor to consider is the ratio of sample volume to scintillation-cocktail volume (i.e., dilution factor). Although this can affect quench as well (especially if there is significant sample dilution), it is more critical that the ratios used for calibration match those in the test-source analysis.

Discussion: The process of scintillation involves the energy transfer from the emitted beta particles, slowing and stopping in the liquid medium as a result of collisions with molecularly bound electrons. The transfer of energy from the beta particle to the electrons results in solvent excitation through thermal, collisional, and photonic interactions. These excited solvent molecules transfer energy through various processes to specific organic molecules known as "fluors." The combination of the solvent and fluor is referred to as the "cocktail." The test source is the combination of the cocktail and sample.

Fluors absorb the energy and are brought to an excited state. The de-excitation of these molecules results in a photon emission that is detected by a photomultiplier tube. Many cocktail combinations contain a second fluor (referred to as a wavelength shifter) which adjusts the emitted photons to a specific bandwidth.

Any component of the cocktail that affects the energy transfer process will have a significant effect on the analysis. This effect is referred to as "quench." The quench of a cocktail can be affected by:

- Color;
- Turbidity;
- Molecules of high electron affinity;
- Solvent;
- Acidity; and
- Dissolved gases.

Quench has the effect of shifting the energy distribution of the beta particle spectrum to lower energies. Quench also can have the effect of reducing the number of net counts.

Excursions: Slowly changing liquid scintillation measurements of a sample may be due to the change in quench because of chemical attack on the cocktail system or to changes in instrument or ambient temperature during a long count. Rapid changes in liquid scintillation measurements include phase separation of the sample in the cocktail, sample precipitation, and light leaks into the instrument. Some causes of excursions in liquid scintillation analysis are listed in Table 18.4.

Examples: Specific examples of these types of excursions as it affects analysis can be seen in the examples below.

<p align="center">TABLE 18.4 — Some causes of excursions in liquid scintillation analysis</p>

Physical Effects	Chemical Effects
Turbidity	Elevated concentrations of Cl^- or NO_3^-
Sample opacity or color	Solvents: $CHCl_3$, methyl ethyl ketone, CCl_4, etc.
Precipitation	Peroxide
Fingerprints on vial	Incorrect fluor
Phase separation	Expired fluor
Light leaks into instrument	Contaminated fluor
Inadequate dark adaptation	
Temperature changes	
Different vial composition	

MEASUREMENT OF ^{55}FE IN RADIOACTIVE WASTE SOLUTIONS. The separation techniques for iron generally use nitric and hydrochloric acids. Both of these acids are eliminated prior to the preparation of the cocktail by boiling down the solution with phosphoric acid. Nitric acid can decompose in room light giving rise to the gas N_2O_4, which can impart a brown color to the solution. High concentrations of chloride can act as electron scavengers in the solution. Both these conditions yield quench. Removing them with phosphoric acid maintains the solution acidity (so the iron does not precipitate) and does not act as a quench agent.

SAMPLES IN CONCENTRATED NITRIC ACID. If samples must be made with high concentrations of nitric acid, they should be measured shortly after preparation, to avoid fluor decomposition. The samples need to have their quench compared to standard samples of the same acid composition and short time following preparation.

TRITIUM IN RAINWATER. Some methods of collecting rainwater involve funneling from a large surface area (like a roof) into a collection bottle through a spout. Rainwater itself contains many contaminants, such as carbon dioxide, sulfur dioxide, and polycyclic aromatic hydrocarbons (PAHs from fossil fuel combustion), which can act as significant quench agents. Furthermore, the surface through which the water is collected may contain accumulated particulate matter that also can affect the quench. Distilling the sample would minimize the effect of their quench. Without this, the quench would be increased and the "apparent" value would have a significant uncertainty associated with it.

18.5.6 Summary Guidance on Instrument Calibration, Background, and Quality Control

Radiation detectors and nuclear instrumentation, such as spectrometry systems, should be

calibrated and maintained according to protocols and procedures documented in the laboratory's standard operating procedures and quality manual. The important calibration parameters, the performance criteria used to monitor these calibration parameters, and the frequency of re-calibrations should be addressed in these documents. Another important parameter that should be addressed is the detector background. Detector background measurements should be taken at an appropriate frequency for the purposes of determining the net count rate of a test source and for controlling contamination.

The following subsections discuss the important calibration and monitoring parameters associated with nuclear instrumentation in common use at radioanalytical laboratories. At the end of each subsection, a table provides some examples of performance criteria for the measurement parameters and the frequency of monitoring of these parameters. The information in these subsections conforms to ASTM E181, ANSI N42.12, and NELAC (2002) and uses the input of the ASTM D19.04 Subcommittee on Methods of Radiochemical Analyses for Radioactivity in Water. A few important concepts should be considered when reviewing the following sections and summary Tables 18.5 through 18.8:

- NIST-traceable radionuclide sources (or traceable to a national standards body) are to be used for all calibrations when possible (see Chapter 15, *Quantification of Radionuclides*). Sources used for QC checks do not have to be NIST-traceable.

- The frequency of performing QC detector-response measurements, or evaluating a detector background, is related to the risk (probability) that a laboratory will accept for not detecting an instrument problem or a change in background, given a certain number of samples analyzed. The acceptable risk for not detecting a problem may vary from one laboratory to another. If an instrument QC response check is performed once every 10 samples (test sources), then there is a possibility that nine samples may be counted on an instrument not meeting quality specifications before a problem is detected. Therefore, it is more appropriate to establish the frequency of instrument QC based on the number of samples processed rather than on time schedules. The examples of instrument QC frequencies presented in the following sections are considered practical for most laboratories.

- Loss of control results from a calibration performance criterion not being met, any repair or maintenance that could affect a calibration parameter, and any event (such as sudden loss of power) that could affect calibration.

- Even without loss of control, a counting or spectrometry system should be re-calibrated for test-source radionuclides, matrices, and counting geometries at a frequency consistent with specifications delineated in the laboratory's quality manual.
- For an accurate measurement of a detector's counting efficiency and resolution, as well as for a detector's QC response checks, the relative counting uncertainty (1σ) of the measurement (net count or net response) or in the individual peaks associated with spectrometry systems

should be 1 percent or less.

- Detector background measurements are used for the calculation of a net measurement response and for detector contamination control. A net measurement response is calculated using a long-duration detector background measurement in order to minimize the counting uncertainty of the measurement. Contamination control background measurements typically are taken more frequently and are of shorter duration than those for net measurement response applications. To determine possible gross contamination, the results from the contamination control background measurements should be evaluated statistically and compared to the long-duration background results.

18.5.6.1   Gas Proportional Counting Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gas proportional counting system:

- Operating voltage settings on the alpha and beta voltage plateaus,
- Detector counting efficiencies, and
- Crosstalk factors.

Initially upon instrument setup, the manufacturer's specifications for these three parameters should be verified. It should be noted that the manufacturer's specifications may be based upon unique calibration sources and operating conditions that may not be similar to those used when analyzing test sources. For example, the manufacturer's detector efficiency and crosstalk factors may be based on electroplated alpha and beta sources. For most laboratories, the typical test source for GP counting is not an electroplated source, so the reference alpha and beta radio-nuclides for calibration are not the same as the radionuclides used by the manufacturer in developing the specifications. However, the detector's alpha and beta voltage plateau settings typically are not changed after instrument setup. The alpha and beta voltage plateau settings are selected from plots of the applied detector voltage versus the observed count rate for pure alpha and beta sources (see Chapter 15, *Quantification of Radionuclides*).

The next parameters to evaluate are the detector's alpha and beta counting efficiencies for various source geometries. Initially, the manufacturer's detector efficiency for both alpha and beta counting modes should be verified using electroplated sources. (Typical electroplated calibration sources include ^{99}Tc and ^{90}Sr for beta sources and ^{230}Th or ^{241}Am for alpha sources.) A detector's counting efficiency should be determined for each radionuclide and method used to analyze test sources. The detector efficiency should be determined for new or changed method protocols and loss of instrument control. For test sources having mass loading, an efficiency curve or mathematical function that describes the detector efficiency versus mass loading, consistent with the expected test source mass range, should be developed. For any mass in the

expected calibration range, the 95-percent confidence limits for the detection efficiency should be within 10 percent of the fitted value for alpha sources and within 5 percent of the fitted value for beta sources.

The crosstalk factors for the alpha counts into the beta channel (alpha crosstalk) and for the beta counts in the alpha channel (beta crosstalk) should be determined when applicable. The manufacturer's specifications for the crosstalk factors using electroplated sources should be verified prior to test source processing. Typical manufacturer specifications for electroplated sources are less than 1 percent alpha counts in the beta channel for ^{210}Po and less than 0.1 percent beta counts in the alpha channel for ^{90}Sr/Y. The alpha crosstalk factor will vary according to the crosstalk parameter setup, decay scheme of the alpha emitting radionuclide, and the mass (weight) of the source. Verify the manufacturer's alpha crosstalk factor using the radionuclide and crosstalk parameters setting specified by the manufacturer. The alpha crosstalk factor for other radionuclides and source masses should be determined for each method, preferably at the same time as determining the detector counting efficiency factors or efficiency versus source mass function. The crosstalk factors may be method specific and should be determined during initial calibration and after re-calibrations.

BACKGROUND

A detector's background should be determined immediately after calibration and at the instrument settings established for each method. An accurate estimate of a detector's background is needed to determine the net count rate of a source. For this application, a very long background, with respect to the nominal counting time for the test sources, typically is needed depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test-source mount long enough to achieve a relative counting uncertainty (1σ) of less than 10 percent for alpha measurements and less than 3 percent for beta measurements. Alternatively, the counting time for a long-duration background measurement should be between one and four times the nominal counting duration of test sources for a given matrix and application. A long-duration background measurement should be conducted on a monthly basis. A statistical test should be used to determine if the detector's background has changed from the initial background determination.

When required, a detector may be evaluated frequently for gross contamination using a short-duration counting interval. When the counting duration of test sources is short (less than one hour), a short-duration background measurement should be conducted prior to processing test sources. When the test-source counting time is longer, the background time interval should be the same as the test sources, and the background should be determined before and after a sample (test source) batch.

CALIBRATION QC CHECKS

Once a GP counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, a tolerance limit or control chart (Section 18.3, "Evaluation of Performance Indicators") is established to monitor the detector's response and to flag responses that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the initial counting efficiency calibration, and after instrument loss of control. A tolerance limit or control chart should be set at ± 3% or 3σ. Once a chart has been established, an instrument or detector response check should be performed after a counting-gas change and daily for short test-source counting intervals. For longer test-source counting times, a detector response check for a multi-sample shelf unit should be conducted prior to test source counting, while a detector response check for a sequential sample counter should be performed before and after the sample batch.

