Radiochemistry Expert Committee (REC)
Meeting Summary

March 1, 2017

1. Roll Call and Minutes:

Bob Shannon, Chair, called the meeting to order at 1:00 pm Eastern on March 1, 2017 by teleconference. Attendance is recorded in Attachment A – there were 6 members present. Associates members Present: Yoon Cha, Jim Chambers, Candy Friday, Carl Kircher, Terry Romanko, Jennifer Western and Carolyn Wong.

The January minutes were distributed by email and will be posted if there are no email comments.

2. Small Lab Handbook

Bob thinks the word "shall" seems too authoritative. This is a guidance document; the word "shall" seems unapproachable. "Shall" should only be used when it is a quote from the Standard.

Dave started reviewing the changes he made based on the conversation during the previous call.

1.5.3 Dave will go through Bob's comments and make changes.

1.5.4 Tom noted that he suggested quite a few changes, but does not see them reflected in the changes made to this section. Dave will go back through it.

1.5.5 – Vas is working on an example.

1.6.2 – The example will be moved up to Keypoints and reworded. Terry noted that the wording is not consistent – low, medium and high? Only two points (low and high) are discussed in other areas. Bob noted that performance checks use low and high. QC is done with low, medium and high. This was done on purpose. Carolyn confirmed that the language is the same as the Standard.

1.7 – This will be rewritten based on Bob's comments. Tom's comments also need to be incorporated. Dave will send Tom a Track Changes version that show the changes made in response to Tom's comments.

1.7.1.4 – Example 1
Delete "performance" and change to: Subsequent performance checks did not indicate and change in <u>efficiency or resolution</u>.

1.7.2.1 – Example 1
Terry commented that it should be method not matrix blank.

The current version of the Small Laboratory Handbook can be found in Attachment D. The attachment reflects any changes made during the call and includes comments made. Time did not permit finishing the review of the document. Dave will take this version and make updates based on today's conversation. He is also waiting for some examples.

3. Committee Membership

Bob introduced two candidates who have applied for membership on the committee: Yoon Cha and Candy Friday. Each candidate introduced herself.

All associates were asked to leave the call for 5 minutes so the committee could freely discuss the candidates and impact on the committee. Any additional members being looked at for the committee should have actual laboratory/hand-on experience.

A motion was made by Marty and seconded by Keith to add both members to the committee. The motion passed unanimously.

The committee can have as many as 15 members.

Ilona will submit the new members to Bob Wyeth and Ken Jackson from the CSDP Executive Committee.

4. Charter

Bob distributed a copy of the DRAFT charter for everyone to review this month. It will be discussed later in the month at the next meeting and hopefully finalized.

5. Checklist

Larry could not be available on today's call and the Checklist will be discussed at the next meeting.

6. New Business

None.

7. Action Items

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

8. Next Meeting and Close

   The next meeting is scheduled for March 22, 2017 at 1pm Eastern.

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

   The meeting was adjourned at 2:38 pm Eastern.

