

DETECTION LIMITS FOR
RADIOISOTOPIC COUNTING TECHNIQUESINTRODUCTION

The problem of validly defining the detection limit of any analytical method has suffered from the lack of a unified approach. The chemical literature contains, as noted by Currie^[1], "a plethora of mathematical expressions and widely-ranging terminology" used to define the detection limit. With the increased interest in environmental monitoring of plant discharges, valid detection limits are very important. The purpose of this paper is to document the method used to define the detection limits reported by the counting room of the 222-S Analytical Laboratory.

SUMMARY AND CONCLUSIONS

The method of defining detection limits which has been adopted by the 222-S Analytical Laboratory counting room is that described by Currie^[1]. Currie develops a system of reporting limits which defines two levels of detection limits:

- The Critical Level (L_C) which must be exceeded before a sample can be said to contain any material above the background level.
- A Detection Limit (L_D) at which we can be 95 percent sure that we will detect material.

The common method of using twice the standard deviation of the background as a lower detection limit was shown to lead to erroneous results. It allows samples which contain no material to be reported as positive and it causes the reporting of "less-than" values which are not really "less-thans".

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The equations relating L_C and L_D to the magnitude and standard deviation of the background were derived. Two examples illustrate the use of these levels.

The reporting method outlined herein is a "common sense" approach to the difficult problem of defining detection limits. While this paper deals exclusively with the application of this method to radioisotopic counting techniques, it is just as applicable in many areas of analytical chemistry. The adoption of this method by all laboratories now active in environmental analysis would help eliminate the confusion surrounding that elusive quantity known as the "detection limit".

DISCUSSION AND THEORY

Definition of Symbols

In general, symbols will be defined as they are used, but it may be helpful to review some of the more important. All equations are derived in count rate (usually counts/minute). The symbols R , σ , and T refer to count rate, standard deviation of the count rate, and length of counting time, respectively. Subscripts S , B , and T are used to denote sample, background, and total, respectively. Thus, R_T is the total count rate ($R_S + R_B$), σ_S is the standard deviation of the sample count rate R_S , etc. In the special case when $R_S = 0$, the subscript 0 is often used, thus R_0 and σ_0 refer to the mean count rate of zero ($R_T = R_B$) and to the standard deviation of R_0 . In the special case when $R_S = L_D$, the subscript D is used, thus R_D and σ_D refer to a mean count rate equal to L_D and its standard deviation.

General

In most analytical radioassay methods, the "detection limit" defined for any given sample or instrument is called upon to perform a number of functions. It is often used to define the sensitivity of the method. At times it sets the maximum limit of sample content. It is used when analyzing data in order to determine if a given result indicates detection. By

examining the functions that a "detection limit" is expected to perform, we can develop the following list of general criteria which must be met before any system of defining limits can be considered to be valid.

A valid system of detection limits should:

- 1) Establish a signal level which when exceeded by the sample, indicates to some desired confidence that material is present.
- 2) Define an upper limit for the content of samples in which no material can be found. This "less-than" value must also be known to some desired confidence level.
- 3) Establish the sample content necessary so that one can be sure to some desired confidence that the material present will be detected.

Currie^[1] has developed a method of defining detection limits which satisfies all three of the criteria outlined above. The method requires the introduction of two different levels of detection limits; 1) an a posteriori (after the fact) limit (L_C) also termed the Critical Level or the Decision Limit, and 2) an a priori (before the fact) limit (L_D) termed the Detection Limit*. One of the more common errors made by chemists in defining detection limits lies in the confusion of these two levels.

In light of the three criteria outlined above, let us examine the failings of a common method of defining detection limits. In the past, the 222-S Analytical Laboratory has used the quantity $2\sigma_B$ as a "lower detection limit", where σ_B is the standard deviation of the background count rate,

*To avoid confusion of this a priori level with various "detection limits" commonly referred to, the term will be capitalized when it refers to the a priori level.

and we referred to this value as the "95 percent limit". If a sample count rate (R_S) was $\leq 2\sigma_B$, we would report that the sample contained $<2\sigma_B$ quantity of material. If $R_S > 2\sigma_B$, we would report R_S as a positive value. Also, if we were asked what amount of material we could be sure of detecting, we would quote a value based on $2\sigma_B$. This procedure violates all three of the criteria specified above.

