# Radiochemistry Expert Committee (REC)
# Meeting Summary

## August 8, 2017

1. Roll Call and Minutes:

Bob Shannon, Chair, called the meeting to order at 1:04 pm Eastern on August 8, 2017 by teleconference. Attendance is recorded in Attachment A – there were 5 members present. Associates: Carolyn Wong and Bill Ray (until 1:20pm).

Meeting minutes are distributed by email for comment/revision for a week and then posted on the TNI website.

Bob had attendees in the room introduce themselves.

2. Status on Revisions of the Standard

Bob would like to have people start thinking about what types of changes are needed to the new 2016 Standard. Vas noted that when the 2016 Standard gets implemented, there will be more input. It may be a bit premature at this point.

Bob pointed out that the committee has a Deferred/Back Burner Items listing that is kept. Any recommendations that arise will be maintained on this listing.

3. Tools for Implementation

The committee has a number of tools available for people implementing the 2016 Standard.

- Comparison of the 2016 Standard vs. 2009 Standard. This was a live training done in Tulsa. There were about 35 people in attendance and the recorded webcast is available on the TNI training website.
- Small Laboratory Handbook (SLH). A final version was voted on by the committee, but Tom asked that a few more items be looked at. Bob will work with Tom to finalize the changes and get it back out to the committee and re-vote. The SLH puts things into layman language and includes examples. The module 6 section is fairly extensive. Vas asked if the Radiochemistry section will be merged into one document with the other modules or if it will be a stand-alone. Bob noted that each module with have a section and it will all be merged together.
- Module 6 Assessment Checklist. This checklist was just recently finished and submitted to TNI. TNI should have a complete checklist available by the end of the year. This committee used another format to prepare its checklist and should be helpful to understand the requirements of Module 6. It will also be helpful to

assessors that are not as familiar with Radiochemistry.

- Understanding 2016 TNI Module 6 Changes. This document helped prepare the Tulsa training and the SLH. It is not currently published. The committee will decide whether to do more with this or consider the SLH and training as the product.

4. New Implementation Tools

Bob asked what other types of implementation tools should be developed. There we no comments. Bob offered the following ideas:

Training for laboratories and assessors. Bob noted that he has had assessors in his labs that were not as familiar with radiochemistry and requirements as they should be. The goal with this training is to provide more knowledge. He would like to start working on some training modules. Richard Sheibley noted that it would be helpful for a training to include looking at real sanitized data. Give them a data package so they know what to expect when they get to a lab. Richard may be able to help with some of this. Roberto would like to see examples of acceptable data.

It was asked how many assessors for Radiochemistry are out there. It depends on what you consider an assessor. Richard has trained at least 40 and Bob has also trained a number at EPA trainings he has done. There is also the question of whether they have the background to assess radiochemistry. A number of assessors are DOE assessors. Bob would like to have a DOE member on the committee again.

Bob noted that there is a general assessors class that all assessors should take. It does complete with a test. What Bob is talking about is specific to Radiochemistry. It has been quite some time since Richard Sheibley last taught this class. This class requires a test. Bob noted that people would like to see a class designed with more than just Drinking Water.

Perhaps modules on specific technical topics could be an included in the training.

Bob has not set a timeline for this class yet. He would like to see this class in 6-12 months.

Discussion with people from the floor continued with people talking about the general need for training.

5. TNI PT Acceptance Criteria SOP

The PTPEC SOP subcommittee would like the committee to review the radiochemistry information in the SOP and to possibly write the information for radiochemistry into the SOP. Keith and Vas volunteered to help with this. Keith volunteered to take a lead.

6. Small Laboratory Handbook (SLH)

Bob decided to begin the review of the concerns raised by Tom in Attachment 1 of the SLH.

He started by correcting the title of the Attachment to Minimum Detectable Activity and Critical Value.

Bob shared the other changes being considered on the Webex screen that was also being shared with the attendees in the room. He also reviewed various examples. (Addition: Attachment D includes the changes made based on the review during the meeting and any additional final considerations that arose based on Tom's comments.)

The changes will be made to the SLH and it will be redistributed to the committee for vote by email.

7. New Business

None.

8. Action Items

A summary of action items can be found in Attachment B.

9. Next Meeting and Close

The next meeting is scheduled for September 27, 2017 at 1 pm Eastern by teleconference.

A summary of action items and backburner/reminder items can be found in Attachment B and C.

The meeting was adjourned at 2:32pm Eastern.