TABLE 18.5 — **Example gas proportional instrument calibration, background frequency, and performance criteria**

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Alpha and beta plateaus and operating voltages	Prior to initial use and after loss of control.	Verify manufacturer's specifications. Plot voltage vs. count rate to determine proper operating voltages.
	Alpha and beta crosstalk factors	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. Determine crosstalk factors for each nuclide, matrix and method. For mass-loaded test sources, determine crosstalk factors for the nuclide as a function of test source mass
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. A 1σ counting uncertainty of ≤1% should be achieved for all detector efficiency determinations.
	a) Weightless sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	Zero-mass sources using the same radio-nuclide of interest.
	b) Mass-loaded sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	For radionuclide of interest, establish mathematical function (curve) of detector efficiency vs. source mass loading. 95% confidence limit of the fitted function (curve) over the calibration range to ≤10% and ≤5% uncertainty for alpha and beta, respectively.
Detector Background		Determine alpha and beta background initially and after efficiency calibration.	Verify manufacturer's specifications.
a) Short count for gross contamina-tion control	Detector background using a contamination-free source mount	Daily for short test-source counting intervals. For longer test-source counts, use the same interval as the test sources before and after a sample batch.	Use a statistical test to determine if the new background count rate is different from the initial (at time of calibration) long background count rate.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
b) Long count for background subtraction of test sources and blanks	Detector background using a contamination-free source mount	Monthly when system is in use.	Establish a background count rate value based on measurement uncertainty or count a long background for a time interval that is 1 to 4 times the typical test-source counting time. Use statistical testing to determine a change in the long background count rate value.
Calibration QC check – detector response check	Count rate using a radionuclide source of appropriate emission and energy	Develop detector response control chart immediately after calibration and loss of control. Perform detector response check daily, prior-to-use, or bracketing a sample batch depending on test source counting time.	Count QC source to reach net 1σ counting uncertainty of $\leq 1\%$. For all detector response checks, compare performance to control chart or tolerance limits: $\pm 3\sigma$ or $\pm 3\%$.

18.5.6.2   Gamma-Ray Detectors and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gamma-ray (photon) detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency calibration for a particular geometry and matrix combination. Initially upon instrument setup, the manufacturer's specifications for the latter two parameters should be verified for a detector. It should be noted that verification of the manufacturer's specifications may require different instrument settings, sources, and geometries compared to those used during normal test-source analyses.

The energy calibration covers the photon energy range of the desired radionuclides expected in test sources. This calibration involves adjusting the gain of the system amplifier so that a specific slope calibration can be achieved (e.g., 0.5 keV/channel). At least two widely spaced photon peaks are needed to determine the energy calibration (Section 17.3.1, "Gamma Spectrometry"). It should be noted that verification of the manufacturer's specification for detector resolution may require a difference in energy calibration (e.g., 0.10 or 0.25 keV per channel) compared to the energy calibration settings used for typical test sources. For most modern spectrometry systems, the instrument energy parameters are very stable. The energy calibration parameter should be monitored as appropriate to support data-reduction algorithm requirements for energy fit and resolution. Typically, the determination of the energy calibration parameter can be made from the data acquired from the daily detector response QC measurement. A tolerance limit on the maximum energy calibration deviation, rather than a QC chart, can be used as an alternate to verifying amplifier output voltages. A pass-fail criterion for peak position also should be established. For example, the channel number that the [137]Cs 661.6 keV peak can change should be less than two channels. Some software applications adjust the energy of the gamma-ray spectrum using the daily energy calibration data. Such applications do not require changes in the settings of the

system's electronics.

The manufacturer's detector resolution, expressed as the FWHM in keV at specific photon energies, should be verified prior to use. Manufacturers of detector systems routinely establish an energy calibration of 0.25 or 0.10 keV/channel by adjusting the gain of the detection system amplifier. The FWHM and the peak-to-Compton ratio are both measured at a specified distance from the detector. Analytical laboratories frequently calibrate energies at approximately 0.50 keV/channel. Thus, prior to initial calibration or when re-calibration is necessary, the analytical laboratory should duplicate the manufacturers conditions for FWHM and peak-to-Compton ratio at the manufacturers stated initial conditions for the detector. It should be noted that the detector resolution varies with energy (Chapter 15) and can be affected by such factors as temperature, humidity, vibration, poor connectors, or poor line-voltage conditioning. The QC check sources used for the detector response check typically are used for resolution measurements during test-sources analyses. For a combined detector response and resolution check, the radionuclides selected for the QC source have photon energies that normally cover the low, middle, and high energies of the desired range (e.g., ^{241}Am, ^{137}Cs, and ^{60}Co). The photon energies selected for the resolution check should be sufficiently separated to avoid other interfering peaks. If the energy calibration settings for routine test source analyses is 0.5 keV per channel or greater, a resolution check may only indicate gross or substantial changes in a detector's resolution (e.g., greater than 10 to 20 percent). Photopeaks with greater than 10,000 counts are needed for routine resolution checks. Once the routine (operational) resolution value has been determined, limiting the maximum resolution deviation with an acceptable tolerance limit may be more suitable than using a QC chart. QC verification of resolution should be performed on a pass-fail basis. Since the FWHM varies as a function of energy, each peak should have its own acceptance criterion.

The peak-to-Compton ratio is an important characteristic of the detector that needs to be compared with the manufacturers specification upon initial detector calibration. This ensures that the maximum sensitivity for full energy peak (FEP) analysis is achieved, and the correct semiconductor crystal has been installed in the detector housing. See Section 15.6.2.1, "Detector Requirements and Characteristics," for the definition and technical basis for the peak-to-Compton ratio determination. This parameter needs to be checked during initial detector setup or prior to detector recalibration.

The next parameter that should be evaluated is the detector's efficiency response as a function of energy and matrix. The manufacturer's specification for detector efficiency is relative the efficiency of a 76 × 76 mm NaI detector responding to to ^{57}Co, ^{137}Cs, and ^{60}Co point sources at a distance of 25 cm from the detector. The standard NaI efficiency for this detector size and a ^{60}Co point source is 0.1 percent. (Gilmore and Hemingway, 1995). For each geometry/matrix combination used for test-source analyses, a gamma-ray efficiency versus energy response function (curve) must be determined. It is important that the same geometry and matrix be used for the calibration and test sources. This includes the container for these sources, as well as their physical placement relative to the detector. The efficiency check should span the energy range of

radionuclides of interest. For commercially available mixed radionuclide calibration sources, 10 data points per calibration curve is typical, covering the range of 59 keV (^{241}Am) to 1,836 (^{88}Y) keV. The 95 percent confidence limit of the fitted curve should be under 8 percent over the calibration energy region. A detector response QC chart should be established immediately after the first calibration for the detector.

DETECTOR BACKGROUND

A detector's background should be determined immediately after calibration with or without a counting container, depending on the inherent radionuclide activity levels in the counting container. An accurate estimate of a detector's background in a radionuclide photopeak is needed when determining the net photopeak count rate of a source. For this application, a very long background with respect to the nominal counting time for the test sources typically is needed, depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test source mount to achieve a relative counting uncertainty (1σ) for major photopeaks that is ≤10 percent. Alternatively, the counting interval for the long count should be between one and four times the nominal counting interval of the test sources. A long detector background measurement should be conducted on a monthly or quarterly basis. A statistical test should be used to determine if the detector background in a photopeak has changed significantly from the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method. The statistical criterion that constitutes a significant change should be stated in the laboratory's quality manual.

When required, the detector's background may be evaluated for gross contamination on a frequent basis using a short counting interval. Once the long background count rate has been determined, a shorter background count can be made and the results compared statistically to the long background count rate to determine possible detector contamination. For the short back-ground, the energy region between about 50 and 2,000 keV is integrated. The counting time for the short background count should be set so that the relative counting uncertainty (1σ) of the integrated counts is ≤3 percent. A limit in the deviation of the integrated background value may be set using a tolerance limit or control chart. It should be verified that no extraneous peaks are identified, indicating lower-level contamination (i.e., no new peaks in the short background spectrum compared to previous spectra)

CALIBRATION QC CHECKS

After the initial detector calibration, a control chart or tolerance limit should be established (Section 18.3, "Evaluation of Performance Indicators"). Such a chart may be generated using a noncalibrated, but reproducible geometry. This source does not necessarily need to be a primary-grade calibration source, but a sealed source that is well characterized and stable. The purpose of this QC source is to validate that the detector performance is reproducible on a day-to-day basis for the detector efficiency, energy response, and resolution. These characteristics can be used on

a relative basis for the QC source as long as it is stable and sealed, so that its only change will be as the result of radioactive decay (which can be accounted for mathematically). It must cover a reasonable energy range (low, middle, and high energies), and the generated QC data should have a relative 1σ uncertainty of under 1 percent. The detector-efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Monitoring of gamma-ray energy resolution (as measured by the FWHM) typically is a tolerance-limit measurement. Thus, an upper bound for this value at specified energies in the calibrated range will serve as the indicator of this parameter. For example, if the acceptable limit for FWHM at the 1,332 energy peak of ^{60}Co is 2.2 keV, any value greater than 2.2 keV at this energy would cause the system to be out of tolerance. A similar situation exists for the energy QC. An upper and lower limit, based on temperature drift of the electronics and detector system, should be used as a tolerance limit. Thus, the example of the ^{60}Co peak the band of acceptable energies that the instrument measures could be from 1,331.5 to 1,333.4 keV. The small changes in parameters such as these do not significantly affect the measurement. The idea of the tolerance limit here puts a bound where an effect can indicate performance issues. It is important to note that some gamma-ray spectrometry software systems use information obtained from the daily energy QC measurement to adjust for the energy response difference when analyzing a spectrum. Any changes to the configuration, integrity or geometry of the QC standard due to age warrants an investigation of its validity.

TABLE 18.6 — Example gamma spectrometry instrument calibration,
background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Detector energy calibration and high resolution peak to Compton measurements	Prior to initial use and after loss of control	Peak resolution; peak-to-Compton ratio (actual vs. manufacturer); equations for energy calibration; and shift in energy vs. channel number.
	Counting efficiency: matrix- and geometry-specific	Prior to initial use, after loss of control, and as required by quality manual.	Efficiency vs. energy for each geometry/matrix. 95% confidence limit of the fitted function: ≤8% over energy range.
Background – Short count for controlling gross contamination	Integrate spectrum from ~50–2,000 keV	Daily or prior to use.	No extraneous peaks; tolerance limit or control chart: ± 3% or 3σ .
Background – Long count for subtracting background from blanks or test sources	Establish background peak/region-of-interest (ROI) count rate and uncertainty for inherent radionuclides in detector, shield, and the counting geometry vessel.	Monthly or quarterly	Statistical test of successive counts and count rates for ROI show no significant difference.
Calibration QC check – Detector response	Energy, efficiency, and resolution	Daily or prior to use	Verify peak shift within tolerance limit; verify efficiency within control parameters; verify resolution in tolerance limit.

18.5.6.3   Alpha Detector and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating an alpha detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency for a particular combination of geometry and matrix. Additionally, a detector's leakage current typically is monitored to detect detector problems and possible detector-chamber light leaks. The manufacturer's specifications for detector resolution and efficiency should be verified initially upon instrument setup. Verifying the manufacturer's specifications may require different instrument settings and sources compared to those used during normal test-source analyses. The instrument setup and source geometry details normally are included in the manufacturer's documentation for a semiconductor alpha detector. The manufacturer's detector resolution (FWHM) in MeV is measured using an electroplated ^{241}Am point source in a near vacuum.

The energy calibration should be applicable to the alpha energies of the radionuclides expected in the test sources. This calibration involves adjusting the gain of the system amplifier so that a specific energy slope calibration can be achieved to cover a desired energy range. A typical energy range is between 3 and 8 MeV for long-lived radionuclides and between 3 and 10 MeV for short-lived radionuclides. At least two widely spaced alpha peaks are needed to determine the energy calibration. An energy calibration should be a linear response. However, the acceptable deviation in the energy gain (MeV per channel) depends on the total number of channels and the range of the energy spectrum.

