4.5.3 Quality Control and Detection Limits

4.5.3 QUALITY CONTROL AND DETECTION LIMITS

QUALITY CONTROL

Quality control (QC) must be included in all aspects of a radiochemical measurement, from the collection of samples to the reporting of data. The exact QC practices that are to be used as part of the radiochemical procedures will vary somewhat, depending upon the chemical and radiological characteristics of the analyte. Some of the general requirements of a QC system for procedures are described here. Where the peculiarities of an analyte necessitate that modifications be made in these requirements, these modifications are discussed in the subsection after the analytical procedure for that analyte. The QC procedures described here are termed "internal" in that they are initiated by the analyst. Similarly, "external" QC procedures should be initiated by project leaders introducing QC samples "blind" into the sample stream. Data from both the internal and external QC procedures must be maintained and tabulated by the party initiating the procedures to document the continuing adequacy of the analytical work.

The QC practices used during radiochemical analyses are intended to assure the analyst that the determinations are under control. They involve continuous testing of those processes that influence the extent to which the results of the analyses remain within the required limits of precision and accuracy. The QC samples that are analyzed consist of five types: instrument calibration standards, blank samples, control samples, "spiked" samples, and replicate samples.

Instrument calibration standards are certified reference materials used primarily to calibrate the measurement apparatus. Standards for radioactivity measurements are discussed in Section 4.5.2. A key requirement of such materials is that they be traceable to the National Institute of Standards and Technology or to other recognized organizations.

Blank samples are commonly "reagent blanks" that are prepared by beginning with deionized water or an empty sample container. All appropriate reagents are added to the sample in the proper sequence and the normal steps involved in the analysis are followed. Ideally, the blank samples would be the same matrix as the routine sample but without the analyte of interest. Normally, the activity of each routine sample is corrected by subtracting the reagent blank activity from it to obtain net activity. All the uncertainties of the measurements obtained throughout the analytical procedure should be propagated when calculating the uncertainty of the final result. However, very often only the Poisson errors of the counts of the reagent blank and of the sample are propagated when they are the most significant contributors to the total uncertainty.

Control samples contain known concentrations of the analyte. If possible, they should be the same matrix as the routine samples, and they should have concentrations in the same range as the routine samples. They usually are samples that are included by the analyst in the sample batches to be analyzed, and their values should be known with an uncertainty better than that which will be required of measurements of the routine samples.

"Spiked" samples are prepared by adding a known amount of the radionuclide of interest to blank samples or to samples that have already been analyzed in order to provide a matrix with a known activity.

Replicate samples usually consist of two or more aliquots of homogeneous solid, liquid or gas samples. Individual samples that are measured by nondestructive techniques, such as γ-ray spectrometry, may be measured more than once to obtain replication of the data.

Analytical instruments, such as analytical balances, must be calibrated regularly. The standards that are used to calibrate any instrument should be traceable to the National Institute of Standards and Technology (NIST), when possible. A record of instrument performance must be maintained by the instrument operator. A record must be kept of any modifications that are made in an instrument, and such modifications must be approved by the analyst's supervisor beforehand and must conform to the safety standards and practices that are specified in the EML Safety Manual.

For most radiochemical procedures, QC samples are added to make up between 10-20% of the sample stream. It is good analytical practice to process high-level and low-level samples in independent batches whenever possible to minimize the possibility of cross contamination. When samples of very low activity are to be analyzed, blank sample analyses and instrument background measurements should be increased.

The best estimates of a reagent blank or blank sample activity, instrument background count rate and detection efficiency are obtained from the mean value of replicate determinations. Whenever possible, the mean and standard error of the replicate determinations should be used in calculating a final value.