As an example, assume that a given counting instrument has a background count rate (R_B) of 9 c/m. For simplicity, assume one minute counts.

$$\begin{aligned} R_B &= 9 \text{ c/m} \\ \sigma_B &= (R_B)^{1/2} = 3 \text{ c/m} \\ 2\sigma_B &= 6 \text{ c/m} \end{aligned}$$

Thus, the "95 percent limit" is 6 c/m. Suppose we have a sample known to contain no radioactive material, i.e., a background level sample. Remember that it is not possible to determine the sample count rate (R_S) directly. R_S is calculated as the difference between a total count rate (R_T) and the background count rate (R_B). Both R_T and R_B must be allowed their statistical fluctuations.

$$\begin{aligned} \text{Thus: } R_S &= R_T - R_B \\ \sigma_S &= (\sigma_T^2 + \sigma_B^2)^{1/2} \\ \text{for a background level sample let } R_T &= R_B = 9 \text{ c/m} \\ \sigma_T &= (R_T)^{1/2} = 3 \text{ c/m} \\ \sigma_S &= (9 + 9)^{1/2} = 4.2426 \text{ c/m} \\ 2\sigma_S &= 8.4853 \text{ c/m} \end{aligned}$$

Therefore, the 2σ limit for the sample count R_S is ± 8.4853 c/m while our "95 percent limit" is 6 c/m. This background level sample could be reported

as positive with much less than the 95 percent confidence implied by the term "95 percent limit". In this sample, the actual confidence level is approximately 84 percent. Thus, the use of $2\sigma_B$ as a "95 percent limit" violates criterion (1).

Now consider what happens if $R_S < 2\sigma_B$. We would report the value of the sample as $< 2\sigma_B$. However the sample count with its 2σ confidence limit is $R_S \pm 2\sigma_S$. Thus, the upper limit for the sample count at the 2σ level is $R_S + 2\sigma_S$. For example if $R_S = 2\sigma_B$, the upper limit is $4\sigma_B$. Therefore, we have violated criterion (2) by not specifying the upper limit of the sample content.

Further, suppose we were asked what amount of material must be present for us to be sure that we would detect it. We would quote an amount based on $2\sigma_B$. However, if we were to receive a sample which gave a mean count rate of $2\sigma_B$, there is only a 50-50 chance that we would detect material in that sample using a single measurement. If by sure we mean 95 percent sure, we have violated criterion (3).

A Priori vs A Posteriori

As previously stated, two levels of detection limits are necessary to satisfy the criteria presented in the previous section - an a priori limit (L_D) and an a posteriori limit (L_C). The relationship between these two levels is best illustrated by Figure 1.

Curve I is the distribution about zero of a sample with a mean count rate $R_S = 0$, i.e., the "background level" sample referred to previously. If k is the factor defining the one-sided 95 percent confidence level of the distribution, then L_C is the maximum limit of the one-sided 95 percent confidence interval and area (A) is 5 percent of the total area under Curve I. Thus, 95 percent of any sample counts recorded above L_C will be due to material present in the sample, and only 5 percent will be due to the statistical fluctuations of the background. Or, stated another way,

