Procedure for Safe Drinking Water Act Program Detection Limits for Radionuclides

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1.0 Introduction

1.1 Background and Objectives

When analyzing radionuclides for the drinking water program, it is important to carefully evaluate method performance at the lowest concentrations attainable for the method. Critical water testing and treatment requirements impacting public health are made based on results that are often near the limits of method detection capability.

The Code of Federal Regulations (CFR) specifies Required Detection Limits (RDLs) for radionuclides. Laboratories must demonstrate their performance at those levels. Many radiochemistry laboratories are accustomed to using a Minimum Detectable Activity (MDA) to achieve this requirement. The MDA is a calculation that is based on counting precision that is scaled by multipliers to account for such factors as sample volumes, chemical yields, and counting times, which may vary. It is therefore a useful, sample-specific tool. However, MDA equations vary and may or may not account for the variability of the whole system (including, for example, the sample separation steps, which often precede instrument counting). Consequently, the Office of Ground Water and Drinking Water (OGWDW), in administering the National Drinking Water Program, emphasizes the need for laboratories to capably and reproducibly demonstrate system performance through detection limit studies. These experimental studies seek to confirm that the system does, in fact, meet the method performance that can be derived mathematically.

Because most radiochemistry methods are based on Poisson distributions rather than Gaussian distributions (as in other chemistry fields), the mechanism of calculating the detection limit for radionuclides differs from that described in 40 CFR 136 Appendix B, which is applied for inorganic and organic analytes. This document provides the derivation of the Safe Drinking Water Act (SDWA) program's radionuclide Detection Limit (herein after referred to as the "SDWA DL"), as well as practical steps for executing the experimental DL study.

1.2 Scope and Application

The procedure provided in this document describes the basis for the SDWA DL for radionuclides and provides an example calculation (see Appendix A) intended to assist laboratories conducting the DL determination for the first time. This procedure describes in detail the calculations associated with the radionuclide detection limit that is defined in 40 CFR 141.25(c). The DL procedure is one part of demonstrating method capability. The evaluation and monitoring of laboratory reagent blanks (LRBs) are also required to verify low system background, and method accuracy and precision are demonstrated through the evaluation of laboratory fortified blanks (LFBs).

2.0 Overview

As an initial estimate, laboratories should calculate their theoretical ability to meet the DL requirement of 40 CFR 141.25(c). Subsequently, they experimentally verify that their analytical system does actually perform consistently with what has been demonstrated in theory. The experimental verification consists of the analysis of at least seven standards spiked at or near the concentration of the RDL. These standards are taken through the entire analytical process, and the results are evaluated against a Chi-square (χ^2) distribution to determine if the experimental results compare favorably with the expected values.

3.0 Calculating Detection Limits for Radiochemical Measurements

3.1 Definition of the Detection Limit for SDWA Radiochemical Measurements

The detection capability of radiochemical measurements used for SDWA drinking water compliance monitoring is defined at 40 CFR part 141.25(c) as a detection limit with the following conditions:

"The detection limit shall be that concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96σ, where σ is the standard deviation of the net counting rate of the sample)."

The SDWA Detection Limit according to this definition differs from other "detection limits," such as the method detection limit or MDL (defined in 40 CFR part 136, Appendix B), and the Minimum Detectable Activity (MDA), which is commonly used by radiochemists. The RDLs for SDWA drinking water compliance monitoring of radionuclides are expressed in terms of the definition given in 40 CFR 141.25(c).

For measurements involving simple nuclear counting with Poisson counting statistics, the procedure given in Section 3.2 below is used to obtain a preliminary estimate of the SDWA DL.

3.2 Derivation of the SDWA Detection Limit Calculation

The **definition of the SDWA DL** may be expressed mathematically as follows:

$$R_{DL} = 1.96 \times \sigma_{DL} \qquad \textbf{(1)}$$

Where:
R_{DL} is the mean net count rate for a sample with concentration at the detection limit
σ_{DL} is the standard deviation of the net count rate

The relationship for the standard deviation of a radiochemical measurement is centered around the fact the gross rate has a background rate subtracted from it to derive a net count rate:

$$R_{DL} = R_G - R_B \qquad \textbf{(2)}$$

Where:
R_G is the mean gross count rate for a sample (with concentration at the DL)
R_B is the mean background count rate for a sample measurement