ESTIMATING THE LOWER LIMIT OF DETECTION

Counting data are like other analytical data in that a series of measurements of background, for example, should show a Gaussian distribution like that in Figure 1. The standard deviation (SD) for the distribution will give an estimate of how well additional background measurements will approach the original mean. In most environmental analyses, however, we cannot afford the luxury of multiple analyses or even duplicates. Fortunately, counting data follow the Poisson distribution and it is possible to estimate the SD from a single measurement. This SD of counting can be used in the same way as the Gaussian SD to establish a confidence interval about the mean value. For example, if the confidence interval chosen is ±1 SD, additional measurements should fall into this interval 68% of the time. An interval of ±2 SD would contain the new value 95% of the time.

Thus, if we establish a background with its associated SD for a counting system, this should give us a way of estimating our lower limit of detection (LLD). For example, a sample count > 1 SD above background should indicate the presence of activity 84% of the time. In the other 16%, there would be a false positive. If the limit of 2 SD is used, the values would be 97.5% real and 2.5% false with 3 SD, 99.85% and 0.15%. This seems to be very simple, but it does not consider the fact that the sample counts also would have a distribution.

The interaction of the two distributions becomes more important as environmental analyses tend toward lower levels of radioactivity. As the activity decreases, the counter background or method blank has to be subtracted from the gross count, and estimating the precision of these measurements and also the limit of detection for a procedure becomes slightly more difficult. Where the total count on a sample approaches the background count, you have a situation as in Figure 2 where the two distributions overlap. [This form of showing the detection limit for counting was given by Healy (1956).]

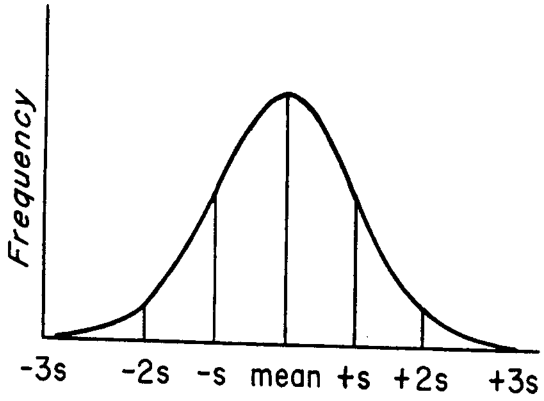

Figure 1. Distribution curve where the relative areas show the fraction of results that should be included within ± s (0.68), ± 2 s (0.95) and ± 3 s (0.997).

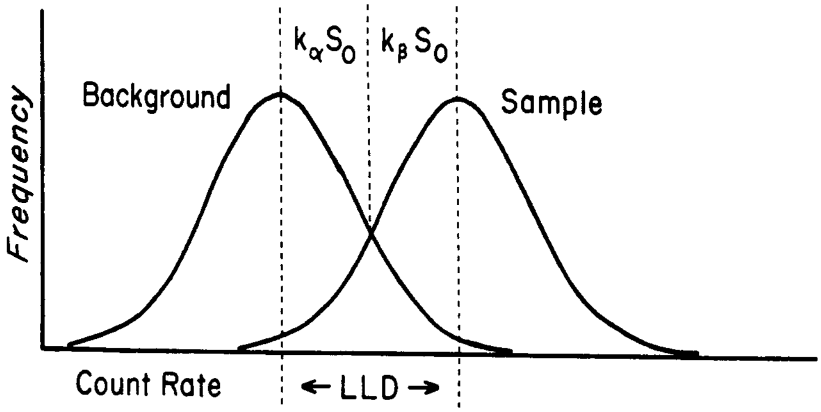

Figure 2. Intersecting distributions for background and sample count rates.

Pasternack and Harley (1971) developed a procedure for calculating what they defined as the LLD, the smallest amount of sample activity that will yield a net count for which there is a confidence at a predetermined level that activity is present. This concept was only practical for γ counting in the original form since they required that the number of counts be sufficient for the Poisson distribution to approach the Gaussian distribution so that Gaussian statistics could be used.

However, the approximation is valid down to a few total counts. Thus, the calculations can be applied to any detection system.