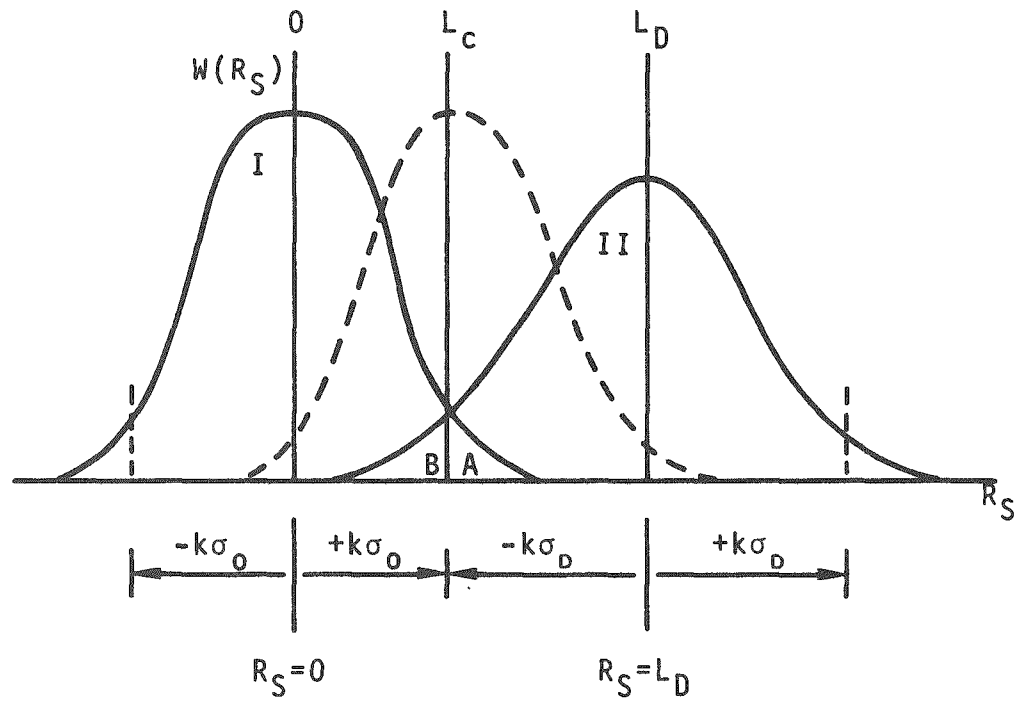


FIGURE 1.

NORMAL DISTRIBUTION CURVES FOR SAMPLES WITH MEAN COUNT RATES $R_S=0$ AND L_D WITH STANDARD DEVIATIONS σ_0 AND σ_D RESPECTIVELY.

any sample counts recorded above L_C are significantly different from zero at the 95 percent confidence level. Therefore, when a sample count rate (R_S) is greater than L_C , we can be 95 percent sure that material has been detected. The L_C level satisfies the requirements of criterion (1).

Now, consider the problem from another viewpoint. Suppose someone calls you on the phone and wants to know what your "lower detection limit" is. He is really asking, "If I send you a sample, how much material must be in that sample for you to be sure (95 percent sure) that you will find it? Since area (B) is 5 percent of the total area under Curve II, the value that you must specify is L_D . A sample containing a quantity of material equivalent to L_D will yield a sample count greater than L_C 95 percent of the time. Indeed, if after the sample had been counted, you found a count rate $>L_C$, you could report a positive value; however, before you count the sample, you can be 95 percent sure that the sample count will be detected ($>L_C$) only if the sample has mean count rate $R_S = L_D$. Assume for a moment that you reply, "Send me a sample with $R_S = L_C$." Since half of the distribution about L_C (dotted curve) is $>L_C$ and half is $<L_C$, the chances that a single measurement will give a positive result are only 50 percent. The decision as to whether or not material will be detected could be made by a simple flip of a coin. Thus, the limit L_D must be employed to satisfy criterion (3).

From the preceding discussion, one can see that L_C is an a posteriori limit, applicable only after the sample has been counted and the data is being analyzed. L_D is an a priori limit which does not depend on the sample result, but rather on the sensitivity of the measurement process.

The astute reader will note that neither L_C or L_D has satisfied criterion (2) - that "less-than" values reported should be the maximum upper limit of the sample content. Indeed this requirement is not satisfied, per se, by either L_C or L_D but rather is satisfied by the method by which we calculate our "less-thans". This will be discussed in a later section of this paper.