However, each count rate is a calculated quantity as specified below:

$$R_G = \frac{C_G}{t_G} \quad \text{and} \quad R_B = \frac{C_B}{t_B} \qquad \textbf{(3)}$$

Where:
R_G is the mean gross count rate for a sample (with concentration at the detection limit)
R_B is the mean background count rate for a sample measurement
C_G is the mean total (gross) sample count
C_B is the mean total background count

t_G is the time of the measurement used to accumulate the sample count
t_B is the time of the measurement used to accumulate the background count

The standard deviation of a count rate is proportional to the square root of the mean of a measurement. Assuming Poisson counting statistics, the standard deviations of the measured values of R_G and R_B are given by:

$$\sigma_G = \frac{\sqrt{C_G}}{t_G} = \sqrt{\frac{R_G}{t_G}} \quad \text{and} \quad \sigma_B = \frac{\sqrt{C_B}}{t_B} = \sqrt{\frac{R_B}{t_B}} \qquad \textbf{(4)}$$

Where:
σ_G is the standard deviation of the measured gross count rate
σ_B is the standard deviation of the measured background count rate

Since the net count rate, R_{DL}, is the difference between R_G and R_B, its standard deviation is given by:

$$\sigma_{DL} = \sqrt{(\sigma_G^2 + \sigma_B^2)} \qquad \textbf{(5)}$$

Where:
σ_{DL} is the standard deviation of the net count rate

Combining equations **(4)** and **(5)**, one arrives at:

$$\sigma_{DL} = \sqrt{\left(\frac{R_G}{t_G} + \frac{R_B}{t_B}\right)} \qquad \textbf{(6)}$$

Substituting equation **(6)** into equation **(1)**, one arrives at:

$$R_{DL} = 1.96 \times \sqrt{\left(\frac{R_G}{t_G} + \frac{R_B}{t_B}\right)} \qquad \textbf{(7)}$$

Equation **(2)** may now be used to eliminate the variable, R_G, from the equation. Since $R_G = R_{DL} + R_B$, equation **(7)** may be rewritten as:

$$R_{DL} = 1.96 \times \sqrt{\left(\frac{R_{DL}+R_B}{t_G} + \frac{R_B}{t_B}\right)} \qquad \textbf{(8)}$$

Equation **(8)** is then solved algebraically for the value of R_{DL}. First, rewrite the radicand:

$$R_{DL} = 1.96 \times \sqrt{\left(\frac{R_{DL}}{t_G} + R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)\right)} \qquad \textbf{(9)}$$

Squaring each side of the equation, one arrives at:

$$R_{DL}^2 = \frac{1.96^2}{t_G} \times R_{DL} + 1.96^2 R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right) \qquad \textbf{(10)}$$

Collecting all items on the left-hand side to put the equation in standard quadratic form, one arrives at:

$$R_{DL}^2 - \frac{1.96^2}{2t_G} \times R_{DL} - 1.96^2 R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right) = 0 \quad \textbf{(11)}$$

The quadratic formula gives two solutions to equation **(11)**, one of which is positive and one of which is negative. The positive solution is required and it is given by the following equation:

$$R_{DL} = \frac{1.96^2}{2t_G} \times \left[1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} \times R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right] \qquad \textbf{(12)}$$

Equation **(12)** provides a reasonable estimate of the count rate at the DL for the net activity that is based on counting statistics alone. This count rate is then divided by the product of the experimental factors, *H*, which can include the following items: the method of detection's counting efficiency, the sample volume, chemical recoveries (measured by gravimetric or tracer techniques), conversion factors to picocuries, etc. The result is used to derive a specific DL of the radioanalyte of interest for a radiochemical method of analysis that is used for SDWA compliance monitoring:

$$SDWA\ DL = \frac{R_{DL}}{H} \qquad \textbf{(13)}$$

Where:

H is the product of the experimental factors (see example calculations in Appendix A)
$SDWA\ DL$ is the SDWA Detection Limit

This SDWA DL is mathematically equivalent to the detection limit specified in 40 CFR part 141.25(c). It is expected that the experimental factors will vary with specific method and sample conditions.