Attachment A
Participants
Radiochemistry Expert Committee

Members	Affiliation		Contact Information	
			Phone	Email
Bob Shannon (Chair) (2019) **Present**	QRS, LLC Grand Marais, MN	Other	218-387-1100	BobShannon@boreal.org
Tom Semkow (Vice Chair) (2019) **Present**	Wadsworth Center, NY State DOH Albany, NY	AB	518-474-6071	thomas.semkow@health.ny.gov
Sreenivas (Vas) Komanduri (2019) **Absent**	State of NJ Department of Environmental Protection Trenton, NJ	AB	609-984-0855	Sreenivas.Komanduri@dep.state.nj.us
Marty Johnson (2019) **Present**	US Army Aviation and Missile Command Nuclear Counting Redstone Arsenal, AL	Lab	865-712-0275	Mjohnson@tSC-tn.com
Dave Fauth (2018) **Present**	Consultant Aiken, SC	Other	803-649-5268	dj1fauth@bellsouth.net
Keith McCroan (2018) **Present**	US EPA ORIA NAREL, Montgomery AL	Lab	334-270-3418	mccroan.keith@epa.gov
Larry Penfold (2018) **Absent**	Test America Laboratories, Inc; Arvada, CO	Lab	303-736-0119	larry.penfold@testamericainc.com
Ron Houck (2018*) **Present**	PA DEP/Bureau of Laboratories	AB	717-346-8210	rhouck@pa.gov
Ilona Taunton (Program Administrator) **Present**	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.	Carolyn	On hold	
80	Combine recent work on Checklist to produce an updated copy of the Checklist and distribute update so that members can look it over prior to the Houston meeting	Larry	1/15/16	1/23/17
81	Update Charter to prepare for new format and prepare DRAFT presentation for Houston. Send to committee members for comment.	All	1/15/17	3/1/2017
82	Provide examples to Dave to incorporate into the small lab handbook prior to the Houston Meeting	As assigned	Ongoing	3/1/2017

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	

Volume 1 Module 6

QUALITY SYSTEMS FOR RADIOCHEMICAL TESTING

1.1 – 1.3 Introduction/Scope/Terms

Key Points - This Standard contains detailed quality control requirements for environmental testing activities involving radiochemical measurements involving detection of the radioactive emissions of the analyte (or indicative daughters) and tracer isotopes. Adherence to the Quality Systems Module 6 procedures, QC requirements specified by the reference method, regulation or project and the laboratory's Quality System requirements shall be met by the laboratory.

Discussion –The lab always has to keep in mind the client's requirements such as analyzing water samples for compliance to a regulation or a specific project. Writing the requirements into SOPs can help ensure that the lab will handle, analyze, and report results within the client's requirements. Be sure you keep your client informed of any deviations from requirements. This will avoid rejection of the results from the Regulators and the need to recollect and/or reanalyze the samples.

Examples: - Under the EPA Radionuclide Rule both Chemical (EPA 200.8) and Radiochemical (SM7500U-B) methods are approved for the analysis of Uranium. If you are using SM7500U-B the lab must adhere to the following requirements; SM7500U-B, TNI Module 2, TNI Module 6, EPA Radionuclide Rule, and the client specific requirements. If you are using EPA 200.8 you would follow TNI Module 4 instead of TNI Module 6.

1.3.1 Key Terms and Definitions

Note: **These definitions are specific to this module. Refer to the previous modules' definitions or the TNI Standard for more guidance.**

Batch, Preparation: A Preparation Batch is composed of one (1) to twenty (20) environmental samples of the same quality system matrix that are prepared together with the same process and personnel, using the same lot(s) of reagents, with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours.

Note: Preparation Batches are only applicable for tests that require physical or chemical preparation that affects the outcome of the test.

Batch, Radiation Measurements (RMB): A Radiation Measurements Batch is composed of one (1) to twenty (20) environmental samples that are counted directly without preliminary physical or chemical processing that affects the outcome of the test (e.g., non-destructive gamma spectrometry, alpha/beta counting of air filters, or swipes on gas proportional detectors). The samples in an RMB share similar physical and chemical parameters, and analytical configurations (e.g., analytes, geometry, calibration, and background corrections). The maximum time between the start of processing of the first and last sample in an RMB is fourteen (14) calendar days.

Critical Value: Value to which a measurement result is compared to make a detection decision (also known as critical level or decision level).

Note: The Critical Value is designed to give a specified low probability α of false detection in an analyte-free sample, which implies that a result that exceeds the Critical Value, gives high confidence (1 – α) that the radionuclide is actually present in the material analyzed. For radiometric methods α is often set at 0.05.