A detector's peak counting efficiency should be determined for each test-source geometry/matrix combination that will be used. Calibration source mounts should be equivalent to the test-source mount (electroplated or microprecipitate) and have the radionuclide of interest or a radionuclide with about the same alpha energy. Most radioanalytical methods using alpha spectrometry incorporate a radioisotope tracer (radiotracer) into the sample processing scheme as a means to determine the sample-specific, chemical-yield detector-efficiency factor. For these methods, a separate detector efficiency calibration is not needed. When radiotracers are not used to deter-mine the chemical-yield-to-detector efficiency factor, a detector should be calibrated for each test-source mounting geometry according to the frequency specified in the laboratory's quality manual. For this calibration, the peak efficiency should be determined using the average of at least two alpha peaks. When measuring a detector's counting efficiency, the source should be counted sufficiently long so that the relative uncertainty (1σ) of the alpha peak(s) count is ≤3 to ≤1 percent.

DETECTOR BACKGROUND

A detector's background should be determined immediately after detector installation, instrument setup, detector calibration, or loss of control. The background counts in an alpha peak or a region of interest for the expected radionuclides should be integrated. A blank test source mount (filter

medium or blank electroplated mount) should be counted for a time interval between one and four times the typical test-source counting time. A detector background measurement should be conducted on a monthly basis, and the results tracked. When test sources contain certain radionuclides that may contaminate the detector (see Chapter 15), a background should be taken after counting the test source. A statistical test should be applied to determine if the detector background in a photopeak or region of interest has changed compared to the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method.

CALIBRATION QC CHECKS

When no radiotracer is used in a method, a detector efficiency determination should be performed at least monthly. The detector efficiency parameter should be recorded and evaluated for changes using a tolerance limit or control chart. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3% or 3σ. In addition, when a radiotracer is not used, a spectral energy response should be performed weekly.

Frequent use of a calibration source may lead to progressive contamination that may become significant, as a result of atom recoil from the source (Chapter 15). An electronic pulser may be used to check the spectrometry system, but not all parameters will be evaluated.

<div align="center">

TABLE 18.7 — **Example alpha spectrometry instrument calibration, background frequency, and performance criteria**

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Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Energy and FWHM peak resolution	Prior to initial use and after loss of control.	Verify manufacturer's specifications for alpha peak resolution and detector leakage current.
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Nonradiotracer applications – calibrate per quality manual For radiotracer applications, use radiotracer with every test source.	Verify manufacturer's specifications point-source efficiency. Nonradiotracer applications, calibrate each test source mounting geometry. For radiotracer and nonradiotracer applications, 1σ relative counting uncertainty ≤ 3% to ≤ 1%.
Detector Background	Detector background – ROIs or alpha peaks	Prior to initial use or after initial calibration and monthly.	Verify manufacturer's specifications. Count a blank test -source mount (filter medium or blank electrodeposited mount) for at least 1–4 times the typical test-source counting time and determine the ROI or alpha peak background levels for background subtraction and contamination control. Track background for each radionuclide's ROI or alpha peak. Use a statistical test to determine a change in the long background count rate value for a ROI or alpha peak.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration QC check – detector response check	Determine peak location, resolution, and ROI/alpha peak efficiency (where counting efficiency is an analytical requirement) using at least two alpha peaks.	When radiotracers are used routinely, the radiotracer can estimate the peak location, gross peak resolution, and provide the detector efficiency–chemical-yield factor. When no radiotracer is used, a detector efficiency check should be performed at least monthly and an energy check weekly.	For nonradiotracer detector response checks, use a tolerance limit or control chart: ±3% or 3σ.

18.5.6.4   Liquid Scintillation Systems

CALIBRATIONS

Following the setup of a liquid scintillation (LS) counting system, the manufacturer's specifications for counting efficiency should be verified with the appropriate reference radionuclides sources, typically unquenched LS cocktails tagged with ^{3}H and/or ^{14}C. As part of the instrument setup, the energy regions of interest (ROIs) or energy windows for the beta spectra of the radionuclides should be established. A tolerance limit or QC chart can be prepared at this time using unquenched LS standards.

The LS counting system should be calibrated specifically for a radionuclide/method application. Verify that the recommended dark-adapt time for each cocktail used in the analyses is consistent with the recommendation of the instrument or cocktail manufacturer. For method calibrations, two different approaches are taken commonly to determine the detector efficiency. These include the development of an efficiency-response/quench curve and the standard addition approach. When establishing a quench curve, a minimum of five calibration sources of different quench factors should be used, and the individual calibration sources should be counted to give a ROI relative counting uncertainty (1σ) of less than 1 percent. A mathematical function and quench curve should be developed so that the 95 percent confidence limit of the function is less than 5 percent over the expected quench range of the sources. For the standard addition approach, where a spike of the radionuclide of interest is added to a duplicate test source (or the original test source after the first analysis), the activity of the spike should be at least four times the anticipated maximum radionuclide activity in a test source. Such standard addition measurements assure that an unknown quench agent or interferent is not having an appreciable affect on the test source quench. The spiked test sources should be counted so that the ROI relative counting uncertainty is less than 3 percent. The deviation in duplicate spiked test source measurements should be evaluated statistically using the methods in Chapter 7 (*Evaluating Methods and Laboratories*) for matrix-spiked duplicates. This ensures that sample homogeneity and sample handling practices are not appreciably affecting the sample analysis.

INSTRUMENT BACKGROUND AND METHOD BLANKS

For methods that have quenched test sources, a quenched method blank (or mean of several quenched blanks) should be used to determine the background count rate that is subtracted from the count rate of the quenched test sources in a batch. A method background is determined by counting a blank sample that has been taken through the analytical process for the radionuclide of interest and determining its quench. When prepared in this manner, the blank will have a quench value similar to that of the test sources in the batch having the approximately the same quench factor. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. Multiple quenched blank measurements should be made to establish a mean quenched-background value and standard uncertainty of the mean (standard error of the mean). These parameters should be used to determine the net count rate (and combined standard uncertainty) of test sources within a batch of samples. The ROI count rate of the quenched blank test source (processed with each batch of test sources) should be recorded and monitored. A statistical test is recommended to determine a change in the quenched background from batch to batch.

For the standard addition approach to analyzing test sources, a blank sample should be processed with each batch of samples. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. The efficiency corrected blank activity (or mean of several batches) should be subtracted from the activities of the test sources uncorrected for chemical yield.

Longer instrument backgrounds with unquenched blank test sources may be taken for instrument-contamination control and to detect light leakage or photomultiplier tube degradation. This background measurement, which is the integral of the total energy spectrum, should be taken after initial instrument setup and monthly thereafter. The counting interval should be sufficiently long to reach an integrated spectrum count that has a relative 1σ counting uncertainty of about 1 percent. The background data should be recorded and monitored. A statistical test to determine a change in the long integrated background count rate value is recommended.

CALIBRATION QC CHECKS

Once a liquid scintillation counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, the unquench-ed reference radionuclides test sources (^{3}H and/or ^{14}C) provided by the manufacturer for instrument setup are used for the QC check sources. The detector's response, measured as the integrated counts in the energy ROIs for the beta spectra of the radionuclides, should be established. A tolerance limit or control chart (Section 18.3) is used to monitor the detector's response and to reveal changes in response that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the instrument setup and after instrument loss of control. Normally, a QC source is counted to reach a relative 1σ counting

uncertainty of under 1 percent in the ROI. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Once a tolerance limit or control chart has been established, an instrument/detector response check should be performed before each sample batch for short test-source counting intervals, and before and after a sample batch for longer counting intervals.

TABLE 18.8 — **Example liquid scintillation counting systems calibration, background frequency, and performance criteria**

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	ROI calibration with unquenched reference standards (typically ^{3}H and ^{14}C)	Prior to initial use and after loss of control and recalibrate per quality manual.	Verify sealed standards activity. Energy distribution of unquenched standard matches manufacturer's.
Method calibration (determining quenching)	Quench curve (at least five points) for each radionuclide and LS cocktail matrix.	Prior to method application, matrix, and cocktail changes. Recalibrate per quality manual.	Count individual calibration source to achieve ROI (1σ) measurement uncertainty of ≤1%. 95% confidence limit of the fitted function <5%
	Internal standard or standard addition – radionuclide of interest.	Add a spike to a duplicate processed sample or add a spike to a sample that has been counted and then recount.	Statistically evaluate replicate test-source analyses.
Background	Method background – quenched.	Each batch.	Use a statistical test to determine a change in the quenched background ROI count rate value.
	Long count background-unquenched blank.	Prior to initial use and monthly.	Monitoring of detector/ instrument contamination and electronic degradation based on integrated counts of entire spectrum.
Calibration QC Check – detector response check	ROI for unquenched reference standards (typically ^{3}H and/or ^{14}C)	Prior to use for short counting intervals. Before and after a test source batch for longer counting intervals.	Control chart or tolerance limit: ± 3σ or ± 3%.

18.5.7 Non-Nuclear Instrumentation

Radionuclides can also be measured using non-nuclear instrumentation such as mass spectrometry, fluorimetry, and phosphorimetry. These methods of analysis are discussed briefly in Chapter 15, *Quantification of Radionuclides*. Analysts can apply many of the laboratory QC techniques discussed in Sections 18.3, 18.4, and 18.6 because they are basic to any laboratory method. A quality program using statistically based control charts of the performance indicators will identify out-of-control situations, assist in improving laboratory performance, and aid in identifying the causes of trends and biases for any laboratory method. Analysts also need to

consider detection capabilities, radionuclide equilibrium, half-life, interferences, and blind samples when using non-nuclear instrumentation.

18.6 Related Concerns

18.6.1 Detection Capability

Issue: The *detection capability* of an analytical procedure is its ability to distinguish small amounts of analyte from zero (Chapter 20). The detection capability of a procedure can be estimated nominally and will depend on many factors.

Discussion: In radioanalysis, the most commonly used measure of detection capability is the minimum detectable concentration (Chapter 20). The MDC is defined as the smallest concentration of an analyte that has a specified probability of detection. The MDC is usually estimated as a nominal scoping performance measure of an analytical procedure, but a sample-specific version is reported routinely by many laboratories.

Detection capability is affected by many factors, including counting times, instrument background levels, aliquant volume, yield, decay times, and interferences. The nominal MDC is presumably based on conservative assumptions about these factors, but measurement conditions vary. The sample-specific MDC is calculated using the actual measured values of all these factors. A high MDC by itself does not indicate that a sample result is invalid or that it cannot be used for its intended purpose. However, if an analysis fails to detect the analyte of interest and the sample-specific MDC is greater than a detection limit required by contract or other agreement, it may be necessary to reanalyze the sample in a way that reduces the MDC. Such decisions should be made case-by-case, since it is not always cost-effective or even possible to reanalyze a sample, or it may not be feasible to achieve the desired MDC.

Excursions: A high sample-specific MDC can be caused by many factors, including:

• Small sample aliquant;
• Low chemical/tracer yield;
• Short counting times;
• Long decay/short ingrowth time;
• High background or blank value; and
• Low counting efficiency or sample self-attenuation.

18.6.2 Radioactive Equilibrium

Issue: It is sometimes necessary to ensure that target radionuclides are in radioactive equilibrium with their progeny, or to establish and correct for disequilibrium conditions. This is particularly

applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny. This is also applicable for nondestructive assays like gamma spectrometry where photon emission from progeny is used to determine the concentration of the non-gamma ray emitting parent (see Attachment 14A following Chapter 14 for a more thorough discussion on radioactive equilibrium).