If an estimate of the SDWA DL described in equation **(13)** does not exceed the required DL, a DL study is performed as described below to verify that laboratory performance in practice can be demonstrated prior to analyzing drinking water samples for compliance. However, if the estimate of the DL exceeds the required DL, the performance will be considered inadequate and there will be little value in completing the experimental DL study. Conditions would need to be adjusted to meet the required DL before proceeding to confirm the DL experimentally. This may entail using a larger sample volume or longer sample counting time.
NOTE: Typical drinking water compliance samples will have very low activity levels and compliance samples should be run under the same conditions as those used to confirm the DL.

4.0 Performing Experimental Confirmation of SDWA Detection Limits for Radiochemical Measurements

4.1 Experimental SDWA Detection Limit Studies

The experimental SDWA DL study will verify that the method is capable of routinely achieving the required detection capability.

The experimental SDWA DL study consists of seven replicate samples. Each sample is prepared with ASTM II grade reagent water, or other blank matrix as appropriate for the method, and using the sample volume described in the method. For example, gross alpha analyses are highly dependent on the total dissolved solids content in the sample matrix. Reagent water can yield artificially low DLs due to higher detector efficiencies. Thus, more realistic gross alpha DLs will be obtained using either laboratory tap water or a synthetic water solids matrix to prepare the DL study samples. Each DL study sample is spiked with NIST traceable source(s) of the method target radionuclide(s) to an activity concentration at or near their RDL. The sample is mixed and then processed through sample preparation, processing and analysis per the test method. The measurements of the DL study samples are then assessed by calculating a precision statistic.

4.2 Statistical Evaluation of Detection Limit Studies

The assessment of the replicate results for each radionuclide uses a chi-square statistic to test whether the relative standard deviation of the results exceeds the maximum value allowed at the RDL.

Calculate the mean, $\bar{X}$, and a chi-square statistic, χ^2, as follows:

$$\bar{X} = \frac{1}{n}\sum_{j=1}^{n} X_j$$

$$\chi^2 = \frac{1.96^2}{\mu^2}\sum_{j=1}^{n}\left(X_j - \bar{X}\right)^2$$

Where:
n is the number of replicate measurements ($\geq$ 7)
μ is the spike concentration (at or near the RDL)
X_j is the result of the j^{th} replicate measurement (j = 1,2,…, n)

To be deemed acceptable, the value of χ^2 must be less than or equal to the 99th percentile of the χ^2 distribution with (n-1) degrees of freedom. When n = 7, the value of this percentile is 16.812.
NOTE: Refer to Appendix A – Example Calculations. Refer to Appendix B for a table of Chi-square values.

5.0 References

1. 40 CFR 141: National Primary Drinking Water Regulations

2. ASTM D1193-99^{E01}: Standard Specifications for Reagent Water. American Society for Testing and Materials. March 1999, with editorial change made in October 2001.

3. MARLAP 2004. *Multi-Agency Radiological Laboratory Analytical Protocols Manual*. NUREG-1576, EPA 402-B-04-001C.

4. Chapter VI, Critical Elements for Radiochemistry. *The Manual for the Certification of Laboratories Analyzing Drinking Water*. (EPA/815-R-05-004).

Appendix A: Example Calculations

The following section provides example calculations for the estimation and experimental confirmation of the SDWA Detection Limit for radionuclide activity. The example uses gross alpha results obtained using EPA Method 900.0. The data was generated by the New Jersey Department of Health (NJDOH) Radioanalytical Services Laboratory, and is used with their permission[1].

1.0 Example Detection Limit Calculation

Equations (12) and (13) in Section 3.2 state:

$$R_{DL} = \frac{1.96^2}{2t_G} \times \left[1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} \times R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right]$$

And

$$SDWA\ DL = \frac{R_{DL}}{H}$$

Combining these equations and considering the experimental factors relevant for gross alpha determination, the following equation is obtained:

$$DL({}^{pCi}/_{L}) = \frac{1.96^2}{2t_G} \times \frac{\left[1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} \times R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right]}{(Efficiency)(Volume)(Chemical\ Recovery)(2.22)}$$

Where:
R_B is the mean background count rate for a sample measurement
t_G is the time of the measurement used to accumulate the sample count
t_B is the time of the measurement used to accumulate the background count
2.22 is the conversion factor from dpm to pCi