The LLD can be approximated as

$$\mathrm{LLD} \cong (k_\alpha + k_\beta)s_0$$

where

k_α is the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present (α),
$k_ß$ is the corresponding value for the predetermined degree of confidence for detecting the presence of activity (1- ß), and
s_0 is the estimated standard deviation for the net sample activity.

A still shorter approximation may be made if the values of α and ß are set at the same level and if the gross activity and background are very close. In this case:

$$s_0 = \sqrt{s_{gross}^2 + s_{bkg}^2} = s_b \sqrt{2}$$

The equation then becomes,

$$\mathrm{LLD} \cong 2\ k\, s_{bkg} \sqrt{2}$$

The values of k for common α's are:

α	$1-\beta$	k	$2k\sqrt{2}$
0.01	0.99	2.327	6.59
0.02	0.98	2.054	5.81
0.05	0.95	1.645	4.66
0.10	0.90	1.282	3.63
0.20	0.80	0.842	2.38
0.50	0.50	0.000	0.00

Routinely, an α value of 0.05 is used at EML for calculating the LLD. The LLD will be provided at the end of each procedure, if appropriate.

The simplest possible case is one where the sample activity is zero. It is sometimes not realized that if a series of counts is taken on such a system, that half of the net values should be less than zero. Negative counts are not possible, of course, but when there is a blank or a background, the entire scale is shifted up and the situation becomes one where half of the sample counts on a zero activity sample would be less than background. This negative net count occurs frequently in low-level measurements, causing considerable concern, but such results are to be expected.

Thus, if we have a counter with a background of 0.003 counts $\sec^{-1}$ (cps) and we count the sample and background for 24000 sec, then

$$s_b = \sqrt{72} = 8.5$$

If we set α at 0.05, accepting a 5% chance of a false positive result for a sample having no activity,

$$\text{LLD} = (4.66)(8.5) = 40 \text{ counts}$$

or ~ 0.002 cps.

Since the simplified formula used sets $k_\alpha = k_\beta$, we are also accepting the chance that we will detect activity when it is present, 95% of the time, but will miss it 5% of the time.

If a 50% chance of finding activity is accepted, the LLD is zero. This is to be expected from the previous qualitative description.

The original paper of Pasternack and Harley (1971) applied the LLD concept to multicomponent γ spectrometry with NaI detectors. They noted particularly the decrease in sensitivity as the number of components in the mixture increased, and observed a decrease when the number of radionuclides in the library was increased, even when the actual sample contained only a single component.

Multicomponent α spectrometry can be performed in accordance with the procedures of Fisenne et al. (1973). Solid state α-spectrometry calculations are simpler, since overlapping spectra are less common. The basic principle is that an interfering radionuclide effectively increases the background for the nuclide sought.

Examples of LLD calculations for three typical measurement situations are given for illustrative purposes in the appendix.

ZERO LEVELS

A. Introduction.

When the measurement of background yields a positive value, its variance and SD may be calculated based on Poisson counting statistics. In any subsequent measurement of a sample, the net activity and its SD may be evaluated to determine whether significant radioactivity is present.

A special case arises when neither counter background nor sample activity is detectable over a reasonably long counter interval. It is of practical interest to be able to quantitate the upper limit of radioactivity that could be present in this sample and yet yield this result, since increasingly more environmental nuclide measurements may fall into this category.

The measurement and identification of low levels (< 0.0001 Bq/sample) of α-emitting nuclides by spectrometry represents a specific example. This measurement is performed with a silicon surface barrier or ion implant detector. Any background counts measured in these detectors usually fall within the energy intervals corresponding to naturally occurring nuclides, primarily radium and its progeny. The background count rate for these detectors usually ranges from 0-5 counts per 6×10^4 sec in any of the energy intervals containing peaks of the U series, Pu isotopes and most other α emitters of interest.

Thorium-232 is a special case, since the energy interval at which it appears (3.9 MeV) normally exhibits very low background. For example, a measurement for ^{232}Th yielded zero counts in 3×10^5 sec and zero background counts over a similar count interval. It is of value to calculate rigorously an upper limit of ^{232}Th activity which could be present in such a sample. Two examples are given here. One, where the counting interval is fixed and the other where the count time can be calculated based upon a desired fixed value for the upper limit of activity in the sample (Harley and Fisenne, 1976).