Detection Limit (DL) for Safe Drinking Water Act (SDWA) Compliance: Laboratories that analyze drinking-water samples for SDWA compliance monitoring must use methods that provide sufficient detection capability to meet

Bob Shannon 3/1/2017 12:15 PM

Comment [1]: Suggest changing shall to a more familiar term that tells the lab what must or have to do. The document will feel more approachable.

the detection limit requirements established in 40 CFR 141. The SDWA DL for radioactivity is defined in 40 CFR Part 141.25(c) as the radionuclide concentration, which can be counted with a precision of plus or minus 100% at the 95% confidence level (1.96σ where σ is the standard deviation of the net counting rate of the sample).

Uncertainty, Counting: The component of Measurement Uncertainty attributable to the random nature of radioactive decay and radiation counting (often estimated as the square root of observed counts) (MARLAP[3]). Older references sometimes refer to this parameter as Error, Counting Error or Count Error (c.f., Total Uncertainty).

Uncertainty, Expanded: The product of the Standard Uncertainty and a coverage factor, k, which is chosen to produce an interval about the result that has a high probability of containing the value of the measurand (c.f., Standard Uncertainty).

Note: Radiochemical results are generally reported in association with the Total Uncertainty or the Counting Uncertainty. Either of these estimates of uncertainty can be reported as the Standard Uncertainty (one-sigma) or an Expanded Uncertainty (k-sigma, where k > 1).

Uncertainty, Measurement: Parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

Uncertainty, Standard: An estimate of the Measurement Uncertainty expressed as a standard deviation (c.f., Expanded Uncertainty).

Uncertainty, Total: An estimate of the Measurement Uncertainty that accounts for contributions from all significant sources of uncertainty associated with the analytical preparation and measurement of a sample. Such estimates are also commonly referred to as Combined Standard Uncertainty or Total Propagated Uncertainty, and in some older references as the Total Propagated Error, among other similar terms (c.f., Counting Uncertainty).

1.3.2 Exclusions and Exceptions

The elements of this module apply to techniques used for the purpose of measuring or monitoring radioactivity, or techniques used to demonstrate compliance with regulations pertaining to radioactivity. The laboratory shall comply with the requirements of Module 4 in cases where technique-specific QA/QC is not defined in Module 6 (e.g., Mass Spectrometry [ICP-MS, TIMS] or Kinetic Phosphorimetry) or by the respective reference method (e.g., calibrations, calibration verifications, determinations of detection statistics, or method-specific quality controls). The laboratory shall identify in its quality system how and when it is complying with the requirements and elements of Chemical Testing (Module 4) and Radiochemical (Module 6), as applicable.

1.4 Method Selection

The TNI Standard generally assumes that the radiochemistry laboratory will use methods based on regulatory drivers. For those situations where a reference method is not specified in a regulation, any applicable reference method may be used. Under these situations the method used must be validated. In all cases, method selection must be approved by the client when doing work for others. For those laboratories where the analytical work is being done to support in-house functions such as for waste water and drinking water facilities, the method must be approved for the regulatory work being conducted. In general, these will be defined in the facility permits.

1.5.1 Validation of Methods

Both reference and non-reference methods require validation. (See Appendix B for an example of method validation study.) This shall be done for each quality system matrix. Whenever a laboratory develops a

Bob Shannon 2/28/2017 2:11 PM
Comment [2]: Convert to text box?

Bob Shannon 2/28/2017 2:11 PM
Comment [3]: This is not really accurate.

The TNI Standard generally assumes that the radiochemistry laboratory will use methods based on regulatory requirements. For those situations where a reference method is not specified in a regulation, any applicable method may be used. Method performance data (i.e., validation data) must be available for all methods used (see 1.5 Method Validation for details).

In all cases, the method selected must be approved in advance by the requesting client. For those laboratories where the analytical work is being done to support in-house functions such as for waste water and drinking water facilities, the method must be approved for the regulatory work being conducted. In general, these will be defined in the facility permits.

Bob Shannon 2/28/2017 2:11 PM
Comment [4]: Move to example section?

method, or modifies a method to meet different data quality objectives, the method must be validated prior to use following a pre-defined process.