**Attachment A**
**Participants**
**Radiochemistry Expert Committee**

| Members | Affiliation | | Contact Information | |
|---|---|---|---|---|
| | | | Phone | Email |
| Bob Shannon (Chair) (2019) **Present** | QRS, LLC<br>Grand Marais, MN | Other | 218-387-1100 | BobShannon@boreal.org |
| Tom Semkow (Vice Chair) (2019) **Absent** | Wadsworth Center, NY State DOH<br>Albany, NY | AB | 518-474-6071 | thomas.semkow@health.ny.gov |
| Sreenivas (Vas) Komanduri (2019) **Present - Webex** | State of NJ Department of Environmental Protection<br>Trenton, NJ | AB | 609-984-0855 | Sreenivas.Komanduri@dep.state.nj.us |
| Marty Johnson (2019) **Absent** | US Army Aviation and Missile Command Nuclear Counting Redstone Arsenal, AL | Lab | 865-712-0275 | Mjohnson@tSC-tn.com |
| Dave Fauth (2018) **Present - Webex** | Consultant<br>Aiken, SC | Other | 803-649-5268 | dj1fauth@bellsouth.net |
| Keith McCroan (2018) **Present - Webex** | US EPA ORIA NAREL,<br>Montgomery AL | Lab | 334-270-3418 | mccroan.keith@epa.gov |
| Larry Penfold (2018) **Absent** | Test America Laboratories, Inc;<br>Arvada, CO | Lab | 303-736-0119 | larry.penfold@testamericainc.com |
| Ron Houck (2018*) **Absent** | PA DEP/Bureau of Laboratories | AB | 717-346-8210 | rhouck@pa.gov |
| Yoon Cha (2020) **Present** | Eurofins Eaton Analytical | Lab | 213-703-5800 | YoonCha@eurofinsUS.com |
| Candy Friday (2020) **Absent** | CdFriday Environmental, Inc. | Lab | 713-822-1951 | candy@fridayllc.com |
| Ilona Taunton (Program Administrator) **Recording Transcription** | The NELAC Institute | n/a | 828-712-9242 | Ilona.taunton@nelac-institute.org |

# Attachment B

## Action Items – REC

| | Action Item | Who | Target Completion | Completed |
|---|---|---|---|---|
| 75 | Prepare copy of Standard annotated with summary document language.<br>9/27/2017 – This item has been superseded by the Small Laboratory Handbook. | Carolyn | On hold | 9/27/2017 |
| 83 | Send SLH to Ilona after final update from today so she can do editing and formatting. | Bob/Dave | 6/10/17 | 7/5/2017 |
| 84 | She will send it back to the committee for further review. | Ilona | 6/28/17 | 8/9/2017 |
| 84 | Check calculation in examples in SLH. | Larry | 8/8/17 | 9/27/2017 |
| 85 | Make updates to SLH and send out for final vote by email. | Bob | 9/5/2017 | 9/8/2017 |
| 86 | | | | |
| | | | | |
| | | | | |

**Attachment C – Back Burner / Reminders**

| | Item | Meeting Reference | Comments |
|---|---|---|---|
| 5 | Form subcommittee of experts in MS and other atom counting techniques to see that these techniques are adequately addressed in the radiochemistry module. | 9/24/14 | |
| | | | |

Attachment 1:

## Minimum Detectable Activity and Critical Value

Radiochemical data are often reported to include minimum detectable activity (MDA) or minimum detectable concentration (MDC) with sample results.[3] The MDA, as an *a priori* parameter, should be used to select a method that will be able to meet a Measurement Quality Objective (MQO) for detection capability (i.e., a Required MDA).

Laboratories frequently misuse the MDA concept by employing MDAs to decide whether a measurement indicates that activity is present in a sample. This practice is incorrect and should be avoided. The TNI standard and MARLAP recommend using the Critical Value (a.k.a. Critical or Decision Level) for detection decisions.

Radiochemical data are often reported in association with a sample-specific MDA. The sample-specific MDA reflects the specific analytical factors used to calculate a sample result. It indicates how well the measurement process is performing under varying real-world measurement conditions when sample-specific characteristics (e.g., interferences) may affect the detection capability. The MDA must *never* be used instead of the Critical Value as a detection threshold.

A number of specific analytical factors can affect the measurement process. Inadequate sample volume, short counting time, low detection efficiency, poor chemical yield, all can affect the detection capability of a method. The laboratory must have procedures in place for determining and documenting the detection capability even when such criteria are not found in the method, regulation or contract. Additionally, projects involving cleanup of contaminated sites often include requirements in contract specifications to report sample-specific MDAs. The laboratory needs to comply with the contract specifications.