Discussion: Some radionuclides that have long physical half-lives decay to species whose half-lives are shorter by several orders of magnitude. Following chemical separation of the parent, the progeny can "grow in" within a time frame relevant to analysis and provide measurable radio-active emissions that should be considered in the analytical method. The condition where the parent and progeny radionuclide are equal in activity is called "secular equilibrium." An example is ^{226}R, a common, naturally occurring radionuclide in the uranium series with a half-life of about 1,600 years. ^{226}Ra is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides that begins with the 3.8-day-half-life ^{222}Rn and ends with stable lead. As soon as ^{226}Ra is chemically separated from its progeny in an analytical procedure via coprecipitation with barium sulfate, its progeny begin to reaccumulate. The progeny exhibit a variety of alpha, beta and gamma emissions, some of which will be detected when the precipitate is counted. The activity due to the ingrowth of radon progeny should be considered when evaluating the counting data (Kirby, 1954). If counting is performed soon after chemical separation, secular equilibrium will be substantially incomplete and a sample-specific correction factor should be calculated and applied. In some cases, it may be necessary to derive correction factors for radioactive ingrowth and decay during the time the sample is counting. These factors are radionuclide specific, and should be evaluated for each analytical method.

Secular equilibrium concerns also apply to non destructive assays, particularly for uranium and thorium series radionuclides. Important radionuclides in these series (e.g., ^{238}U and ^{232}Th) have photon emissions that are weak or otherwise difficult to measure, while their shorter-lived primary, secondary or tertiary progeny are easily measured. This allows for the parents to be quantified indirectly, i.e., their concentration is determined by measuring their progeny and accounting for the amount of parent-progeny equilibrium. The amount of parent-progeny secular equilibrium is fundamental to these analyses, and data should be scrutinized to insure that the amount is valid.

When several radionuclides from one decay chain are measured in a sample, observed activity ratios can be compared to those predicted by decay and ingrowth calculations, the history of the sample and other information. For example, undisturbed soil typically contains natural uranium with approximately equal activities of ^{238}U and ^{234}U, while water samples often have very different ^{238}U/^{234}U ratio. Data from ores or materials involved in processing that could disrupt naturally occurring relationships require close attention in this regard.

All numerical protocols (electronic and manual) should be evaluated to determine if there is bias

with respect to correction factors related to equilibrium concerns. This includes a check of all constants and units used to derive such correction factors, as well as the use of input data that unambiguously state the time of all pertinent events (chemical separation and sample counting). The analyst should ensure that samples requiring progeny ingrowth are held for sufficient time before counting to establish secular equilibrium. Limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. For ingrowth, the limits should reflect the minimum time required to ensure that the radionuclide(s) of interest has accumulated sufficiently to not adversely affect the detection limit or uncertainty. Conversely, the time for radioactive decay of the radionuclides of interest should be limited such that the decay factor does not elevate the MDC or adversely affect the measurement uncertainty. These will vary depending on the radionuclide(s) and analytical method.

Excursions: Samples where equilibrium is incorrectly assumed or calculated will produce data that do not represent the true sample concentrations. It is difficult to detect errors in equilibrium assumptions or calculations. Frequently, it takes anomalous or unanticipated results to identify these errors. In these cases, analysts need to know the sample history or characteristics before equilibrium errors can be identified and corrected. Some samples may not be amenable to nondestructive assays because their equilibrium status cannot be determined; in such cases, other analytical methods are indicated.

Examples:

> **Isotopic Distribution – Natural, Enriched and Depleted Uranium**: Isotopic distribution is particularly important with respect to uranium, an element that is ubiquitous in nature in soils and also a contaminant in many site cleanups. The three predominant uranium isotopes of interest are ^{238}U, ^{234}U, and ^{235}U, which constitute 99.2745, 0.0055, and 0.72 atom percent, respectively, of "natural" uranium,[3] i.e., uranium as found in nature (Parrington et al., 1996). However, human activities related to uranium typically involve changing the ratio of natural uranium by separating the more readily fissionable ^{235}U from natural uranium to produce material "enriched" in ^{235}U, for use in fuel cycle and nuclear weapons related activities.[4] Typical ^{235}U enrichments range from 2 percent for commercial reactor fuels to greater than 90 percent ^{235}U for weapons. The enrichment process also produces material that is "depleted" in ^{235}U, i.e., the uranium from which the ^{235}U was taken. While the ^{235}U concentrations of depleted uranium are reduced relative to natural ores, they still can be measured by several assay techniques. This gives rise to uranium with three distinct distributions of ^{238}U, ^{235}U, and ^{234}U, referred to as "natural," "enriched," and "depleted" uranium. Because ^{238}U, ^{235}U, and

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[3] The "natural abundance" of ^{235}U of 0.72 atom percent is a commonly accepted average. Actual values from specific ore samples vary.

[4] Enriched and depleted refer primarily to ^{235}U.

^{234}U are alpha emitters with considerably different physical half-lives and specific activities, a measurement of a sample's total uranium alpha activity cannot be used to quantify the sample's isotopic composition or uranium mass without knowing if the uranium is natural or has been enriched or depleted in ^{235}U. However, if this information is known, measurement and distribution of the sample's uranium alpha activity can be used to infer values for a sample's uranium mass and for the activities of the isotopes ^{238}U, ^{235}U, and ^{234}U. This ratio can be determined directly or empirically using mass or alpha spectrometry, techniques which are time and cost intensive, but which provide the material's definitive isotopic distribution. It is often practical to perform mass or alpha spectrometry on representative samples from a site to establish the material's isotopic distribution, assuming all samples from a given area are comparable in this respect. Once established, this ratio can be applied to measurements of uranium alpha activity to derive activity concentrations for ^{238}U, ^{234}U, and ^{235}U data.

18.6.3 Half-Life

Issue: Radionuclides with short half-lives relative to the time frame of the analysis may decay significantly from the time of sample collection or chemical separation to counting. In some cases, this decay will cause the ingrowth of other short-lived radionuclides. In both instances, sample-specific factors should be applied to correct the sample's observed counting/disintegration rate. Also, determination of half-life could indicate sample purity. If radioactive impurities are not appropriately corrected, analytical errors will occur. Repetitive counting of the test source may confirm the radionuclide's half-life, and thus the radioactive purity of the test source.

Discussion: When assaying for short-lived radionuclides, data should be corrected for decay over the time period between sample collection and counting. For example, operating power reactors routinely assay environmental samples for ^{131}I, a fission product with about an eight-day half-life. Samples may be counted for several days up to two weeks, during which time their ^{131}I concentration is decreasing via radioactive decay. Using the eight-day half-life, the counting data should be decay-corrected to the ending time of collection in the field and corrected for decay before and during counting. If desired, environmental samples can be decay-corrected to a time other than sample collection.

Half-life considerations also apply to radionuclide ingrowth. Certain radionuclides are assayed by an initial chemical separation, which begins a time period over which their direct progeny are allowed to reach a near-secular equilibrium condition. This is followed by additional chemical separation, purification, and counting of the progeny. The degree of the progeny's ingrowth is calculated based on the radionuclides' half-lives and the elapsed time between the two chemical separations. Allowance should also be made for the progeny's decay from separation to counting and for decay that occurred while counting, if applicable. Two examples are the beta emitting radionuclides ^{228}Ra and ^{90}Sr: they are quantified by measuring the direct progeny of each, ^{228}Ac and ^{90}Y, respectively. For airborne concentrations of ^{222}Rn, sample collection and analytical

methods should incorporate concerns related to the short-lived progeny of other radon species, such as ^{220}Rn. Other half-life related considerations apply to alpha spectrometry when assaying samples for uranium and thorium chain radionuclides. Samples that have been allowed to sit for several weeks may accumulate short-lived radionuclides that have alpha emissions whose energies are in close proximity to target radionuclides. These can interfere with quantitative analyses of the target radionuclides. Chemical yield tracers used in alpha spectrometry, such as ^{234}Th and ^{232}U, can cause this effect due to their short-lived progeny and all chemical yield tracers should be scrutinized for this potential prior to their use in analytical methods. Radionuclide specific limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. These should be based on limiting the adverse effect of such calculations on the detection limit and measurement uncertainty. All analytical methods involving computational corrections for radioactive decay of the target species should be evaluated relative to half-life and secular equilibrium related concerns. This evaluation should be incorporated in the routine data review process that is performed on all analytical results.

A good source for radionuclide half-lives and other nuclear data can be found at the Brookhaven National Laboratory's National Nuclear Data Center (www.nndc.bnl.gov/nndc/nudat/). Using this data source will ensure consistency within and among laboratories, and will provide analysts with the current values.

Excursions: Samples that are assayed by "non destructive" techniques like gamma spectrometry may provide indications of potential complications due to half-life related considerations. Because the assay provides information on photon emitting radionuclides in the sample, the analyst can develop appropriate corrections for half-life related phenomena. However, non-spectrometric techniques like gas flow proportional counting are essentially gross counting procedures that record all events without any indication of their origin. Therefore, these data should be evaluated to ensure they are free from half-life related considerations (e.g., radionuclide purity).

Samples with short-lived radionuclide concentrations at or near environmental background will experience elevated detection limits and increased measurement uncertainty if there is excessive elapsed time between sample collection and counting. Because of the magnitude of the additional correction (decay) factor for these samples, they usually have a larger measurement uncertainty compared to longer-lived radionuclides, given equal measurement and sample conditions and parameters.

18.6.4 Interferences

Issue: Chemical or radionuclide interferences can produce erroneous results or increased measurement uncertainty.

Discussion: Analytical samples, particularly environmental samples, are often chemically complex. This complexity may include chemical constituents that interfere with an analytical method to the point that they require modification of the method. Examples of modifications include limiting the size of the sample aliquant, quantifying interfering compounds through other analyses (radiometric and non-radiometric) and changing time periods to allow adequate ingrowth of target radionuclides or decay of interferences.

A common example is groundwater or well water that contains high concentrations of salts or dissolved solids, so that screening for gross alpha activity produces erratic or anomalous results. For such samples, it may be necessary to limit the aliquant volume with the resulting increase in detection limit and measurement uncertainty. There is a salt concentration at which this procedure cannot overcome the interferences and should not be used.

Samples that contain natural concentrations of stable or radioactive compounds that are added during an analytical procedure (e.g., carrier or tracer) may also cause interference problems. Because barium is used as a carrier, water samples that contain a high concentration of barium may provide inaccurate carrier yields when screened for alpha-emitting radium isotopes. Quantifying the sample's barium content prospectively via a non-radiometric technique (e.g., atomic absorption) would be required to correct for this interference. With respect to radioactive compounds, two examples are provided. The first involves the radiochemical procedure for determining ^{228}Ra in drinking water that separates radium via coprecipitation with barium sulfate. The precipitate is allowed to come to equilibrium with its direct progeny ^{228}Ac, which is separated via co-precipitation with yttrium oxalate, purified, mounted and counted. The yttrium precipitate also carries ^{90}Y, the direct progeny of ^{90}Sr, a fission product often found in environmental samples as a result of atmospheric weapons testing and nuclear fuel cycle activities. The results of samples assayed for ^{228}Ra that contain measurable amounts of ^{90}Sr require corrections because of the differences in half-lives (^{228}Ac with a 6-hour half-life versus ^{90}Y with a half-life of about 64 hours) or other parameters. The second example involves alpha spectrometry procedures that use tracers to determine chemical yield. For example, ^{234}Th is used as a chemical yield tracer for isotopic thorium analyses. The approach assumes that the sample's inherent concentration of the tracer radionuclide is insignificant such that it will not interfere with the tracer's ability to accurately represent the sample's chemical yield. Samples that contain measurable amounts of these radionuclides may produce excessive interference and may not be amenable to this procedure.