Key Points:

- The validation must follow a documented procedure.
- The validation must address detection capability, precision, bias, measurement uncertainty, and selectivity (consistent with published guidelines such as MARLAP, FEM, EUROCHEM) where possible the activity range shall include zero activity
- The validation records must be maintained for the life of the method and be readily retrievable.

Discussion:

- The standard requires all methods be validated including reference methods regardless if they are used within or outside the scope of the method.
- Methods as published in literature or developed by the laboratory can be used, but must be fully validated. Clients must be informed and agree with the lab on the selected method.
- Introduction of laboratory-developed methods should be introduced following a plan.
- The following parameters should be considered for validating in-house developed methods: detection capability, accuracy, selectivity, repeatability and/or reproducibility, and robustness.
- Exact validation experiments should be relevant to sample and required information.
- All methods used outside their approved scope must be validated before being placed into use.
- Validation includes specification of the requirements and scope, determination of the characteristics of the methods, appropriate tests to prove that the requirements can be fulfilled by using the method and a statement on the validity.

LOOK AT PAGE 2 OF CHECKLIST AND ADD LANGUAGE TO EXAMPLE

Examples:

1. Use external performance testing (PT) samples to verify lab performance.

2. The use of non-TNI accredited PT providers is strictly for method validation purposes, and not for laboratory accreditation.

1.5.2 Detection Capability

Detection capability refers to terms commonly used in radiochemistry such as Critical Value, Minimum Detectable Activity (MDA) or Safe Drinking Water Act (SDWA) Detection Limit. See Appendix A for information on the key term, Minimum Detectable Activity. Methods and associated MDAs will vary as implemented from lab to lab. The Standard does not specify the procedure to use to determine the Detection Capability. It is left to the laboratory to select any method that they can defend as being technically sound as long regulatory, method, contractual, or laboratory quality system requirements.

Key Points:

- The laboratory detection capability must be verified initially as part of the method capability study for each matrix.
- The Laboratory detection capability must be re-verified when there is a change in the method or when there are substantial changes to the instruments used.
- The laboratory is required to document the procedure used to determine detection capability.
- The method used shall be appropriate and relevant for the intended use of the data recognizing that project-specific or client-specific requirements may be unique.
- Software used for the detection capability must be identified

The Standard requires that the detection capability be initially determined for each analyte in each matrix. As long as the method is being run throughout the year and ongoing QC data does not indicate a change in method performance, there is no annual requirement for determination of the detection capability. All steps of the analytical process must be included in the detection capability determination and confirmation. This

Bob Shannon 2/28/2017 2:11 PM

Comment [5]: Possible language

Both reference and non-reference methods must be supported with data on the method's detection capability, precision, bias, Measurement Uncertainty, and selectivity. Such method validation data is required for each analyte / quality system matrix combination. Whenever a laboratory develops a method, or modifies a method to meet different data quality objectives, the new method must be validated prior to use.

In the case of reference methods, published performance data taken from the method may be used in lieu of data generated by method validation (where available). Performance data, however, are frequently not published in radiochemical reference methods. Alternatively, the laboratory may have modified the method. In such cases the laboratory may need to generate the required method performance data by validating the method.

Other "validation" approaches have been used to generate some or all of the performance validation data needed to satisfy validation requirements including analysis of historical internal quality control data.

Bob Shannon 2/28/2017 2:11 PM

Comment [6]: Key Points:

·All methods must be validated and data on the detection capability, precision, bias, Measurement Uncertainty, and selectivity of the method (consistent with published guidelines such as MARLAP, FEM, EUROCHEM) available at the laboratory to document method performance at the laboratory.

·The validation must follow a pre-defined process that is consistent with Sections 1.5.2 through 1.5.5 of V1M2 of the TNI Standard.

·Generally, the activity range must include performance at zero activity since most radiochemical methods generate results that include zero activity.