There are multiple formulations used to calculate MDAs and critical values. Several variants of nearly the same formula may all satisfy the definition of MDA and critical value included in the Standard depending on details of the measurement. The discussion below provides an example for the determination of Critical Value and MDA.

[3] The MDC is the MDA expressed in terms of activity concentration instead of activity. For the purposes of the TNI Standard and the discussion that follows, both concepts will be referred to as MDA.

A laboratory receives a 1 L wastewater sample from one of its customers. The chain of custody indicates that it is a ground water sample from site near an operating nuclear power plant. The analysis required on the sample is $^{3}H$. The laboratory analyzes the sample 66 days after sample collection by distilling the water sample and analyzing a portion of the purified sample in a liquid scintillation counter. The critical level and MDA may be calculated as follows:

*Sample counting time: $t_s$ = 45 minutes*
*Subtraction background counts: $C_B$ = 193 counts*
*Subtraction background count time, $t_B$ = 90 minutes*
*Sample volume: V = 0.008 L*
*Counting efficiency in the tritium window: ε = 0.25*
*Decay factor for 66 days elapsed between collection and analysis, DF: 0.9899*
*Factor to convert from dpm to pCi: 2.22 dpm/pCi*

The decay correction factor, DF, for 66 days between sample collection and the count (valid for unsupported decay) was calculated as follows:

$$DF = e^{-\lambda \Delta t}$$

Where:

e = base of the natural logarithm – 2.7183
λ = decay constant for tritium
= ln2 / half-life of tritium
= 0.69315 / (12.32 years × 365.24 days/year) = 0.00015404 $d^{-1}$
Δt = time elapsed between the activity reference date and the count in days (the same time units used for decay constant)

Substituting the data into the formula, DF is 0.9899.

The laboratory calculates the Critical Level, $L_C$, using the following formula:

$$L_c \frac{1.645 \times \sqrt{C_B \times \frac{t_S}{t_B} \times \left(1 + \frac{t_S}{t_B}\right)}}{t_s \times \varepsilon \times V \times DF \times 2.22}$$

The numerator term in this formula calculates critical net signal, $S_C$ (e.g., counts or count rate). The same factors used to calculate the sample result from sample net counts or count rate, represented using a generic collective term K, are applied to $S_C$ to calculate the Critical Level in the same reporting units as the sample result. Thus,

$$S_c = 1.645 \times \sqrt{\frac{R_B}{t_S} \times \left(1 + \frac{t_S}{t_B}\right)} \quad and \quad L_c = \frac{S_c}{K}$$

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *100 Min.*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *200*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *%*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *9882*

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Font:Italic

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Left

Several algebraically equivalent expressions for $S_C$ are in common use including:

$$S_C = 1.645\times\sqrt{\frac{R_B}{t_S}\times\left(1+\frac{t_S}{t_B}\right)} = \left[1.645\times\sqrt{C_B\times\frac{t_S}{t_B}\times\left(1+\frac{t_S}{t_B}\right)}\right]/t_S$$

This expression is valid for any sample and subtraction background count times (although subtraction background counts should always be at least as long as the sample count. This expression simplifies to the following commonly used critical level formula when $t_S$ and $t_B$ are equal:

$$S_C = 1.645\times\sqrt{\frac{R_B}{t_S}\times(1+1)} = 2.33\times\sqrt{\frac{R_B}{t_S}}$$

Similar considerations apply also to the MDA and SDWA calculations.

Substituting the data into the formula, the $L_c$ would be 100 pCi/L. When the sample result is equal to or greater than $L_c$, one would conclude that analyte was detected by the measurement.

Results and uncertainty are generally reported "as measured" regardless of their magnitude (positive, zero or negative). It may be appropriate to flag results with qualifiers to indicate, for example, that the measurement did not detect activity (i.e., the result was less than the critical level).

The laboratory calculates the MDA using the following formula:

$$\text{MDA} = \frac{2.71 + 3.29\times\sqrt{C_B\times\frac{t_S}{t_B}\times\left(1+\frac{t_S}{t_B}\right)}}{t_s\times\varepsilon\times V\times DF\times 2.22}.$$

Substituting the data into the formula, the value for the MDA would be 214 pCi/L. Although a sample specific MDA may by reported, the laboratory should never compare a result to, or censor a result relative to an MDA (e.g., "<MDA").

A detailed discussion of the Critical Value and MDA concepts is presented in Chapter 18 of the MARLAP Manual and is strongly recommended to the reader.