Alpha spectra should be checked for radionuclide interferences (e.g., a ^{232}Th peak in uranium spectra). If the ^{232}Th peak is present due to incomplete chemical separation, ^{230}Th may represent interference in the ^{234}U determination. Data should be corrected or the samples reanalyzed with better target-radionuclide purification.

Each analytical method should be evaluated with respect to interferences during the method-

validation stage. Such evaluations can be based on available information and, if properly documented, can serve as the basis for developing the range of applicability, which becomes an integral part of the protocol. Evaluating performance indicators aids in the identification of samples that have interferences. All performance criteria would be protocol specific, and have clearly established acceptance ranges that incorporate the potential interferences discussed above.

Excursions: Interfering elements can affect measurement results in several ways. For example, large amounts of non-analyte elements may overload ion exchange resins, affecting the resin's ability to collect all of the analyte. In addition, spiking elements, already in the sample prior to preparation, may cause matrix spike results to exceed acceptance limits.

Carrier/tracer yields exhibiting gradual changes that appear to be correlated with a batch or group of samples from the same sampling location may indicate potentially interfering conditions. A significant decrease in the carrier/tracer yield may indicate that the analytical method is not functioning as planned. Yields that are significantly low or in excess of 100 percent may be caused by competing reactions within the sample matrix, or by the presence of an inherent carrier or tracer within the sample.

For screening analyses, e.g., gross alpha or beta, large changes in counting efficiencies or erratic counting data can reflect the presence of salts. Samples of this type are hygroscopic and continue to gain weight following preparation as they absorb moisture from the air. These changes could be detected by reweighing the planchets directly prior to counting. These samples can be converted to oxides by carefully holding them over the open flame of a laboratory burner; however, this will cause losses of volatile radionuclides, such as ^{210}Po and ^{137}Cs, which have alpha and beta emissions, respectively. An alternative approach is to thoroughly dry each planchet, record the weight and count it immediately, followed by a post-counting weighing to ensure that the weight did not change significantly over the measurement period. This approach may not be practical for all laboratories.

18.6.5 Negative Results

Issue: When an instrument background measurement is subtracted from a measurement of a low-activity sample, it is possible to obtain a net activity value less than zero.

Discussion: Many factors influence the evaluation of negative results. The simplest case occurs when the background measurement is unbiased and both the gross counts and background counts are high enough that the distribution of the net count rate is approximately normal. In this case, normal statistics can be used to determine whether a negative result indicates a problem. For example, if a sample contains zero activity, there is a very small probability of obtaining a net count rate more than two-and-a-half or three standard deviations below zero (i.e., negative value). Since the combined standard uncertainty is an estimate of the standard deviation, a result

$$\frac{2\sigma}{\sqrt{\pi}} \approx 1.128\,\sigma \tag{18.8}$$

which may be estimated by

$$\overline{MR} = \frac{1}{n-1} \sum_{i=1}^{n-1} \left| X_{i+1} - X_i \right| \tag{18.9}$$

So, σ is estimated by $\overline{MR} / 1.128$. The moving-range estimate of σ may be preferred because it is less sensitive to outliers in the data. Furthermore, when consecutive values of X_i are correlated, as for example when a trend is present, the moving-range estimate may produce narrower control limits, which will tend to lead to earlier corrective action.

Procedure 18.1 (*X* chart). Determine the central line, control limits, and warning limits for an X chart based on a series of n independent measurements, which produce the measured values $X_1, X_2, \ldots, X_n$, during a period when the measurement process is in a state of statistical control. At least 2 measurements *must* be used. Ideally, at least 20 measurements should be used.

Procedure:
1. Calculate the sum $\sum_{i=1}^{n} X_i$
2. Calculate the arithmetic mean $\overline{X}$ using the formula

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

3. Calculate an unbiased estimate $\overline{\sigma}$ of the standard deviation (e.g., s / c_4 or $\overline{MR} / 1.128$)
4. Define the central line, control limits, and warning limits as follows:

$$CL = \overline{X} \qquad \begin{array}{ll} UCL = \overline{X} + 3\overline{\sigma} & LWL = \overline{X} - 2\overline{\sigma} \\ LCL = \overline{X} - 3\overline{\sigma} & UWL = \overline{X} + 2\overline{\sigma} \end{array}$$

If n is less than 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. So, fewer than 20 measured values should be used only if 20 values cannot be obtained; and the limits should be recalculated when 20 values become available.

EXAMPLE

Problem: Suppose a series of 20 observations of a parameter yield the following normally distributed values:

1,118.9 1,110.5 1,118.3 1,091.0 1,099.8 1,113.7 1,114.4 1,075.1 1,112.8 1,103.7
1,120.5 1,104.0 1,125.7 1,117.6 1,097.6 1,099.8 1,102.3 1,119.9 1,107.8 1,114.9

Determine the central line and warning and control limits for future measurements.

Solution:

Step 1   Calculate ΣX_i = 22,168.3

Step 2   Calculate the mean $\overline{X}$ = 22,168.3 / 20 = 1,108.415

Step 3   Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20-1}\sum_{i=1}^{20}(X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18.1 (or estimate $c_4 \approx \frac{4n-4}{4n-3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4   Define the central line, control limits, and warning limits as follows:

CL = 1,108.415
UCL = 1,108.415 + 3(12.2037) = 1,145.0
LCL = 1,108.415 − 3(12.2037) = 1,071.8
UWL = 1,108.415 + 2(12.2037) = 1,132.8
LWL = 1,108.415 − 2(12.2037) = 1,084.0

18A.3 $\overline{X}$ Charts

When subgroup averages are plotted on a control chart, Steps 1 and 2 of Procedure 18.1 may be used to determine the arithmetic mean $\overline{X}$ and the standard deviation $\overline{\sigma}$ of a prior set of data $X_1, X_2, \ldots, X_n$. If k denotes the size of the subgroup, the central line, control limits, and warning limits for the subgroup average are calculated using the formulas

$$CL_{\overline{X}} = \overline{X}$$

$$UCL_{\overline{X}} = \overline{X} + 3\overline{\sigma} / \sqrt{k} \qquad UWL_{\overline{X}} = \overline{X} + 2\overline{\sigma} / \sqrt{k}$$

$$LCL_{\overline{X}} = \overline{X} - 3\overline{\sigma} / \sqrt{k} \qquad LWL_{\overline{X}} = \overline{X} - 2\overline{\sigma} / \sqrt{k}$$

If n is less than about 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. For this reason fewer than 20 measured values should be used only if 20 values cannot be obtained.

EXAMPLE

Problem: Use the data from the preceding example to determine warning and control limits for subgroup averages when the subgroup size is $k = 5$.

Solution:

Step 1   Calculate $\sum X_i = 22{,}168.3$

Step 2   Calculate the mean $\overline{X} = 22{,}168.3 / 20 = 1{,}108.415$

Step 3   Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20-1} \sum_{i=1}^{20} (X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18A-1 (or estimate $c_4 \approx \frac{4n-4}{4n-3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4   Define the central line, control limits, and warning limits as follows:

$$CL_{\overline{X}} = 1{,}108.415$$
$$LCL_{\overline{X}} = 1{,}108.415 - 3(12.2037) / \sqrt{5} = 1{,}092.0$$
$$UCL_{\overline{X}} = 1{,}108.415 + 3(12.2037) / \sqrt{5} = 1{,}124.8$$
$$LWL_{\overline{X}} = 1{,}108.415 - 2(12.2037) / \sqrt{5} = 1{,}097.5$$
$$UWL_{\overline{X}} = 1{,}108.415 + 2(12.2037) / \sqrt{5} = 1{,}119.3$$

18A.4 *R* Charts

The *range* of a set of values is defined as the difference between the largest value and the smallest value in the set. When data are collected in subgroups, as described above, the range of each subgroup may be plotted on a *range chart*, or *R chart*, to monitor within-group variability.

The central line for an *R* chart can be obtained by averaging the observed ranges for a series of subgroups. Then the upper control limit for the chart can be obtained by multiplying the average range, $\overline{R}$, by a factor, denoted by D_4, whose value depends on the subgroup size, *N*. When $N \geq 7$, there is another factor, D_3, by which $\overline{R}$ can be multiplied to give the lower control limit. When $N < 7$, the *R* chart has no lower control limit. Values for D_3 and D_4 are tabulated in *Manual on Presentation of Data and Control Chart Analysis* (ASTM MNL7), as well as many other references.

For example, if an analyst makes a series of duplicate measurements of some quantity ($N = 2$), the central line of the *R* chart equals the average of the measured ranges, $\overline{R}$; the upper control limit equals the product of $\overline{R}$ and the factor D_4, whose value is 3.267 for duplicate measurements. The steps for calculating the central line and upper control limit when $N = 2$ are shown explicitly in Procedure 18.2 below.

Procedure 18.2 (*R* chart). Determine the central line and control limits for a *R* chart based on a series of *n* independent sets of duplicate measurements, which produce the values R_1, R_2, …,R_n, during a period when the measurement process is in a state of statistical control.

Procedure:
1. Calculate the range, R_i, of each pair of duplicate measurements, (x_i, y_i)

$$R_i = |x_i - y_i|$$

2. Calculate the mean range, $\overline{R}$, using the formula

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

3. Calculate the upper control limit as $\text{UCL} = 3.267\,\overline{R}$

This approach may also be used for the moving range of a series of individual results.

EXAMPLE

Problem: Suppose a series of 20 duplicate observations of a parameter yield the following pairs of values.

(0.501, 0.491) (0.490, 0.490) (0.479, 0.482) (0.520, 0.512) (0.500, 0.490)
(0.510, 0.488) (0.505, 0.500) (0.475, 0.493) (0.500, 0.515) (0.498, 0.501)
(0.523, 0.516) (0.500, 0.512) (0.513, 0.503) (0.512, 0.497) (0.502, 0.500)
(0.506, 0.508) (0.485, 0.503) (0.484, 0.487) (0.512, 0.495) (0.509, 0.500)

Determine the central line and upper control limit for the range of future pairs of measurements.

Solution:

Step 1   Calculate the range of each of the 20 pairs:

0.010	0.000	0.003	0.008	0.010
0.022	0.005	0.018	0.015	0.003
0.007	0.012	0.010	0.015	0.002
0.002	0.018	0.003	0.017	0.009

Step 2

Calculate the mean range $\overline{R} = \dfrac{1}{20} \sum_{i=1}^{20} R_i = \dfrac{0.189}{20} = 0.00945$

Step 3   Calculate the upper control limit: UCL $= 3.267\,\overline{R} = (3.267)(0.00945) = 0.0309$

18A.5 Control Charts for Instrument Response

A radioactive check source should be used to monitor the radiation response/efficiency of every radiation counting instrument. MARLAP recommends that the activity and count time for the source be chosen to give no more than 1 percent counting uncertainty (ANSI N42.23). In other words, at least 10,000 counts should be obtained in each measurement of the source. There may be cases when placing a high-activity source in a detector is undesirable, so obtaining 10,000 counts is impractical.

The instrument response may not have a Poisson distribution. In this case, if the check source is long-lived, an X or $\overline{X}$ chart based on replicate measurements should be set up. For example, an X or $\overline{X}$ chart is the appropriate radiation response/efficiency chart for a high-purity germanium detector when the area of a specific photopeak is monitored, since the calculated size of the photopeak may have significant sources of uncertainty in addition to counting uncertainty. An X or $\overline{X}$ chart may be used even if the response is truly Poisson, since the Poisson distribution in this case is approximated well by a normal distribution, but slightly better warning and control limits are obtained by using the unique properties of the Poisson distribution.