·In the case of reference methods, performance data published in the method may be used in lieu of method validation at the laboratory. Where performance data is not available, or if the reference method is modified, the laboratory must generat ... [1]

Bob Shannon 1/23/2017 2:32 PM

Deleted: It is analyte- and matrix-specific and will

Bob Shannon 2/28/2017 2:11 PM

Comment [7]: Is this correct? I was under the impression that there is no frequency requirement to reevaluate the detection capability as long as the process does not change.

confirmation takes into account any analyte losses during sample preparation and prevents the use of a detection capability that is unrealistically low.

Many methods and/or regulatory programs require a detection capability determination. See Appendix A for more details on Detection Capability.

1.5.3 Evaluation of Precision and Bias

The laboratory shall evaluate the precision and bias of a method for each analyte of concern for each quality system matrix.

Key Points:

- The laboratory must establish the laboratory precision and bias for all measurements and all matrix types.
- The initial demonstration of capability (DOC) does not replace the method validation where the precision and bias are determined
-

Examples:

1. The initial documentation of capability is generally considered to meet the requirement for DOC.
2. For non-reference methods, the Standard enumerates the method for establishing precision and bias.
3. Precision and bias can be derived and monitored from the LCS performance data.
4. Acceptance criteria for performance should be based on one of the following:
   -DQOs/MQOs
   -Applicable regulations (e.g., SDWA)
   -Published guidelines, such as MARLAP or FEM
5. One approach might involve using LCS performance data to generate precision and bias results.
6. Blanks shall be analyzed to test for absolute bias.

1.5.4 Measurement Uncertainty

All radiochemical measurement results shall be reported with an estimate of total uncertainty expressed either as a standard deviation or a multiple thereof.

Key Points:

- The laboratory is required to document its procedure for estimating uncertainty in its quality system documentation.
- The reported results must also explicitly specify the total uncertainty. The results of the precision evaluation shall be compared to the uncertainty estimates as a check on the validity of the uncertainty evaluation procedure.

Discussion:
Add discussion of difference between counting and total uncertainty

Examples:

1. The intent here is that the laboratory will report total uncertainty unless they are specifically required to report counting uncertainty.
2. Reports must specify the type of uncertainty reported (counting or total) and coverage (e.g, 95% or 1 sigma, or k=1).

Bob Shannon 2/28/2017 2:11 PM
Comment [8]: The procedure a laboratory uses to determine the detection capability of a method must comply with the specific requirements of Volume 1, Module 6, Sections 1.5.2.1 and 1.5.2.2.

Bob Shannon 2/28/2017 2:11 PM
Comment [9]: Some regulatory programs, such as the SDWA compliance program, may prescribe acceptable approaches for detection capability determinations.

Bob Shannon 2/28/2017 2:11 PM
Comment [10]: Precision and bias must be characterized across the range of activities that brackets those applicable in samples, including zero activity.

Bob Shannon 1/23/2017 2:45 PM
Deleted: Precision and bias can be derived and monitored from the LCS performance data.

Bob Shannon 2/28/2017 2:11 PM
Comment [11]: 1 does not seem to make sense.
2 and 4 are more requirements than examples.
On 2 - The standard does not isolate reference methods for different treatment.
3 could be developed into example of how a lab might go about using existing QC data to generate performance data for bias and precision but it needs more detail to be clear.
3 is redundant with 5.
3 could also be grouped with 6 and more detail added.

Bob Shannon 2/28/2017 2:11 PM
Comment [12]: Sometimes counting is required. Suggest deleting total and just saying uncertainty.

Bob Shannon 2/28/2017 2:10 PM
Deleted: combined standard

Bob Shannon 2/28/2017 2:11 PM
Comment [13]: Add discussion and examples (appendix) of uncertainty: difference between counting and total uncertainty, and coverage factors and reporting?

Bob Shannon 2/28/2017 2:14 PM
Comment [14]: This will not help labs not familiar with this concept. At least list something other than standard uncertainty. 2-sigma, k=2 or 95% confidence level

Add an example or two of uncertainty – work with Keith (NIST Tech bulletin 1297???, GUM, MARLAP,

Bob Shannon 2/28/2017 2:11 PM
Comment [15]: Keith is working on this.