B. Predetermined count interval.

We may apply the binomial distribution to a group of N_o atoms to calculate the probability that there will be no α decays in counting interval, t.

The binomial distribution for the probability of x number of disintegrations out of a total of N_o atoms is:

$$\Pr(x) = \frac{N_0!}{(N_0 - x)!\,x!}\, p^x\, q^{(N_0 - x)} \qquad (1)$$

where

Pr(x) = probability of x disintegrations during time, t,
N_0 = initial number of radioactive atoms,
p = probability that an atom will decay in time, t, and
q = probability that an atom will not decay in time, t.

Since the probability, q, that an atom will not decay is:

$$q = e^{-\lambda t}$$

then,

$$p = \left(1 - e^{-\lambda t}\right)$$

and

$$\Pr(x) = \frac{N_0!}{\left(N_0 - x\right)!\ x!}\left(1 - e^{-\lambda t}\right)^x \left(e^{-\lambda t}\right)^{N_0 - x}$$

The probability of no disintegrations in time t is then:

$$\Pr(0) = \frac{N_0!}{N_0\ 0!}\left(1 - e^{-\lambda t}\right)^0 \left(e^{-\lambda t}\right)^{N_0} = e^{-\lambda N_0 t} \tag{2}$$

Because the detector efficiency is <100%, there is also the possibility that one or more disintegrations occur but that they are not detected. If the detector efficiency is G and one disintegration occurs, the probability of no count being detected is (1-G). If two disintegrations occur, the probability of zero counts is $(1\text{-}G)^2$. In general, whenever x disintegrations occur, the probability that zero counts will be seen is $(1\text{-}G)^x$. Then the probability that one or more of N_o atoms present disintegrates during time, t, but that none is detected is:

$$\Pr(1)\cdot(1 - G) + \Pr(2)\cdot(1 - G)^2 + \Pr(3)\cdot(1 - G)^3 + \ldots \tag{3}$$

From (1), the probability of one disintegration occurring is:

$$\Pr(1) = \frac{N_0!}{\left(N_0 - 1\right)!\ 1!}\left(1 - e^{-\lambda t}\right)^1 \left(e^{-\lambda t}\right)^{N_0 - 1} \tag{4a}$$

The probability of two disintegrations occurring is:

$$\Pr(2) = \frac{N_0!}{(N_0 - 2)!\, 2!} \left(1 - e^{-\lambda t}\right)^{N_0 - 2} \tag{4b}$$

and so on.

If the assumption can be made that t is small and that N_o is much greater than one, then Pr(1), Pr(2), etc., simplify to:

$$\Pr(1) \cong N_0\ (\lambda t)^{-1} \left(e^{-\lambda N_0 t}\right) \tag{5a}$$

$$\Pr(2) = \frac{N_0 N_0}{2!} (\lambda t)^2 \left(e^{-\lambda N_0 t}\right) \tag{5b}$$

$$\Pr(3) = \frac{N_0 N_0 N_0}{3!} (\lambda t)^3 \left(e^{-\lambda N_0 t}\right) \tag{5c}$$

The probability for observing zero counts is the sum of the probabilities for no disintegration to occur plus those for the occurrence of one or more disintegrations which are not detected.

$$P = \Pr(0) + \Pr(1) \cdot (1\text{-}G) + \Pr(2) \cdot (1\text{-}G)^2 + \Pr(3) \cdot (1\text{-}G)^3 + \ldots$$

$$\cong \quad e^{-\lambda N_0 t} + \lambda N_0 t e^{-\lambda N_0 t}\ (1 - G) + \frac{\left[\lambda N_0 t (1 - G)\right]^2}{2!} e^{-\lambda N_0 t} + \ldots$$

$$\cong \quad e^{-\lambda N_0 t} \left[1 + \frac{\lambda N_0 t (1 - G)}{1!} + \frac{\left[\lambda N_0 t (1 - G)\right]^2}{2!} + \frac{\left[\lambda N_0 t (1 - G)\right]^3}{3!} + \ldots \right]$$

$$\cong e^{-\lambda N_o t} \cdot e^{+\lambda N_o t(1-G)} \tag{6a}$$

$$\cong e^{-\lambda N_o tG} \tag{6b}$$

$\lambda N_o tG$ is the number of counts to be expected during the interval t.