Standard guidance documents recommend two types of control charts for Poisson data. A "*c* chart" typically is used in industrial quality control to monitor the number of manufacturing defects per item. A "*u* chart" is used to monitor the number of defects per unit "area of opportunity," when the area of opportunity may vary. Thus, the values plotted on a *c* chart are counts and those plotted on a *u* chart are count rates. The same two types of charts may be adapted for monitoring counts and count rates produced by a radioactive check source. When a *u* chart is used, the "area of opportunity" equals the product of the count time and the source decay factor. In radiation laboratories a variant of the *u* chart is more often used when the count time remains fixed but the decay factor changes during the time when the chart is in use.

Before using control limits derived from the Poisson model, one should use Procedure E1, described in Section 18B.2 of Attachment 18B, to confirm experimentally that the Poisson approximation is adequate and that any excess variance is relatively small at the expected count rate. Factors such as source position that may vary during routine QC measurements should be varied to the same degree during the experiment.

Calculation of warning and control limits using the Poisson model requires only a precise measurement of the source at a time when the instrument is operating properly at the time of calibration. The precision can be improved either by counting the source longer or by averaging several measurements. In principle both approaches should provide equally good estimates of the count rate; however, an advantage of the latter approach is that it can provide the data needed to detect excess variance (using Procedure E1).

Procedures 18.2 and 18.3, listed below, may be used to determine warning and control limits for measurements of a radioactive check source when the total count follows the Poisson model. Procedure 18.2 is for control charts and should be used only when the expected count in each measurement is the same, for example when the source is long-lived and all count durations are equal. Procedure 18.3, which implements an alternative to the *u* chart, may be used in all other cases.

Procedure 18.2 (Control chart for Poisson efficiency check data with constant mean). A check source is counted n times on an instrument, producing the measured counts N_1, N_2, …, N_n. (Ideally, n is at least 20.) Determine control limits and warning limits for future measurements of the source count on the same instrument.

Procedure:
1. Estimate the central line by

$$\text{CL} = \frac{1}{n} \sum_{i=1}^{n} N_i$$

and the standard deviation by

$$s = \sqrt{CL}$$

NOTE: The estimate s is biased, but the bias is negligible for the large number of counts typically obtained from a check source.

2. Define the control limits and warning limits (in counts) as follows:

$$UCL = CL + 3s \qquad UWL = CL + 2s$$
$$LCL = CL - 3s \qquad LWL = CL - 2s$$

If n is less than 20, a higher rate of false warnings and failures may occur because of the uncertainty in the estimate of the mean. So, fewer than 20 measurements should be used only if 20 measured values are not available.

Procedure 18.3 (Control chart for Poisson efficiency check data with variable mean). A check source is counted n times ($n \geq 1$) on an instrument, producing the measured counts N_1, N_2, …, N_n. (It is assumed that the background level is negligible when compared to the source count rate.) Let t_i denote the duration of the i^{th} measurement and d_i the decay factor [for example, $\exp(-\lambda(\Delta t + 0.5\,t_i))$]. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is T and the decay factor is D.

Procedure:
1. Compute the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i d_i$.
2. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$CL = \hat{r}\,TD$$

and the standard deviation s by

$$s = \sqrt{CL}$$

4.   Define the control limits and warning limits as follows:

$$UCL = CL + 3s \qquad UWL = CL + 2s$$
$$LCL = CL - 3s \qquad LWL = CL - 2s$$

If $\Sigma t_i d_i < 20\,TD$, a higher rate of false warnings and failures may occur because of increased uncertainty in the estimate of the count rate $\hat{r}$.

EXAMPLE

Problem: A source containing ^{90}Sr and ^{90}Y in equilibrium is used for efficiency checks on a proportional counter. Near the time of calibration, a series of twenty 600-s measurements are made. The observed counts are as follows:

12,262 12,561 12,606 12,381 12,394 12,518 12,399 12,556 12,565 12,444
12,432 12,723 12,514 12,389 12,383 12,492 12,521 12,619 12,397 12,562

Assume all twenty measurements are made approximately at time 0, so the ten decay factors d_i are all equal to 1. Use Procedure 18.3 to calculate lower and upper control limits for a 600-s measurement of the same source at a time exactly 1 year later.

Solution:

Step 1   Compute the sums $\Sigma N_i = 249{,}718$ and $\Sigma t_i d_i = 12{,}000$.

Step 2   Calculate $\hat{r} = \dfrac{\Sigma N_i}{\Sigma t_i d_i} = \dfrac{249{,}718}{12{,}000} = 20.80983$

Step 3   The decay time for the final measurement is 1 y = 31,557,600 s. The corresponding decay factor is $D = 0.976055$. The count time is $T = 600$ s. So, compute
$$CL = (20.80983)(600)(0.976055) = 12{,}187$$
and
$$s = \sqrt{12{,}187} = 110.39$$

Step 4   The control limits and warning limits are
$$UCL = 12{,}187 + 3 \times 110.39 = 12{,}518$$
$$LCL = 12{,}187 - 3 \times 110.39 = 11{,}856$$
$$UWL = 12{,}187 + 2 \times 110.39 = 12{,}408$$
$$LWL = 12{,}187 - 2 \times 110.39 = 11{,}966$$

If substantial excess (non-Poisson) variance is present in the data, the simple Poisson charts described above should not be used. The *c* chart may be replaced by an *X* chart or $\overline{X}$ chart, but a new type of chart is needed to replace the *u* chart. To determine warning and control limits for this chart, one must determine the relative excess variance of the data ξ^2. A value of ξ^2 may be assumed or it may be estimated using procedures described in Attachment 18B. Then Procedure 18.3 may be replaced by the Procedure 18.4, shown below.

Procedure 18.4 (Control chart for Poisson efficiency check data with excess variance). A check source is counted *n* times on an instrument, producing the measured counts $N_1, N_2, \ldots, N_n$. Let t_i denote the duration of the i^{th} measurement and d_i the decay factor. Let the data follow an approximately Poisson distribution with relative excess variance ξ^2. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is *T* and the decay factor is *D*.

Procedure:
1. Compute the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i d_i$
2. Estimate the mean decay-corrected count rate $\hat{r}$ by

$$\hat{r} = \frac{\displaystyle\sum_{i=1}^{n} \frac{N_i}{1 + r_0 t_i d_i \xi^2}}{\displaystyle\sum_{i=1}^{n} \frac{1}{1 + r_0 t_i d_i \xi^2}} \qquad \text{where} \qquad r_0 = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$\text{CL} = \hat{r} \, T D$$

and the standard deviation *s* by

$$s = \sqrt{\text{CL} + \xi^2 \text{CL}^2}$$

4. Define the control limits and warning limits as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

18A.6 References

American National Standard Institute (ANSI) N42.23. "Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories." 2003.

American Society for Testing and Materials (ASTM) D6299. *Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance*, 2000, West Conshohocken, Pennsylvania.

American Society for Testing and Materials (ASTM) E882, *Standard Guide for Accountability and Quality Control in the Chemical Analysis Laboratory*, 1998, West Conshohocken, Pennsylvania.

American Society for Testing and Materials (ASTM) MNL 7, *Manual on Presentation of Data and Control Chart Analysis* ASTM Manual Series, 7th Edition, 2002

National Bureau of Standards (NBS). 1964. *Handbook of Mathematical Functions*. M. Abramowitz and Stegun, I., Editors.

ATTACHMENT 18B
Statistical Tests for QC Results

18B.1 Introduction

Attachment 18A describes several types of control charts that may be used for statistical quality control in the laboratory. This attachment describes additional statistical methods that may be used, where appropriate, to test the performance of measurement results from blank, replicate, LCS, spikes, CRM, yield-monitor, background, efficiency, calibration, or peak resolution results, with special emphasis on instrumentation results.

18B.2 Tests for Excess Variance in the Instrument Response

As noted in Chapter 19, the counting uncertainty given by the Poisson approximation does not describe the total variability in a counting measurement. A number of factors may generate a small excess component of variance. When a large number of counts are obtained in the measurement, the relative magnitude of the Poisson variance is small; so, the excess component may dominate.

Regardless of whether replication or the Poisson approximation is used to estimate counting uncertainties, MARLAP recommends that a series of check source measurements be made on each instrument periodically to test for excess variance. Procedure E1, which is presented below, may be used to evaluate the measurement results. To check the stability of the instrument itself, one should perform the measurements while holding constant any controllable factors, such as source position, that might increase the variance. To check the variance when such factors are not constant, one may use Procedure E1 but vary the factors randomly for each measurement.

Assume n measurements of the source produce the counts $N_1, N_2, \ldots, N_n$. If the expected count for each measurement is at least 20, so that the Poisson distribution is approximated by a normal distribution, and if the average decay-corrected count rate $\hat{r}$ is determined with adequate precision, then the quantity

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i d_i} - \hat{r} \right)^2 t_i d_i \tag{18.10}$$

where t_i and d_i are the count time and source decay factor for the i^{th} measurement, respectively, should be distributed approximately as chi-square with $n - 1$ degrees of freedom.[5] The precision

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[5] If r denotes the true mean decay-corrected count rate, then under the null hypothesis each measured count rate $N_i / t_i d_i$ is approximately normal with mean r and variance $r / t_i d_i$, and the least-squares estimator for r is $\hat{r} = \sum N_i / \sum t_i d_i$. So, the sum $\sum (N_i / t_i d_i - \hat{r})^2 / (r / t_i d_i)$ is approximately chi-square with $n - 1$ degrees of freedom.

of the estimate $\hat{r}$ should be adequate for the test as long as the expected count for each measurement is at least 20. Since a check source is involved, the expected count is usually much greater than 20.

Procedure E1. The χ^2 (chi-square) analysis can be used to determine whether a series of measurements of a check source provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement. Let $w_i = t_i d_i$, where t_i denotes the count time and d_i denotes the source decay factor (if relevant). If all the values w_i are equal, one may use $w_i = 1$ instead for all i. It is assumed either that the background count rate is negligible or that the decay factors are all nearly equal, so that the expected count in each measurement is proportional to w_i.[6] The procedure tests the null hypothesis that the total measurement variance is the Poisson counting variance.

Procedure:
1. Choose the significance level α
2. Calculate the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} w_i$
3. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} w_i} \tag{18.11}$$

4. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i \tag{18.12}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case conclude that the variance is greater than predicted by the Poisson model.

If $\hat{r}$ is determined accurately, the true mean count rate r may be replaced in the formula by its estimated value $\hat{r}$ to obtain the formula that appears in the text. If all the products $t_i d_i$ are equal, they cancel out of the sum, which becomes $\sum(N_i - \overline{N})^2 / \overline{N}$, as described by Evans (1955), Goldin (1984), and Knoll (1989).

[6] The expected gross count for the i^{th} measurement equals $R_B t_i + r w_i$, where r is the mean net count rate at time 0. The expected count is proportional to w_i if $R_B = 0$, or if all the decay factors are equal so that $t_i \propto w_i$.

EXAMPLE

Problem: A long-lived source is counted $n = 20$ times in a gross radiation detector and the duration of each measurement is 300 s. The following total counts are measured:

> 11,189 11,105 11,183 10,910 10,998 11,137 11,144 10,751 11,128 11,037
> 11,205 11,040 11,257 11,176 10,976 10,998 11,023 11,199 11,078 11,149

Are these data consistent with the assumption that the measurement variance is no greater than predicted by the Poisson model? Use 5 percent as the significance level.