1.5.5 Evaluation of Selectivity

The laboratory shall qualitatively evaluate selectivity, if applicable, by addressing the following sample and matrix characteristics:

- the effect of matrix composition on the ability of the method to detect analyte;
- the ability of the method to chemically separate the analyte from the interfering analytes; and
- spectral and instrumental interferences.

The evaluation of selectivity may be accomplished by testing matrix blanks, spiked matrix blanks, worst-case samples, or certified reference materials. If applicable, a qualitative selectivity statement shall be included in the SOP.

Vas suggests added an example – for example alpha or LS spectrometry shows interfering analytes have been addressed – not present, resolution or quench not affected

This is where we stopped our review at the Houston meeting.

1.6 Demonstration of Capability (DOC)

1.6.1 General

The laboratory analyst must have constant, close supervision until a satisfactory DOC has been completed.

Key Point:

- All DOCs shall be documented, retained and readily available at the laboratory.

1.6.2 Initial DOC

An initial DOC shall be made prior to using any method and at any time there is a change in instrument type, personnel, or method and any time that a method has been performed by the laboratory or analyst in a twelve month period.

Bob Shannon 2/28/2017 2:17 PM
Comment [16]: Point out that DOC is not validation – serves to document that analyst is capable of running validated method.

Might also note that generally, validation is more extensive and would provide enough detail to simultaneously meet requirements for I-DOC for analyst performing it.

Key Points:

- Performance requirements are generally defined by method, regulation, contract, or accreditation requirements.
- Documented DOC is performed for each unique method and quality system matrix combination.
- Each analyst must perform a DOC before analyzing any samples.
- A new DOC is required whenever there is a change in method, instruments, or personnel.

Bob Shannon 2/28/2017 2:17 PM
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Discussion:

The laboratory shall document each initial DOC in a manner such that the following information is readily available for each analyst:

- Analyst(s)
- Matrix
- Analyte(s), class of analyte(s), or measured parameters
- Identification of method(s) performed
- Identification of laboratory-specific SOP used for analysis, including revision number
- Date(s) of analysis
- Summary of analyses

If the method, regulation or contract does not specify an initial DOC, the following procedure would be one acceptable approach. It is the responsibility of the laboratory to document that other approaches to initial DOC meet applicable requirements.

1. Prepare 4 test samples consistent with Section 1.7.2.3 Positive Control and 4 method blanks of clean quality system matrix in which no target analytes or interferences are present.
2. Analyze the samples according to the method.
3. Calculate the mean recovery and standard deviation of the spikes.
4. Compare the data to acceptance criteria specified in the method/regulation or contract.

Where no acceptance criteria exist, the laboratory shall compare the data with criteria established in the laboratory quality system.

Example:

1. When performing multi-elemental analysis by gamma spectrometry, the DOC need not involve every radionuclide. The standard specifically states the test sample shall contain gamma-emitting radionuclides that represent the low, medium, and high energy range of the analyzed gamma-ray spectra.

1.6.3 Ongoing DOC

The laboratory shall have a documented procedure describing ongoing DOC that includes procedures for how the laboratory will identify data associated with ongoing DOCs. The analyst(s) shall demonstrate on-going capability by routinely meeting the quality control requirements of the method, regulation or contract, or as established by this Standard and by the laboratory's quality system. It is the responsibility of the laboratory to document that other approaches to ongoing DOC are adequate.

Key Points:

- Performance is generally defined by the method, regulation, contract or the Laboratory's quality system and relies on Performance Testing samples.
- Ongoing DOC is by method, analyst and matrix.
- If the method has not been performed by the analyst in a 12-month period, an initial DOC shall be performed.