The Critical Level (L_C)

From Figure 1: $L_C = R_0 + k\sigma_0$

Since $R_0 = R_T - R_B = 0$

$$\sigma_0^2 = \sigma_T^2 + \sigma_B^2$$

$$\sigma_T = \left(\frac{R_0 + R_B}{T_T} \right)^{1/2} = \left(\frac{R_B}{T_T} \right)^{1/2}$$

$$\sigma_B = \left(\frac{R_B}{T_B} \right)^{1/2}$$

Thus,

$$\sigma_T = \sigma_B \left(\frac{T_B}{T_T} \right)^{1/2}$$

$$\sigma_0 = \left(\frac{T_B}{T_T} \sigma_B^2 + \sigma_B^2 \right)^{1/2} = \sigma_B \left(1 + \frac{T_B}{T_T} \right)^{1/2}$$

Therefore,

$$L_C = k\sigma_B \left(1 + \frac{T_B}{T_T} \right)^{1/2} \quad [1]$$

Where $k = 1.65$ and refers to the one-sided 95 percent confidence level.

When $T_B = T_T$, Equation [1] reduces to

$$L_C = k\sqrt{2} \sigma_B = 2.33\sigma_B \quad [2]$$

The Detection Limit (L_D)

Referring again to Figure 1. $L_D = L_C + k\sigma_D$

Where σ_D is the standard deviation of the difference between R_D and R_0 .

Thus,

$$\sigma_D^2 = \sigma_T^2 + \sigma_0^2$$

$$\sigma_T = \left(\frac{R_0 + R_D}{T}\right)^{1/2} = \left(\frac{R_D}{T}\right)^{1/2}$$

but, $R_D = L_D$

Then,

$$\sigma_D = \left(\frac{L_D}{T} + \sigma_0^2\right)^{1/2}$$

$$L_D = L_C + k \left(\frac{L_D}{T} + \sigma_0^2\right)^{1/2}$$

But,

$$L_C^2 = k^2 \sigma_0^2$$

Thus,

$$L_D = L_C + \left(k^2 \frac{L_D}{T} + L_C^2\right)^{1/2}$$

Rearranging and solving for L_D :

$$L_D = \frac{k^2}{T} + 2L_C \quad [3]$$

or

$$L_D = \frac{k^2}{T} + 4.65\sigma_B \quad [4]$$

Reporting Method

The reporting of analytical results from our counting room requires that the value of the Critical Level (L_C) be calculated from background data using equation [1] (or equation [2] if applicable). The sample count rate is then tested against L_C and the sample result computed as follows:

- 1) If $R_S > L_C$, the result is calculated and reported as positive along with its symmetric 95 percent confidence interval. Thus, the value reported is $R_S \pm k_1 \sigma_S$ where $\sigma_S = (\sigma_T^2 + \sigma_B^2)^{1/2}$, and k_1 refers to the two-sided 95 percent CL ($k_1 = 1.96$).
- 2) If $R_S \leq L_C$, the upper 95 percent limit, R_{Max} , is reported. $R_{Max} = R_S + k_2 \sigma_S$ where σ_S is calculated as in (1), and k_2 refers to the one-sided confidence interval ($k_2 = 1.65$ @ 95 percent CL). The sample is then reported to contain $<R_{Max}$ quantity of material. This method of reporting "less-than" values satisfies criterion (2) for valid detection limits.

There is one important exception to the general method outlined above. Refer to Figure 1, and note that it is possible for R_S to be less than zero for very low samples. If we followed the method outlined above, the R_{Max} reported could be $<L_C$. We have modified the reporting method so that when $R_S < 0$, we report R_{Max} as L_C . This is a reasonable procedure because of our knowledge of the sample character, and is less confusing than reporting "less thans" which are far below our Critical Level.

An interesting result of this method of reporting which could cause confusion unless the method is adequately understood, is that it is quite possible (even probable) that the positive values reported on some samples may be lower than the "less thans" reported on others. This is consistent with the procedure, since the positive values reported are assumed to be the mean of the sample content, and the "less thans" are the upper 95 percent confidence limit.