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Subscript

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** 113

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** Sample results may be compared to

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** to determine whether or not

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** to be

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** ".

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** 227

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** i.

**Attachment 2:**

**METHOD VALIDATION STUDY**

INTRODUCTION

The example in this document is for illustrative purpose and not necessarily the only approach that can be used for method validation. Historically, radioanalytical, regulations and even contract(s) have not consistently provided requirements for method performance and method validation. Therefore, laboratories are often forced to develop their own procedure(s) for method validation. Such method validation should be as extensive as necessary depending upon the method, regulation or contract to which a laboratory has agreed to be bound. The example in this document is one such model for the validation.

THE EXAMPLE

Let us assume XYZ Labs is a NELAP laboratory. The laboratory is seeking accreditation for Gross Alpha analysis of drinking water samples by co-precipitation method. The laboratory performed a method validation study and documented the results. Following is an excerpt from the study.

- Parameter: Gross Alpha
- Applicable Matrix: Drinking Water
- Reference Method: SM 7110C, Laboratory SOP XYZ123. Rev 2
- Method Description: Co-Precipitation

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** - NJ Parameter Code: DW10.00130

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** Technique

Study description: The XYZ Lab QA Manual includes a method validation study procedure. Per the Manual, the following elements comprise method validation study.

A) Detection Limit study,
B) Precision & Bias (Accuracy) Study,
C) Measurement Uncertainty,
D) Selectivity, and
E) Analysis of an external QC (or a PT) Sample.

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** study

A) CALCULATION OF THE SDWA DETECTION LIMIT AND DETECTION LIMIT STUDY

CALCULATION OF SDWA DETECTION LIMIT

The detection limit for compliance monitoring purposes under the Safe Drinking Water Act is the SDWA Detection Limit (DL). Best laboratory practices include reporting SDWA compliance sample results for radiochemical parameters not only in association with their measurement uncertainty but also with the sample-specific SDWA detection limit.

The SDWA DL is defined in the 40 CFR Part 141.25(c) as 'that concentration which can be counted with a precision of ±100% at the 95% confidence level (1.96σ where σ is the standard deviation of the net counting rate of the sample)'. A generic equation for SDWA DL is:

$$\text{SDWA DL} = \frac{\frac{1.96^2}{2t_S} \times \left(1 + \sqrt{1 + \left[\frac{4t_S^2}{1.96^2} \times R_B \times \left(\frac{1}{t_S} + \frac{1}{t_B}\right)\right]}\right)}{K}$$

where

$R_B$ is the background subtraction sample count rate,
$t_S$ and $t_B$ are counting times for sample and background, min.,
K is a collective term that converts net count rate to sample activity in the desired reporting units.

The generic formula calculates the detection limit in units of net count rate (e.g., background subtracted counts per minute) and then applies a collective term, K, that combines all of the factors that would be used to convert net count rate to sample activity in the desired reporting units (e.g., pCi/L, Bq/g, etc.) The equation must be modified for each method to parallel the equation used to calculate the measurement result.

Thus, for the gross alpha co-precipitation method 7110C, the formula used to calculate the sample activity concentration in pCi/L is:

$$\text{Activity Concentration} = \frac{R_S - R_B}{K} = \frac{R_S - R_B}{2.22 \times \varepsilon \times V}$$

Where K is the product of 2.22, the efficiency and the volume of the sample aliquot. The corresponding formula for the SDWA DL would then be:

$$\text{SDWA DL} = \frac{\frac{1.96^2}{2t_S} \times \left(1 + \sqrt{1 + \left[\frac{4t_S^2}{1.96^2} \times R_B \times \left(\frac{1}{t_S} + \frac{1}{t_B}\right)\right]}\right)}{2.22 \times \varepsilon \times V}$$

Where:

*Gross count rate for the sample, $R_S$: (not used in this example*
*Background subtraction sample count rate, $R_B$: 0.11 cpm*
*Volume of the sample, V: 1.0 L*
*Calibrated efficiency for alpha particles for detector used, ε: 0.1800*
*Conversion factor for dpm to pCi: 2.22 dpm/pCi*