1.7 Technical Requirements

The initial calibration and calibration verification of equipment are the most important steps of an analytical process. If not done adequately, all of the subsequent steps are suspect. Unfortunately, many reference methods contain sketchy requirements for calibration and quality control. Laboratories performing radiochemical measurements must rely more on laboratory-developed methods than reference methods for any matrix other than drinking water.

1.7.1 Instrument Set-Up, Calibration, Performance Checks and Background Measurements

These requirements ensure that the measurements will be of known and appropriate quality for meeting regulatory and contractual requirements and for supporting decision making. This section does not specify detailed procedural steps for these operations, but establishes essential elements for selection of the appropriate technique(s). This allows flexibility and permits employment of a wide variety of analytical procedures and statistical approaches. Where there are no established mandatory requirements, the laboratory shall incorporate guidelines consistent with MARLAP or other consensus standard organizations.

The structure of this section parallels the stages of the calibration life cycle

- Instrument set-up
- Initial calibration

Bob Shannon 2/28/2017 2:20 PM
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Bob Shannon 2/28/2017 2:20 PM
Deleted: are adequate

Bob Shannon 2/28/2017 2:21 PM
Comment [17]: This is not an example.

Bob Shannon 2/28/2017 2:26 PM
Comment [18]: Non-sequitur – qc and calibration / calibration verification do not drive this. The lab may have to supplement a reference method with a QC approach which could result in lab developed method if. I think this raises more questions than it answers. Also, why is this talking about calibration and cal ver and then calibration and QC when it is the general header for the technical requirements.

How about:

The set-up, calibration, performance checks of instrumentation, and background determinations are all critical steps of an analytical process. If not done adequately, all subsequent analyses are suspect. Many reference methods, however, contain no or incomplete requirements. The laboratory may need to supplement the method to satisfy applicable program, regulatory, or contractual requirements, in addition to those specified in Module 6.

- Calibration verification
- Instrument checks

The approach in the standard parallels that in ASTM D7282 – Standard Practice for Set-up, Calibration and Quality Control of Instruments Used for Radioactivity. Refer to this standard to better understand the logic used here.

1.7.1.1 Initial set-up of Instrumentation

Many of these requirements address procedures and documentation for set-up and configuration. They might be implicit in requirements for procedures and documents but they are routinely overlooked and impact quality of results produced.

Key Points:

- The laboratory shall maintain the required radiation measurement systems for each method it performs.
- The laboratory shall document radiation measurement system configuration and maintainable values for hardware- and software- related operational parameters prior to initial calibration
- The laboratory must ensure the continued integrity of system configuration and perform corrective actions to determine and ameliorate any potential impact if any changes are made or identified.

1.7.1.2 Initial Calibration

This section specifies the essential elements for initial calibration of radiation measurement systems. Although standards of varying activity are not needed to calibrate radiometric techniques, multiple points may be needed to correlate parameters other than activity. Here are six common examples:

i) channel-energy calibration of alpha or gamma spectrometers;

ii) energy-efficiency calibration of gamma spectrometers;

iii) mass-efficiency (mass-attenuation) calibration of gas-flow proportional or x-ray detectors;

iv) quench-efficiency calibration of liquid scintillation detectors;

v) mass-crosstalk calibration of gas-flow proportional; and

vi) quench-crosstalk calibration of liquid scintillation detectors.

This section reiterates the need for physical calibration of instruments against traceable reference materials but opens the door for applying mathematical or statistical corrections based on mathematical techniques such as Monte Carlo simulations.

Key Points:

- The laboratory shall establish and document in written procedures and in records the details of the initial calibration. Details shall include , at a minimum:
  1. the type of calibrations to be performed;
  2. the number of calibration points required;
  3. a description of the calibration standards required;
  4. the preparation of the calibration standards;
  5. the counting of the calibration standards;
  6. the maximum permissible uncertainty for calibration measurements (e.g., a maximum relative total uncertainty of the calibration parameter or a minimum number of counts collected); and
  7. all calculations.
- The laboratory shall document the criteria for conditions that initiate (re)calibration in its SOPs.
- The laboratory shall quantitate sample results only from the initial instrument calibrations unless otherwise allowed by regulation, method or contract.