We would like the occurrence of zero counts, when activity is actually present, to have a small probability. If this probability is arbitrarily set to 0.05 so that zero counts will be detected only 5% of the time, when N_o atoms are actually present and the counting interval is t minutes, then (6b) becomes:

$$e^{-\lambda N_0 tG} = 0.05$$

$$\lambda N_0 tG = -1n(0.05)$$

$$(\lambda N_0) = A_0 = -\frac{1}{tG} 1n(0.05) \tag{7}$$

$$A_0 = \frac{3}{tG}$$

where $\lambda N_o = A_o$ is the upper limit of sample activity in Bq at the 95% confidence level, when t is in seconds and G is expressed as fractional efficiency.

C. Predetermined upper limit of activity.

It may be of interest to establish the counting time required to determine that a chosen upper limit of activity is present. Solving (7) for the counting time yields:

$$t = \frac{3}{A_0 G} \tag{8}$$

As an example, the measured data for the ^{232}Th sample will be used. The efficiency of the surface barrier detector is 0.30 and zero counts were recorded in $3 \mathrm{x} 10^5$ sec. From (7):

$$A_0 = \frac{3}{\left(3 \text{ x } 10^5\right)(0.3)} = 3 \text{ x } 10^{-5} \text{ Bq} \tag{9}$$

The upper limit of activity in this sample is thus $3 \mathrm{x} 10^{-5}$ Bq at the 95% confidence level.

BACKGROUND NOT ZERO

All of the above expressions apply equally well to background activity. It is possible that either a background count did not occur during the count interval or that one or more occurred but were not detected. In this case, the upper limit to background activity is the same as that calculated in (9), except that there is no efficiency for background and the background activity is expressed as counts sec^{-1}. Expression (9) would then become:

$$A_0 G = \frac{3}{\left(3 \text{ x } 10^5\right)} = 1 \text{ x } 10^{-5} \text{ counts sec}^{-1}$$

Then according to the convention at EML, any value of net activity equal to zero would be evaluated in comparison with:

$$S_{net} = \sqrt{\frac{1x10^{-5}}{3x10^{5}} + \frac{1x10^{-5}}{3x10^{5}}} = 8 \text{ x } 10^{-6} \text{ counts sec}^{-1}$$

and the activity would be reported as:

$$\frac{\leq 8 \text{ x } 10^{-6}}{0.3},$$

or ≤ $2x10^{-5}$ Bq at the 95% confidence interval.[1]

**This convention would be used for reporting single values. For averaging purposes, the actual value of the net activity, positive or negative, would be used.*

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APPENDIX

LOWER LIMIT OF DETECTION[2]

In the analyses of samples for naturally occurring radionuclides, it is rare that the sample activity and background are the same. Reagent blanks processed through the chemical procedure will show activity in excess of the background of the detection system. Multiple measurements of the background and multiple reagent blank analyses are used to obtain the respective standard errors of these variables. In this case, the equation is

$$S_S = \left[S_{gross} + S_{\overline{BK}}^{\,2} + S_{\overline{Bl}}^{\,2} \right]^{1/2} \tag{1}$$

where

S_{gross} = the mean background plus mean reagent blank counts for a specified counting time,

$S_{\overline{BK}}$ = the standard error of the background from multiple measurements (n), corresponding to the same counting time as above, $([s_{BK}^2]/[n])^{1/2}$, and

$S_{\overline{Bl}}$ = the standard error of the blank from multiple analyses (n), also with the same counting time, $([s_{Bl}^2]/[n]^{1/2})$.