Solution:

Step 1   The significance level is specified to be $\alpha = 0.05$

Step 2   Since the source is long-lived and all the count times are equal, let $w_i = 1$ for each i. Calculate $\Sigma N_i = 221{,}683$ and $\Sigma w_i = 20$

Step 3   Calculate the mean count rate $\hat{r} = 221{,}683 / 20 = 11{,}084.15$

Step 4   Calculate the chi-square statistic

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i = \frac{1}{11{,}084.15} \sum_{i=1}^{20} (N_i - 11{,}084.15)^2 = 24.87$$

Step 5   The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $24.87 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the assumption of Poisson counting statistics at the 5 percent significance level.

A two-sided version of Procedure E1 may also be used to test whether the measurement variance is either greater than or less than predicted by the Poisson model. Step 5 must be changed so that the null hypothesis is rejected if the value of the test statistic χ^2 does not lie between the two quantiles $\chi^2_{\alpha/2}(n - 1)$ and $\chi^2_{1-\alpha/2}(n - 1)$.

A chi-square test may require many measurements or long count times to detect a small excess variance component. When all measurements have the same expected count μ, the detection limit for the *relative* excess variance, or its minimum detectable value, is equal to

$$\xi_D^2 = \frac{1}{\mu} \left(\frac{\chi^2_{1-\alpha}(n - 1)}{\chi^2_{\beta}(n - 1)} - 1 \right) \tag{18.13}$$

where β is the specified probability of a type II error (failure to detect) (Currie,1972). Note that since ξ_D^2 represents a relative variance, its square root ξ_D represents a relative standard deviation.

EXAMPLE: A long-lived source is counted 20 times, and each measurement has the same duration. The average of the measured counts is 10,816. If $\alpha = \beta = 0.05$, the minimum detectable value of the relative excess variance is estimated by

$$\xi_D^2 = \frac{1}{10{,}816}\left(\frac{\chi_{0.95}^2(19)}{\chi_{0.05}^2(19)} - 1 \right) = \frac{1}{10{,}816}\left(\frac{30.14}{10.12} - 1 \right) = \frac{1.978}{10{,}816} = 1.829 \times 10^{-4}$$

which corresponds to a relative standard deviation $\xi_D = \sqrt{1.829 \times 10^{-4}} = 0.01352$, or about 1.35 percent.

If (1) the relative excess variance in a measurement is not affected by count time, (2) a fixed total count time is available, and (3) all measurements have the same expected count (e.g., when all count times are equal and the source is long-lived), then it is possible to determine the number of measurements that minimizes ξ_D^2 (Currie, 1972). The optimal number is the number n that minimizes the quantity

$$F(n) = n\left(\frac{\chi_{1-\alpha}^2(n-1)}{\chi_{\beta}^2(n-1)} - 1 \right) \tag{18.14}$$

The solution may be found by computing $F(n)$ for $n = 2, 3, 4, \ldots$, until the computed value begins to increase. When $\alpha = \beta = 0.05$, the optimal number of measurements is $n = 15$, although the improvement as n increases from 6 to 15 is slight. If n is increased further, the detection limit ξ_D^2 worsens unless the total count time is also increased.

A chi-square test may also be used to test whether the total source measurement variance consists of a Poisson component and a specified excess component (Currie 1972). Procedure E2, described below, implements this test. If the specified component is zero, Procedure E2 is equivalent to E1.

Procedure E2. Determine whether a series of measurements of a check source provide evidence that the measurement variance is greater than the Poisson component plus a specified excess component. (Refer to the notation used in Procedure E1.) Let ξ^2 denote the value of the relative excess variance under the null hypothesis H_0.

Procedure:

1. Choose the significance level α.

2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} w_i$, where $N_1, N_2, \ldots, N_n$ are the measured values.

3. Estimate the mean decay-corrected count rate $\hat{r}$ in two steps by

$$r_0 = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} w_i} \qquad \text{and} \qquad \hat{r} = \sum_{i=1}^{n} \frac{N_i}{1 + r_0 w_i \xi^2} \bigg/ \sum_{i=1}^{n} \frac{w_i}{1 + r_0 w_i \xi^2} \qquad (18.15)$$

(If $w_1 = w_2 = \cdots = w_n$ or $\xi^2 = 0$, then $\hat{r} = r_0$.)

4. Calculate the chi-square statistic as follows:[7]

$$\chi^2 = \sum_{i=1}^{n} \frac{(N_i / w_i - \hat{r})^2}{\hat{r} / w_i + \hat{r}^2 \xi^2} \qquad (18.16)$$

5. Determine the quantile $\chi_{1-\alpha}^2(n-1)$ (see Table G.3). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi_{1-\alpha}^2(n-1)$. In this case conclude that the relative excess variance is greater than ξ^2.

Procedure E2, like E1, can easily be converted to a two-sided test by changing Step 5.

The excess component may be estimated by solving Equations 18.15 and 18.16 for the value of ξ that gives $\chi^2 = n - 1$. An iterative computer algorithm, such as bisection, which repeatedly tries values of ξ and computes χ^2 can be used.[8] An approximate confidence interval for the relative excess variance may similarly be found by solving for values of ξ which give $\chi^2 = \chi_{(1\pm\gamma)/2}^2(n-1)$, where γ is the desired confidence coefficient (Currie, 1972).

If $w_1 = w_2 = \cdots = w_n$, the iterative algorithm is unnecessary. In this case the value of ξ may be estimated directly using the formula

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[7] In Currie (1972), the variance of N_i is estimated by $N_i + \xi^2 N_i^2$. The estimated variance used here is calculated by pooling the counting data to reduce any small bias caused by the correlation between N_i and $N_i + \xi^2 N_i^2$.

[8] Newton's method, which converges more rapidly, can also be used, but its use is more practical if one replaces $\hat{r}$ by r_0 in the denominator of each term of Equation 18.16.

$$\xi^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{n-1}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.17}$$

or by $\xi = 0$ if the preceding formula gives a negative result. Similarly, the approximate lower confidence limit is given by the formula

$$\xi_{\text{lower}}^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi_{(1+\gamma)/2}^2(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.18}$$

and the approximate upper confidence limit is given by

$$\xi_{\text{upper}}^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi_{(1-\gamma)/2}^2(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.19}$$

EXAMPLE

Problem: A long-lived efficiency check source is counted once a day for 20 days, and each measurement has the same duration. Suppose the measured counts (N_i) are:

14,454 15,140 15,242 14,728 14,756 15,040 14,768 15,128 15,150 14,872
14,845 15,511 15,032 14,746 14,731 14,982 15,047 15,272 14,765 15,143

Use these data to estimate ξ and determine a 95 percent two-sided confidence interval for its value.

Solution: Since the source is long-lived and all the measurements have the same duration, $w_1 = w_2 = \cdots = w_{20}$ and Equations 18.17 through 18.19 may be used. So, calculate $\sum N_i = 299{,}352$ and $\overline{N} = 299{,}352 / 20 = 14{,}967.6$. Then the value of ξ is estimated as

$$\xi = \frac{1}{14{,}967.6}\sqrt{\frac{1}{20-1}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2 - 14{,}967.6} = 0.014463$$

The 95 percent confidence limits are calculated as follows:

$$\xi_{lower} = \frac{1}{\overline{N}} \sqrt{\frac{1}{\chi^2_{0.975}(20-1)} \sum_{i=1}^{20} (N_i - \overline{N})^2 - \overline{N}}$$

$$= \frac{1}{14,967.6} \sqrt{\frac{1}{32.852} \sum_{i=1}^{20} (N_i - 14,967.6)^2 - 14,967.6}$$

$$= 0.0096334$$

$$\xi_{upper} = \frac{1}{\overline{N}} \sqrt{\frac{1}{\chi^2_{0.025}(20-1)} \sum_{i=1}^{20} (N_i - \overline{N})^2 - \overline{N}}$$

$$= \frac{1}{14,967.6} \sqrt{\frac{1}{8.9065} \sum_{i=1}^{20} (N_i - 14,967.6)^2 - 14,967.6}$$

$$= 0.022846$$

For most practical purposes the excess variance may be considered negligible in a counting measurement if the total count N is less than $1/10\xi^2$, since, in this case, the excess variance increases the standard deviation of the measured count by less then 5 percent. Similarly, the counting variance may be considered negligible if $N \geq 10/\xi^2$.

EXAMPLE: Suppose $N = 1,000$ counts observed in a measurement and ξ has been estimated to be 0.01. Then $N = 1/10\xi^2$. The standard uncertainty of N is evaluated as

$$u(N) = \sqrt{N + \xi^2 N^2} = \sqrt{1,000 + 10^{-4}10^6} = \sqrt{1,100} \approx 1.05\sqrt{N}$$

If $N = 100,000$, then $N = 10/\xi^2$ and

$$u(N) = \sqrt{10^5 + 10^{-4}10^{10}} = \sqrt{1,100,000} \approx 1.05(\xi N)$$

So, $u(N) \approx \sqrt{N}$ for $N \leq 1,000$, and $u(N) \approx \xi N$ for $N \geq 100,000$.

18B.3 Instrument Background Measurements

This section presents statistical tests related to measurements of instrument background levels. The tests are intended for single-channel detectors but may be applied to multichannel systems if wide spectral regions are integrated. Tests are described for comparing background levels to preset limits, for detecting changes in background levels between measurements, and for detecting the presence of variability in excess of that predicted by the Poisson model.

Each of the statistical tests in this section includes different instructions depending on whether the number of background counts in a measurement is at least 20. The reason for this is that when the expected number of counts is high enough, the Poisson distribution can be approximated by a normal distribution, which simplifies the test procedure. For more information about the Poisson distribution and the normal approximation, see Section 19A.2.9, "Poisson Distributions."

18B.3.1   Detection of Background Variability

The chi-square test (Procedure E1) used to detect excess variance in measurements of a check source may be adapted for background measurements. Procedure B1 implements a chi-square test for backgrounds. This test is one-sided, although Step 6 can be modified to implement a two-sided test.

Procedure B1. Determine whether a series of measurements of an instrument's background provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement, and let t_i denote the count time.

Procedure:
  1.   Determine the significance level α
  2.   Calculate the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i$
  3.   Estimate the mean background count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i} \qquad (18.20)$$

  4.   Let t_{min} be the smallest value of t_i. If $\hat{r} t_{min} \geq 20$, go to Step 5. Otherwise, discard all measured values N_i for which $\hat{r} t_i < 20$. If possible, restart the test at Step 2; if not, stop.

  5.   Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i \tag{18.21}$$

6. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case, conclude that the instrument background does not follow the Poisson model.

EXAMPLE

Problem: Twenty overnight background measurements are performed on a proportional counter. The duration of each measurement is 60,000 s, and the following alpha counts are measured:

14	23	23	25	28	22	19	26	20	27
30	21	34	32	24	27	25	19	19	25

Are these data consistent with the assumption that the measurement variance is attributable to Poisson counting statistics? Use 5 percent as the significance level.

Solution:

Step 1   The significance level is specified to be $\alpha = 0.05$

Step 2   Calculate $\sum N_i = 483$ and $\sum t_i = 20 \times 60{,}000 = 1{,}200{,}000$

Step 3   Calculate the mean count rate $\hat{r} = 483 / 1{,}200{,}000 = 0.0004025$

Step 4   Since $t_{min} = 60{,}000$, $\hat{r}t_{min} = 24.15$. Since $24.15 \geq 20$, go to Step 5

Step 5   Calculate the chi-square statistic
$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i = \frac{1}{0.0004025} \sum_{i=1}^{20} \left(\frac{N_i}{60{,}000} - 0.0004025 \right)^2 60{,}000 = 18.49$$

Step 6   The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $18.49 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the Poisson model.