Deleted: The
Bob Shannon 8/31/2017 10:27 AM
Moved (insertion) [1] ... [1]
Bob Shannon 8/31/2017 10:27 AM
Deleted: SDWA DL $\left(\frac{pCi}{L}\right)$ = ... [2]
Bob Shannon 8/31/2017 10:27 AM
Deleted: net
Bob Shannon 8/31/2017 10:27 AM
Deleted: $\left(\frac{pCi}{L}\right) = \frac{R_S - R_B}{K} = \frac{R_S - R_B}{K}$ ... [3]
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [4]
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [5]
Bob Shannon 8/31/2017 10:27 AM
Deleted: of...or the SDWA DL parallel this ... [6]
Bob Shannon 8/31/2017 10:27 AM
Deleted: SDWA DL $\left(\frac{pCi}{L}\right)$ = ... [7]
Bob Shannon 8/31/2017 10:27 AM
Moved up [1]: where
Bob Shannon 8/31/2017 10:27 AM
Deleted: $R_S$ is the gross
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [8]
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [9]
Bob Shannon 8/31/2017 10:27 AM
Deleted:
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [10]
Bob Shannon 8/31/2017 10:27 AM
Deleted: $R_B$ is the background
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [11]
Bob Shannon 8/31/2017 10:27 AM
Deleted: of
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [12]
Bob Shannon 8/31/2017 10:27 AM
Deleted: CPM,
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [13]
Bob Shannon 8/31/2017 10:27 AM
Deleted: V is the volume
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [14]
Bob Shannon 8/31/2017 10:27 AM
Deleted: in L. It is recommended to use
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [15]
Bob Shannon 8/31/2017 10:27 AM
Deleted: for co-precipitation method.
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [16]
Bob Shannon 8/31/2017 10:27 AM
Deleted: ε is the detection
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [17]
Bob Shannon 8/31/2017 10:27 AM
Deleted: Is determined during ... [18]
Bob Shannon 8/31/2017 10:27 AM
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [19]
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [20]
Bob Shannon 8/31/2017 10:27 AM
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [21]
Bob Shannon 8/31/2017 10:27 AM
Bob Shannon 8/31/2017 10:27 AM
Formatted ... [22]
Bob Shannon 8/31/2017 10:27 AM

*Count times for sample and background, $t_S$ and $t_B$: 200 and 600 min. respectively.*

Substituting the values for our sample into the above equation gives an SDWA DL of 0.053005 pCi/L (unrounded). Since this value is less than the required detection limit (RDL) of 3 pCi/L for Gross Alpha, the method would meet requirements for detection capability.

*Note: $L_C$ and MDA/MDC, and SDWA DL are very different concepts. See Attachment 1 for a discussion of the $L_C$ and MDA/MDC.*

*How is the DL affected by limited sample volume or shorter counting intervals? Too often, all laboratories find themselves having less than 1 L of sample or perhaps one of their instruments suddenly goes down requiring tight control over count time for the functioning equipment(s).*

*Let us assume that the laboratory has limited sample. An aliquot of 0.5 L is only available for the test. We assumed 1 L in our example. How will the reduced volume impact our DL? By substituting 0.5 L in the above equation, we find the DL is now 0.10601 pCi/ L (unrounded). Although the DL has just doubled, it is still low enough to meet the RDL of 3 pCi/L.*

*It is possible in advance to calculate DL for optimum counting time, or sample volume, or both. Can the laboratory count the sample and background for only 1 hour? All other parameters being the same as the example with decreased volume, the DL is now 0.7755 pCi/L (unrounded), which still falls below the RDL. Being able to optimize count times in advance is advantageous for laboratories with limited resources of equipment and manpower, and when additional challenge of higher than normal workload is received by the laboratory.*

DETECTION LIMIT STUDY:

The SDWA DL calculation assumes that the only contributor to the uncertainty of the background is the random nature of radioactive decay (i.e., counting uncertainty). In a perfect world, the counting uncertainty would be approximated by a Poisson distribution where the square root of the number of counts is a good estimator of the standard deviation of the counts. In reality, however, there may be additional uncertainty from other sources.

Thus, drinking water laboratories may be required to perform detection limit studies to demonstrate that the detection capability of the methods, as run, is sufficient to meet SDWA program requirements. Describing this study in detail goes beyond the scope of this document. Instead, we will point readers to a recent EPA document, *Procedure for Safe Drinking Water Act Program Detection Limits for Radionuclides*





Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $t_c$ and $t_B$ are counting

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** minutes

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Font:Italic

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** of

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Font:Italic

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Font:Italic

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** .

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Font:Italic

Bob Shannon 8/31/2017 10:27 AM
**Formatted:** Normal

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** 16

Bob Shannon 8/31/2017 10:27 AM
**Deleted:**

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** .

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *or*

Bob Shannon 8/31/2017 10:37 AM
**Deleted:** *on*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *32*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** .

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *will*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *be*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *63*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** *for a 1 hour count,*

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** .