The reader should also note that in (1) above, the confidence interval calculated is the two-sided interval and $k_1 = 1.96$, but in (2) the interval is one-sided and $k_2 = 1.65$. Chemists are often confused as to the proper usage of these two types of confidence intervals. In (1) we wish to define an interval such that 95 percent of the area under the normal distribution curve will lie between the limits $R_S - k_1\sigma_S$ and $R_S + k_1\sigma_S$. This means that only 2.5 percent of the area under the curve may lie above $R_S + k_1\sigma_S$ while 2.5 percent of the area will lie below $R_S - k_1\sigma_S$. In (2) we wish to define a limit such that 5 percent of the area will be above $R_S + k_2\sigma_S$. Thus, the interval defined in (1) must be wider than that defined in (2).

Examples

Suppose we wish to determine the activity of two low level samples of ^{60}Co . We will assume that the measurement is by total beta counting on a proportional counter with a mean background of 10 c/m and an efficiency for ^{60}Co of 0.32 counts per disintegration. Both samples and backgrounds were counted for five minutes. Samples 1 and 2 gave count rates of 12 c/m and 14 c/m, respectively. If $R_B = 10$ c/m from a five-minute count, then $\sigma_B = (10/5)^{1/2} = 1.414$ c/m. Since $T_T = T_B$, we can use equation [2] for calculation of the critical level. Thus, $L_C = (2.33)(1.414) = 3.29$ c/m. Consider sample 1 where $R_T = 12$ c/m. Since $R_S = R_T - R_B$, $R_S = 2$ c/m. For this sample, $R_S < L_C$ and we must report a "less-than" value. We calculate the standard deviation of R_S , $\sigma_S = \left(\frac{12 + 10}{5}\right)^{1/2} = 2.10$ c/m and $R_{\text{Max}} = 2.0 + (1.65)(2.10) = 5.46$ c/m or 17.1 d/m. Sample 1 is then reported as containing <17.1 d/m ^{60}Co . For sample 2, $R_T = 14$ c/m, thus $R_S = 4$ c/m and $R_S > L_C$. A positive value with its two-sided 95 percent confidence interval should be reported. Calculating σ_S as before, $\sigma_S = \left(\frac{14 + 10}{5}\right)^{1/2} = 2.19$ c/m and $k_1\sigma_S = 4.29$ c/m. Thus, $R_S = 4 \pm 4.29$ c/m or, in terms of activity, 12.5 ± 13.4 d/m.

Note that the positive value reported for sample 2 is less than the "less-than" value reported for sample 1. If one wished to define an a priori detection limit for this system, $L_D = 2.71/5 + (2)(3.29) = 7.12$ c/m or 22.3 d/m.

APPLICATIONS

At the time of writing, this method of detection limit reporting is being used on all total beta and total alpha counts reported by the 222-S Analytical Laboratory counting room. Of primary importance are total beta and total alpha counts on environmental water samples. These samples are of two basic types - process control samples which are run daily, and environmental monthly composites run once a month. The results on the monthly composites are used to assess the total quantity of radioactive material released to the environment by the processing plants in the 200 areas. A computer program, titled ENVSAM*, is in place to calculate sample results on environmental composites, while a program, titled WATSAM* has been written to calculate results on the daily process control samples. Since the critical level, L_C , depends on the magnitude of the background, both ENVSAM and WATSAM contain routines to aid in background control. The calculation methods and required changes made in ENVSAM and WATSAM have been documented elsewhere^[2]. Work is proceeding to apply this method to gamma energy analysis results.

A Further Note

For those readers who are sufficiently motivated to refer to the source document by Currie^[1], a further note is in order. Currie actually defines, not two, but three levels of detection limits. The third limit which he terms the "Determination Limit (L_Q)" is that amount of material which must be present in order that the final result will have a statistical error of less than a given amount (for Currie, ± 10 percent at the 1σ level). To aid in the understanding of this type of a detection limit, references [3,4,5] are recommended.

*ENVSAM and WATSAM are BASIC programs which were written and updated by G. L. Troyer, ARHCO.