All the background tests described below are based on the assumption of Poisson counting statistics. If Procedure B1 indicates the Poisson assumption is invalid, each test requires modification or replacement. In most cases, unless the observed background counts are very low, standard statistical tests for normally distributed data may be used instead (e.g., NBS, 1963; EPA, 2000).

18B.3.2   Comparing a Single Observation to Preset Limits

High background levels on an instrument degrade detection capabilities and may indicate the presence of contamination. Unusually low levels on certain types of instruments may indicate instrument failure. When these issues are of concern, one or both of the two statistical tests described below may be performed to determine whether the true background level is outside of its desired range.

The result of the background measurement in counts is assumed to have a Poisson distribution. In both of the following tests, t denotes the count time, and r denotes the preset lower or upper limit for the true mean background count rate R_B. Given an observed count N_B, Procedure B2 determines whether $R_B > r$ and B3 determines whether $R_B < r$.

Procedure B2 should be used when r is an upper limit and B3 should be used when r is a lower limit. Thus, the background level is assumed to be within its acceptable limits unless there is statistical evidence to the contrary. The alternative approach, which changes the burden of proof, may be used if rt is large enough.

If rt is extremely large (e.g., if $rt \geq 2{,}500$), there is probably no justification for a statistical test. Instead, the observed count rate may be compared directly to r.

Procedure B2. Determine whether the mean background count rate R_B is greater than r. Test the null hypothesis H_0: $R_B \leq r$ against the alternative hypothesis H_1: $R_B > r$.

Procedure:
1.   Choose the significance level α.

2.   If $N_B \leq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3.   Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}}$$

(18.22)

4.   Determine $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5.   Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

> NOTE: If the background count time t is always the same, a fixed upper control limit may be calculated using the formula

$$\text{UCL} = \textbf{round}\left(rt + z_{1-\alpha}\sqrt{rt}\right)$$

where **round** denotes the function that rounds its argument to the nearest integer. Then Steps 3–5 are effectively performed by comparing the observed value N_B to UCL.

6. Determine $\chi_\alpha^2(2N_B)$, the α-quantile of the chi-square distribution with $2N_B$ degrees of freedom (see Table G.3 in Appendix G), and calculate $Q = 0.5\,\chi_\alpha^2(2N_B)$.

7. Reject the null hypothesis if and only if $Q > rt$.

EXAMPLE

Problem: To ensure adequate detection capabilities, a laboratory establishes an upper limit of 0.02 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 125 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.02 cps.

Solution: The values of the variables are $N_B = 125$, $t = 6{,}000$ and $r = 0.02$

Step 1   The significance level α is $1 - 0.95 = 0.05$

Step 2   Since $N_B \geq rt = 120$ and $rt \geq 20$, go to Step 3

Step 3   Calculate $Z = (0.5 + 125 - 120) / \sqrt{120} = 0.5021$

Step 4   Table G.1 shows that $z_{0.95} = 1.645$

Step 5   Since $0.5021 \leq 1.645$, do not reject the null hypothesis. There is insufficient evidence to conclude that the beta background exceeds 0.02 cps

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EXAMPLE

Problem: The same laboratory establishes an upper limit of 0.002 cps for alpha backgrounds on the same counter. A 6,000-s background measurement is performed, during which 19 alpha counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.002 cps.

Solution: The values of the variables are $N_B = 19$, $t = 6{,}000$ and $r = 0.002$

Step 1   The significance level α is $1 - 0.95 = 0.05$

Step 2   Since $N_B \geq rt = 12$ and $rt < 20$, go to Step 6

Step 6   Table G.3 shows that $\chi^2_{0.05}(38) = 24.88$. So, $Q = 0.5 \cdot 24.88 = 12.44$

Step 7   Since $12.44 > 12$, reject the null hypothesis. The data give 95 percent confidence that the alpha background is greater than 0.002 cps.

Procedure B3. Determine whether the mean background count rate R_B is less than r. Test the null hypothesis H_0: $R_B \geq r$ against the alternative hypothesis H_1: $R_B < r$.

Procedure:

1.   Choose the significance level α.

2.   If $N_B \geq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3.   Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}}$$

(18.23)

4.   Determine $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5.   Reject the null hypothesis if and only if $Z < -z_{1-\alpha}$. Stop.

> NOTE: If the background count time t is always the same, a lower control limit may be calculated using the formula
> $$\text{LCL} = \textbf{round}\left(rt - z_{1-\alpha}\sqrt{rt}\right).$$
>
> Steps 3–5 are then effectively performed by comparing N_B to LCL.

6.   Determine $\chi^2_{1-\alpha}(2N_B + 2)$, the $(1 - \alpha)$-quantile of the chi-square distribution with $2N_B + 2$ degrees of freedom (see Table G.3), and calculate $Q = 0.5\,\chi^2_{1-\alpha}(2N_B + 2)$.

7.   Reject the null hypothesis if and only if $Q < rt$.

EXAMPLE

Problem: A laboratory establishes a lower limit of 0.01 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 50 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is less than 0.01 cps.

Solution: The values of the variables are $N_B = 50$, $t = 6,000$ and $r = 0.01$

Step 1 The significance level α is $1 - 0.95 = 0.05$

Step 2 Since $N_B \leq rt = 60$ and $rt \geq 20$, go to Step 3

Step 3 Calculate $Z = (0.5 + 50 - 60)/\sqrt{60} = -1.226$

Step 4 Table G.1 shows that $z_{0.95} = 1.645$

Step 5 Since $-1.226 \geq -1.645$, do not reject the null hypothesis.

18B.3.3 Comparing the Results of Consecutive Measurements

If consecutive measurements of the background level on an instrument give significantly different values, one should be concerned about the accuracy of any laboratory sample measurements made between the two background measurements. If the background has increased, the laboratory sample activities may have been overestimated. If the background has decreased, the activities may have been underestimated. For very low background applications, when the number of observed counts per measurement approaches zero (as encountered in alpha spectrometry), the tests for comparing statistical equivalence of paired backgrounds can be confounded. In these cases, it may be better to examine populations of blanks with $N \geq 20$.

Let N_1 and N_2 denote the counts observed in two independent background measurements on the same instrument, and assume they represent Poisson distributions with unknown means. Let t_1 and t_2 denote the corresponding count times. The following two procedures may be used to determine whether the difference between the two observed values is significantly larger than would be expected on the basis of the Poisson model. Procedure B4 determines whether the second value is significantly greater than the first. Procedure B5 determines whether there is a significant difference between the two values.

Procedure B4. Determine whether the second mean background count rate R_2 is higher than the first R_1. Test the null hypothesis H_0: $R_1 \geq R_2$ against the alternative hypothesis H_1: $R_1 < R_2$.

Procedure:
1.   Choose the significance level α.

2.   If $N_1 / t_1 \geq N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3. If $N_1 < 20$ or $N_2 < 20$, go to Step 6.

3.   Calculate

$$Z = \left(\frac{N_2}{t_2} - \frac{N_1}{t_1} \right) \Big/ \sqrt{\frac{N_1 + N_2}{t_1 t_2}} \tag{18.24}$$

4.   Determine $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution.

5.   Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

6.   Let $p = t_1 / (t_1 + t_2)$ and $q = t_2 / (t_1 + t_2)$. If $N_1 < N_2$, calculate

$$S = \sum_{k=0}^{N_1} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{18.25}$$

If $N_1 \geq N_2$, calculate S more efficiently using the formula

$$S = 1 - \sum_{k=N_1+1}^{N_1+N_2} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{18.26}$$

NOTE: For any nonnegative integers n and k, the notation $\binom{n}{k}$ denotes a *binomial coefficient*, usually read "n choose k," which is the number of possible combinations of n objects chosen k at a time. For example, $\binom{4}{1} = 4$, $\binom{4}{2} = 6$, $\binom{4}{3} = 4$, and $\binom{4}{4} = 1$. In general, for $0 \leq k \leq n$, the value of $\binom{n}{k}$ equals $\frac{n!}{k!(n-k)!}$, where the symbol ! denotes the "factorial" operator. The number of combinations of n objects chosen k at a time is also denoted sometimes by $_nC_k$.

7.   Reject the null hypothesis if and only if $S \leq \alpha$.

EXAMPLE

Problem: A 60,000-s background measurement is performed on an alpha spectrometer and 15 total counts are observed in a particular region of interest. After a test source is counted, a 6,000-s background measurement is performed and 3 counts are observed. Assuming Poisson counting statistics, is the second measured count rate (0.0005 cps) significantly higher than the first (0.00025 cps) at the 5 percent significance level?

Solution: The variables are $N_1 = 15$, $t_1 = 60,000$, $N_2 = 3$, and $t_2 = 6,000$

Step 1   The significance level α is specified to be 0.05

Step 2   Since $N_1 / t_1 = 0.00025 < 0.0005 = N_2 / t_2$, $N_1 < 20$, and $N_2 < 20$, go to Step 6

Step 6 $p = \frac{60,000}{66,000} = \frac{10}{11}$ and $q = \frac{6,000}{66,000} = \frac{1}{11}$. Since $N_1 \geq N_2$, calculate S using the second formula.

$$S = 1 - \left(\binom{18}{16}\left(\frac{10}{11}\right)^{16}\left(\frac{1}{11}\right)^2 + \binom{18}{17}\left(\frac{10}{11}\right)^{17}\left(\frac{1}{11}\right)^1 + \binom{18}{18}\left(\frac{10}{11}\right)^{18}\left(\frac{1}{11}\right)^0 \right)$$

$$= 1 - 0.7788 = 0.2212 .$$

Step 7   Since $S \geq \alpha$, there is not enough evidence to reject the null hypothesis. The second measured count rate is not significantly higher than the first.

Procedure B5. Determine whether the mean background count rates are different. Test the null hypothesis H_0: $R_1 = R_2$ against the alternative hypothesis H_1: $R_1 \neq R_2$.

Procedure:
1.   Choose the significance level α.

2.   If $N_1 / t_1 = N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 < 20$ or $N_2 < 20$, go to Step 6. If $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3.

3.   Calculate Z using Equation 18.24.

4.   Determine $z_{1-\alpha/2}$, the $(1 - \alpha / 2)$-quantile of the standard normal distribution.

5.   Reject the null hypothesis if and only if $|Z| > z_{1-\alpha/2}$. Stop.

6. If $N_1 / t_1 < N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ to determine whether $R_1 < R_2$. If $N_1 / t_1 > N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ and with the observations reversed to determine whether $R_2 < R_1$.

18B.4 Negative Activities

When the measured count rate for a test source is less than that of the corresponding instrument background, giving a negative value for the source activity, Procedure B4 may be used to determine whether the difference between the two count rates is significantly more than should be expected on the basis of the Poisson model and the assumption that the source is a blank. (Let N_1 and t_1 be the source count and counting time and let N_2 and t_2 be the background count and counting time.). If a significant difference is found, it may indicate that the background measurement was biased, the true background is variable or non-Poisson, or the instrument is unstable. As background counts approach zero, the assumption of Poisson statistics begins to fail. This mean-centered approach may lead the analyst to an inappropriate conclusion. In these cases, an examination of a larger population of blanks is more appropriate.

18B.5 References

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