*(EPA 815-B-17-003),* which describes in detail a process that can be used to statistically demonstrate the detection capability of the method is adequate to meet the SDWA RDL.

B) PRECISION & BIAS (ACCURACY) STUDY:

Section 1.5.1 requires the laboratory to validate each method in each quality system matrix for which it is applicable by demonstrating the method's detection capability, precision, bias, Measurement Uncertainty, and selectivity using the procedures specified in Sections 1.5.2 through 1.5.5.

Evaluating bias and precision are critical elements of method validation. While there are many approaches that can be taken, a relatively straightforward one is presented here. By analyzing seven replicates in the quality systems matrix, spiked at each of several different activity levels, the laboratory can produce representative data that forms the basis for the evaluation of bias and precision. Thus, bias and precision are characterized across a range of activities the laboratory expects to encounter in samples. If known, the range should ideally include the activity at which important decisions will be made (e.g., whether contamination is present above a specified limit). The Standard specifically mentions that the range should include zero activity since, generally, all results must be reported as measured in association with their measurement uncertainty even if they are negative or zero.

For example, the laboratory might perform replicate analysis to evaluate bias and precision for the gross alpha coprecipitation method. The laboratory would analyze seven replicates at the MCL for gross alpha in drinking water (15 pCi/ L) as well as seven replicates at each of two concentration levels, one above and one below the action level. They also would analyze seven replicate blanks to evaluate absolute bias at background. Bias and precision can be evaluated at all levels.

EVALUATION OF SPIKED SAMPLES FOR RELATIVE BIAS:

In general, relative method bias is determined by calculating the arithmetic mean recovery of the seven replicates at each activity level using the formula:

$$Relative\ Bias\ (\%) = \left(\frac{\overline{X}}{\mu} - 1\right) \times 100$$

Where,

$\overline{X}$ is the mean recovery of the seven replicates, and

μ = true value for the test sample

The output of this equation yields values for relative bias at three concentrations. The target value for relative bias is 0%.

Bob Shannon 8/31/2017 10:27 AM

**Deleted:** $\overline{X}$

Unknown

**Formatted:** Font:+Theme Body, Lowered by 2 pt

It is strongly recommended that laboratories test their relative bias results to determine whether the test statistically detects "bias" or not. If bias is not detected, there is no need to take action. They can state whether or not bias was detected in their documentation/reports, and if it was, the magnitude of the bias.

Again, describing in detail the tests for relative bias goes beyond the scope of this document. One approach that has been used is discussed in detail in Section 5.6.2 of *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities*, (EPA 402-R-09-006).

EVALUATION OF BLANKS FOR ABSOLUTE BIAS:

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** .

The concept of relative bias, as defined above, is meaningless for blank samples since the target activity is zero and dividing by zero will yield an undefined result. A more commonly used approach calculates the arithmetic mean activity of the seven blank samples, generally in the same reporting units as sample results (e.g., pCi/L or Bq/g).

Similar to the relative bias above, these results can be tested for "absolute bias". Once again, this test is beyond the scope of this discussion but is described in detail in Section 5.6.1 of *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities*, (EPA 402-R-09-006).

Alternatively, a laboratory could calculate a z-score for blanks by dividing the average absolute bias by the standard deviation of the replicate measurements. The z-score shows the magnitude of the mean value for blanks normalized to the uncertainty (i.e., standard deviations from zero). Z-score is generally evaluated by comparing to critical values of ±2 and ±3 (a.k.a., warning and control limits) which correspond to the 95% and 99.7% confidence levels for the distribution.

If bias is detected, it is recommended that the lab work to identify and eliminate (or correct) the cause for the bias. This may include changing materials or procedure, or applying a correction for bias as described in the document above.

EVALUATION OF PRECISION

Similar to the evaluation of bias, precision can be evaluated in a number of valid ways. The approach presented here is straightforward. The precision of the method is determined by calculating the percent relative standard deviation (%RSD) of the spiked analyte recoveries of the seven replicates at each of the levels evaluated.

Relative Precision = $\frac{\sigma}{\overline{X}} \times 100\%$,

where

$\overline{X}$ = Arithmetic mean value for the seven replicates

σ = Standard deviation for the seven replicates

If there are external requirements for relative precision, the calculated relative precision can be directly compared to the limits to determine whether the method will provide sufficient precision. In cases where the laboratory sets their own limits, it may be sufficient to calculate the relative precision and to use that as the limit, thereafter.