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REFERENCES

- [1] L. A. Currie, "Limits for Qualitative Detection and Quantitative Determination", Anal. Chem., Vol. 40, No. 3, 586-593, (1968).
- [2] Letter, J. K. Hartwell and G. L. Troyer to R. E. Wheeler, "ENVSAM and WATSAM", June 1972 (See Appendix).
- [3] D. E. Watt and D. Ramsden, High Sensitivity Counting Techniques, Macmillan Co., New York, NY, (1964).
- [4] W. H. Zimmer, "Limits of Detection of Isotopic Activity", ARHCO Analytical Methods Standard, Code EA001, (1972).
- [5] J. A. Cooper, "Factors Determining the Ultimate Detection Sensitivity of Ge(Li) Gamma-Ray Spectrometers", BNWL-SA-2940, January 23, 1970.

APPENDIX

ENVSAM AND WATSAM

Date: June 6, 1972
To: R. E. Wheeler
From: G. L. Troyer/J. K. Hartwell
Subject: COMPUTER PROGRAMS ENVSAM AND WATSAM

The computer program ENVSAM was written to automatically provide valid statistical analyses of environmental level radioactive samples. The original techniques utilized least squares, gap over range and modified "T" test to determine average background, eliminate flyers and calculate the standard error in the results. This original package was recently modified to improve the statistical validity of results according to work by L. A. Currie¹. Also, an additional program, WATSAM, has been written for higher activity samples in which background is more difficult to control.

ENVSAM - A program to calculate results for monthly composites of environmental water samples.

The primary problem in analyzing environmental level samples is accurate knowledge and control of counting backgrounds. Of major concern is the fact that at low count rates, statistical errors on the order of the square root of the total count yield high percent values. In our automatic sample changing system, we have taken steps to assure that these statistical errors are minimized.

We have the capability of counting up to 60 samples automatically using a Beckman Wide Beta II analyzer. We have established that 10 percent of the sample positions contain standards for instrument control. Half of the remaining positions are backgrounds using clean planchets without

¹Currie, L. A., Anal. Chem., 40, No. 3, March 1968, pp. 586-593

R. E. Wheeler
Page 2
June 6, 1972

sample, randomly selected. In the past, the background planchets and their holders were reused each time a set of samples was run. To overcome suspected low bias of background, we have gone to the random selection of planchets, planchet holders, and positions in the sample load. This, hopefully, will provide a more valid background determination.

The statistical treatment is handled in the following manner. The backgrounds are first tested for flyers using gap over range or deviation divided by standard deviation depending on the number of backgrounds, n . After testing for normal distribution, the average background and its deviation is calculated. The program notes that when a flyer is found, all planchets must be washed to 1) reduce background and 2) to reduce the standard deviation.

A critical limit is calculated to provide a test level for accepting and calculating a true positive answer. This value is 2.33 times the standard deviation of the background. If the net count rate (sample less ave. background) is less than zero, this value is used to calculate a "less than" result. No error range is attached.

If the net count is positive but less than the test level, a less than value is calculated using the net count plus 1.65 times the combined standard deviations of the total count and the average background. This allows the statement that in only 5 percent of all tests will the less than be exceeded.

For net counts greater than the test level, a positive value along with its two-sided 95 percent confidence interval is calculated along with a \pm percent error.

WATSAM - A program to calculate results for routine environmental water samples.

Unlike ENVSAM, WATSAM is associated with daily monitoring of radioactive process control water samples. By nature, these samples present higher potentials for background contamination. Also, the samples have a

R. E. Wheeler
Page 3
June 6, 1972

much higher activity and can be counted more rapidly than the low level monthly composites. The equipment is similar, however.

Once each day, the background is taken on each sample holder and stored for computer access. Instead of the rigorous statistical evaluation, each sample is tested against its prerecorded background. The less than values are generated from this point as in ENVSAM.

When the backgrounds are stored, the average and 2σ deviation are calculated and added to a file of up to 30 sets. This data is inspected periodically to determine if there indeed are gross changes in the background characteristics.

It should be noted that the + percent error referred to in both ENVSAM and WATSAM is only the statistical counting error and should not be considered to be the total measurement error. When compared to other measurement errors (notably sampling), the statistical counting error is relatively insignificant.

GLT:JKH:ss

cc: TR Garland
JJ Roemer