Then, the LLD at the 95% confidence level is

$$LLD_{95\%} = \left(k_a + k_b\right) S_S = 3.29\ S_S \tag{2}$$

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[*] *Taken from Pasternack and Harley (1971).*

where

k_α = the preselected risk for concluding falsely that activity present. At the 95% confidence level (α) = 1.645, and

k_β = the predetermined degree of confidence for detecting the presence of activity. At the 95% confidence level ($1-\beta$) = 1.645.

Thus, at $\mathrm{LLD}_{95\%}$

$$k_\alpha = k_\beta = 1.645$$

and

$$(k_\alpha + k_\beta) = 3.29$$

The $\mathrm{LLD}_{95\%}$ must be converted to activity (Bq) using the appropriate conversion factors.

$$\mathrm{LLD}_{95\%}\ (\mathrm{Bq}) = \frac{3.29\, s_S}{(\mathrm{CT})\,(\epsilon)(\mathrm{Y})} \tag{3}$$

where

CT = the counting time or counting interval in seconds,

ϵ = the detection efficiency of the measurement system (counts $\mathrm{sec}^{-1}\ \mathrm{Bq}^{-1}$), and

Y = the average radiometric or chemical yield obtained for the separation method.

The applications of Equations 1 and 3 to solid state α-spectrometry measurements are illustrated below.

In ^{239}Pu measurements, a manmade radionuclide, there is no measurable blank and the mean background count from multiple measurements is used. Then, the term s_{Bl} does not appear and Equation 1 reduces to

$$s_S = [s_{\text{gross}} + s_{\text{Bk}}^2]^{1/2} \tag{4}$$

For this situation s_{gross} is the mean background counts and s_{Bk} is the standard error of multiple measurements.

Given the following variables:

counter efficiency:	40%
counter background (in the ^{239}Pu energy region):	$3.3 \times 10^{-5} \pm 1.7 \times 10^{-5}$ counts sec^{-1} (0.002 ± 0.001 counts min^{-1})
tracer yield:	75%
counting time:	60,000 s (1,000 min)

$$s_S = (2 + 1 \text{ counts})^{½} = (3 \text{ counts})^{½} \tag{5}$$

and

$$\text{LLD}_{95\%} = \frac{3.29(3 \text{ counts})^{1/2}}{(60000 \text{ sec})(0.40 \text{ counts sec}^{-1} \text{ Bq}^{-1})(0.75 \text{ yield})} = 0.0003 \text{ Bq}$$

In ^{210}Po measurements there usually is a measurable blank and all variables in Equation 1 must be taken into account.

Given the following variables:

counter efficiency:	40%
counter background (in the ^{210}Po energy region):	$8.3 \times 10^{-5} \pm 5.0 \times 10^{-5}$ counts sec^{-1} (0.005 ± 0.003 counts min^{-1})

blank:	$1.6 \times 10^{-4} \pm 1.0 \times 10^{-4}$ Bq ($5.0 \times 10^{-5} \pm 3.3 \times 10^{-5}$ counts $\sec^{-1}$) (0.003 ± 0.002 counts $\min^{-1}$)
tracer yield:	80%
counting time:	60,000 s (1,000 min)

Again, mean background from multiple measurements and the mean reagent blank from multiple analyses are to be used.

$$s_S = [(5+3 \text{ counts}) + (2 \text{ counts})^2 + (3 \text{ counts})^2]^{½} = 4.6 \text{ counts}$$

$$\text{LLD}_{95\%} = \frac{3.29\,(4.6 \text{ counts})}{(60000 \text{ sec})\,(0.40 \text{ cps Bq}^{-1})\,(0.80 \text{ yield})} = 0.0008 \text{ Bq}$$

The LLD can be reduced by: (1) increasing the number of background and reagent blank measurements, assuming these do not increase over time; (2) increasing the counting time; (3) increasing the counting efficiency; and (4) increasing the sample yield.