It is important to remember that the precision is a function of concentration. The precision will decrease (i.e., relative uncertainty will increase) as the concentration of samples approaches background. This thought will be discussed further under measurement uncertainty below. The reader may also wish to refer to the discussion of precision under Sample Specific QC measures (1.7.2.4) including RPD and DER illustrated for precision.

DOCUMENTATION AND USE OF BIAS AND PRECISION TESTING RESULTS

Many laboratories present the results of bias and precision testing in their Quality System documents. Bias and precision are quantitative performance criteria that can be incorporated into scope and applicability statements of SOPs or method capability tables in quality manuals. Laboratories can also use them to evaluate and present method performance to clients and data users and during the evaluation of contracts and tenders prior to accepting work.

The laboratory should be cautious about assessing the acceptability of bias and precision results by comparing to a required acceptance range. Externally established limits for laboratory control samples may give a skewed or misleading picture of method capability. Consider, for example, a requirement for the acceptance of LCS results that states that measured results must fall within 25% of the true value. We analyze our QC data and observe an average relative bias of 24% - just 1% below the acceptable upper limit. Although the calculated average appears to fall within the specified range, nearly half of all results will fall outside the acceptable range and this would not meet the MQO provided.

C) Measurement Uncertainty:

Similar to above, there are different ways that one could demonstrate that the experimentally observed standard deviation (σ) is not statistically greater than the maximum combined uncertainty of the measurement results. The simplest test is to compare the largest uncertainty value for a group of 7 validation samples at a given concentration to the standard deviation of those values. If the largest value is greater than the standard deviation,the criterion is met.

D) Selectivity:

Selectivity refers to the degree to which the method can quantify the target analyte in the presence of other analytes, matrices, or other potentially interfering materials. For the

gross alpha technique being a screening technique, the selectivity is achieved by the radiochemical separation that isolates the analytes of interest in the medium. Additionally, when counting samples with a gas flow proprotional counter (that is capable of distinguishing alpha emsision and beta emissions on the basis of the energy deposition in the sensitive volume of the detector), the selecivity is enhanced substantially. And, the cross talk correction by the counting system further enhances selectivity of the method. Therefore, the selectivity of the method is adequate and acceptable.

**Attachment 3.**

**Measurement Uncertainty**

**Example: Standard counting uncertainty and total combined standard uncertainty**

Scenario: A lab analyzes water samples for tritium using liquid scintillation counting. The method involves distillation of each sample and provides for a single-point calibration without a quench curve. The tritium activity concentration is calculated using the equation

$$AC = \frac{C_S/t_S - C_B/t_B}{(2.22\ dpm/pCi)\times t\times\varepsilon\times V\times DF} \quad (1)$$

where

- $AC$ is the tritium activity concentration as of the sample reference date (pCi/L),
- $C_S$ is the number of sample counts,
- $C_B$ is the number of background counts,
- $t_S$ is the sample count time (min),
- $t_B$ is the background count time (min),
- $\varepsilon$ is the tritium counting efficiency,
- $V$ is the sample aliquot volume (L), and
- $DF$ is the decay factor (for decay from collection).

The standard counting uncertainty, $u_{cC}(AC)$, is calculated by propagating only the uncertainties of the counts, $C_S$ and $C_B$. Assuming Poisson counting statistics, the uncertainty of $C_S$ is $\sqrt{C_S}$ and the standard uncertainty of $C_B$ is $\sqrt{C_B}$. The counting uncertainty is then given explicitly by the equation:

$$u_{cC}(AC) = \frac{\sqrt{C_S/t_S^2 + C_B/t_B^2}}{2.22\times\varepsilon\times V\times DF} \quad (2)$$

The total combined standard uncertainty, $u_c(AC)$, may include not only the counting uncertainty but also uncertainty components due to the efficiency $\varepsilon$ and the aliquot volume $V$. For example:

$$u_c(AC) = \sqrt{\frac{C_S/t_S^2 + C_B/t_B^2}{2.22^2\times\varepsilon^2\times V^2\times DF^2} + AC^2\times\left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2}\right)} \quad (3)$$

where $u(\varepsilon)$ is the standard uncertainty of the efficiency and $u(V)$ is the standard uncertainty of the aliquot volume. Here we assume that any uncertainty in the count times or the decay factor is negligible.