For this DL study, gross alpha recovery is assumed to be 100%. R_B = 0.03 cpm, Volume = 1.0 L, and t_G = t_B = 200 minutes. The detection efficiency was 0.177 cpm/dpm. Substituting these values into the equation produces the following:

$$DL\ ({}^{pCi}/_{L}) = \frac{1.96^2}{(2 \times 200)} \times \frac{\left[1 + \sqrt{1 + \frac{4(200)^2}{1.96^2} \times 0.03 \times \left(\frac{1}{200} + \frac{1}{200}\right)}\right]}{(0.177)(1)(1)(2.22)}$$

$= 9.6x10^{-3} \times \frac{1+\sqrt{1+12.5}}{0.393}$

$= 2.44x10^{-2} \times 4.7$

= **0.11 pCi/L**

The Required Detection Limit (RDL) for gross alpha is **3 pCi/L**. Because 0.11 pCi/L is a smaller quantity than 3 pCi/L, it is theoretically true that the counting times, volumes, and efficiencies assumed for this example would lead to acceptable precision at the RDL concentration.

2.0 Example Experimental SDWA Detection Limit Study

The instructions for performing an experimental SDWA DL study are given in Sections 4.1 and 4.2. The following example illustrates how the evaluation criteria are applied.

Table 1. Experimental Values for Seven Spiked Replicates

Replicates	Measured Gross Alpha (Th-230) Activity (pCi/L)	Spike Amount (pCi/L)
BS 1	2.89 $\pm$ 0.30	3.0
BS 2	5.51 $\pm$ 0.45	3.2
BS 3	2.88 $\pm$ 0.31	3.3
BS 4	3.72 $\pm$ 0.36	3.2
BS 5	3.42 $\pm$ 0.34	3.0
BS 6	3.11 $\pm$ 0.32	3.1
BS 7	3.17 $\pm$ 0.32	3.1
Average:	3.53	3.13

The mean gross alpha activity is calculated using the equation:

$$\bar{X} = \frac{1}{n}\sum_{j=1}^{n} X_j$$

Substituting the data, this produces:

$\bar{X} = \frac{1}{7}(2.89 + 5.51 + 2.88 + 3.72 + 3.42 + 3.11 + 3.17) = 3.53$ pCi/L

The Chi-square statistic is calculated using the equation:

$$\chi^2 = \frac{1.96^2}{\mu^2}\sum_{j=1}^{n}\left(X_j - \bar{X}\right)^2$$

Where:
n is the number of replicate measurements (7)
μ is the spike concentration (at or near the RDL; in this case 3.13 pCi/L)
X_j is the result of the j^{th} replicate measurement

Substituting the data, this produces:

$$\chi^2 = \frac{1.96^2}{3.13^2} \times [(2.89 - 3.53)^2 + (5.51 - 3.53)^2 + (2.88 - 3.53)^2 + (3.72 - 3.53)^2 + (3.42 - 3.53)^2 + (3.11 - 3.53)^2 + (3.17 - 3.53)^2]$$

$= \frac{3.84}{9.8} \times (5.1)$

= 2.0

This data set has seven replicates and thus, six degrees of freedom. So, the critical value for the statistic is the 99th percentile of the χ^2 distribution with six degrees of freedom, which equals

16.812. (see Chi-Square Table provided in Appendix B). Since the calculated χ^2 value of 2.0 does not exceed 16.812, the method passes the experimental DL study.

1. Detection Limit Study, Gross Alpha, Evaporation, EPA Method 900.0. Dr. Bahman Parsa, NJDOH Laboratory, 3 Schwarzkopf Drive, West Trenton, NJ 08628. June 14, 2011.

Appendix B: Chi-Square Values at the 99th Percentile

Table 2. Chi-Square Values (99th Percentile)

Degrees of Freedom	χ^2
1	6.635
2	9.210
3	11.345
4	13.277
5	15.086
6	16.812
7	18.475
8	20.090
9	21.666
10	23.209
11	24.725
12	26.217
13	27.688
14	29.141
15	30.578
16	32.000
17	33.409
18	34.805
19	36.191
20	37.566

Appendix C: Abbreviations and Acronyms

ASTM	ASTM International
CFR	*Code of Federal Regulations*
DL	Detection Limit
EPA	U.S. Environmental Protection Agency
MARLAP	*Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MDA	Minimum Detectable Activity
NJDOH	New Jersey Department of Health
NIST	National Institute of Standards and Technology
OGWDW	Office of Groundwater and Drinking Water
RB	Reagent Blank
RDL	Required Detection Limit
SDWA	Safe Drinking Water Act