Equation 1 is a special case of a general type of activity equation of the form:

$$AC = \frac{C_S/t_S - C_B/t_B}{K_1\times K_2\times\ldots\times K_n} \quad (4)$$

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $u_{cC}(AC) = \frac{\sqrt{C_S/t_S^2 + C_B/t_B^2}}{(2.22\,\mathrm{dpm/pCi})\times\varepsilon\times V\times}$ (2)

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $u_c(AC) = \sqrt{\frac{C_S/t_S^2 + C_B/t_B}{(2.22\,\mathrm{dpm/pCi})^2\times\varepsilon^2\times}}$ (3)

Unknown
**Formatted:** Font:+Theme Body, Lowered by 17 pt

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $AC = \frac{C_S/t_S - C_B/t_B}{K_1\times K_2\times\cdots\times K_n}$ (4)

Unknown
**Formatted:** Font:+Theme Body, Lowered by 15 pt

where $t_S$ denotes the sample count time, $t_B$ denotes the background count time, and the factors $K_1$ through $K_n$ depend on the method. The standard counting uncertainty for equation 4 is given by:

$$u_{cC}(AC) = \frac{\sqrt{C_S/t_S^2 + C_B/t_B^2}}{K_1 \times K_2 \times \ldots \times K_n} \quad (5)$$

and the total combined standard uncertainty is given by:

$$u_{cC}(AC) = \sqrt{\frac{C_S/t_S^2 + C_B/t_B^2}{K_1 \times K_2 \times \ldots \times K_n} + AC^2 \times \left(\frac{u^2(K_1)}{K_1^2} + \frac{u^2(K_2)}{K_2^2} + \cdots + \frac{u^2(K_n)}{K_n^2}\right)} \quad (6)$$

MARLAP Section 19.4.3 discusses *Special Forms of the Uncertainty Propagation Formula*. MARLAP Example 19.10 presents an example based on Equation 19.16 that is very similar to one presented here.

To calculate uncertainties for more general types of activity equations, see the guidance in documents such as:

*Guide to the Expression of Uncertainty in Measurement* (available at http://www.bipm.org/en/publications/guides/gum.html),

NIST Technical Note 1297 "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results" (available at https://www.nist.gov/pml/nist-technical-note-1297), or

Chapter 19 ("Measurement Uncertainty") of the *Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual* (available at https://www.epa.gov/radiation/multi-agency-radiological-laboratory-analytical-protocols-manual-marlap).

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $u_{cC}(AC) = \frac{\sqrt{C_S/t_S^2 + C_B/t_B^2}}{K_1 \times K_2 \times \ldots \times K_n}$ (5)

Unknown
**Formatted:** Font:+Theme Body, Lowered by 15 pt

Bob Shannon 8/31/2017 10:27 AM
**Deleted:** $u_c(AC) = \sqrt{\frac{C_S/t_S^2 + C_B/t_B^2}{K_1^2 \times K_2^2 \times \cdots \times K_n^2} + AC$

Unknown
**Formatted:** Font:+Theme Body, Lowered by 17 pt

**Page 45: [1] Moved from page 45 (Move #1)** **Bob Shannon** **8/31/17 10:27 AM**

where

**Page 45: [2] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

$$\text{SDWA DL}\left(\frac{\text{pCi}}{\text{L}}\right) = \frac{\frac{1.96^2}{2t_G} \times \left(1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} R_B \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right)}{K}$$

**Page 45: [3] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

$$\left(\frac{\text{pCi}}{\text{L}}\right) = \frac{R_S - R_B}{K}$$

**Page 45: [3] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

$$\left(\frac{\text{pCi}}{\text{L}}\right) = \frac{R_S - R_B}{K}$$

**Page 45: [4] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Cambria Math

**Page 45: [5] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Indent: First line: 0"

**Page 45: [6] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

of

**Page 45: [6] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

of

**Page 45: [7] Deleted** **Bob Shannon** **8/31/17 10:27 AM**

$$\text{SDWA DL}\left(\frac{\text{pCi}}{\text{L}}\right) = \frac{\frac{1.96^2}{2t_G} \times \left(1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} R_B \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right)}{2.22 * \varepsilon * V}$$

**Page 45: [8] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Indent: Left: 0.88", Hanging: 0.38"

**Page 45: [9] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Italic

**Page 45: [10] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Italic

**Page 45: [11] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Italic

**Page 45: [12] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Italic

**Page 45: [13] Formatted** **Bob Shannon** **8/31/17 10:27 AM**

Font:Italic

| Page 45: [14] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [15] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [16] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [17] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [18] Deleted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Is determined during calibration of the

| Page 45: [19] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [20] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [21] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [22] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic

| Page 45: [23] Formatted | Bob Shannon | 8/31/17 10:27 AM |
|---|---|---|

Font:Italic