1.7.1.3 Calibration Verification

Bob Shannon 2/28/2017 2:29 PM
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Bob Shannon 2/28/2017 2:30 PM
Comment [19]: No guidance on this? This is a big item which is new… I think Tom at least made reference to an approach under performance checks. Move that here? Supplement?

Bob Shannon 2/28/2017 2:30 PM
Deleted: combined

The TNI Standard: Guidance for Small labs

This section establishes requirements for verification of initial calibrations independent of instrument performance and prior to use for analyzing samples. Requirements for calibration verification were poorly differentiated from and frequently confused with instrument performance checks. Calibration verifications verify the integrity of initial method-specific calibrations relative to established criteria that is based on measurement of independently produced calibration verification sources.

Key Points:

- Initial instrument verifications must be verified prior to use of an initial calibration for analysis of samples
- If at all possible, the standard used must be from a source or lot independent of the reference standard used in the initial calibration.
- The laboratory must specify the maximum permissible uncertainty for calibration verification measurements (e.g., the minimum number of counts collected for each measurement) in their SOPs.
- The laboratory shall specify verification acceptance criteria in their SOPs and when corrective actions are necessary.

EXAMPLE:

The laboratory performed initial calibration of Ge gamma spectrometer (Section 1.7.1.2b)ii)), using a reference mixed gamma standard (Am, Cd, Co, Ce, Hg, Sn, Sr, Cs, Mn, Y, Zn, Co) (Sections 1.7.1.2c) and 1.7.2.6c)). However, the vendor was not able to provide a reference standard of the relatively short-lived mixed gamma radionuclides from another lot for calibration verification (Section 1.7.1.3a).

Comment: Therefore, the laboratory performed calibration verification by quantifying a set of LCS samples (Sections 1.7.1.3a)ii) and 1.7.2.3) and ensuring that the acceptance criteria were met.

1.7.1.4 Instrument Performance Checks

This section was called Continuing Calibration Verification, a misleading term. Instrument performance checks measure and track the stability of key detector response-related parameters over time. The continuing validity of initial calibrations is established by demonstrating the stability of the detection system from the point of initial calibration to the time of the Test Source measurement, whether it be days, months or even years because it is based on demonstrated evidence of instrument stability over time.

Key Points:

- Essential elements of instrument performance checks are

1. The check source used for instrument performance checks need not be a reference standard as defined in this module.
2. The laboratory shall use the same check source for ongoing performance checks as the one in the preparation of the tolerance or control chart limits at the point of the initial calibration.
3. The laboratory shall prepare, handle, seal and/or encapsulate check sources to prevent damage, loss of activity and contamination.
4. The laboratory shall minimize the uncertainty of the check source count to allow detection of small changes in detector response relative to the acceptance criteria. The count duration and check source activity should be sufficient to provide adequate counting statistics over the life of the source.
5. Where significant, the radioactive decay in the check source shall be taken into account when evaluating count-rate sensitive parameters such as efficiency.

Bob Shannon 2/28/2017 2:33 PM
Comment [20]: How about : Unless reference standards cannot be procured or obtained, …

Bob Shannon 2/28/2017 2:40 PM
Comment [21]: This just reiterates the requirements. Why not emphasize why making sure the source does not change provides one of the most reliable ways of detecting small changes in response at the instrument.

6. The laboratory shall monitor the results of instrument performance checks using control or tolerance charts to ensure that instrument performance has not changed significantly since the point of the initial calibration.

7. The laboratory procedure shall specify what corrective actions are to be taken when performance check acceptance criteria are not met.

EXAMPLE 1. Change of operational parameter

Laboratory established an initial conversion gain of 4096 channels for a full energy range of 2 MeV for a Ge gamma spectrometer (Section 1.7.1.1b)). The gamma energy calibration was then performed using $^{125}Sb/^{154,155}Eu$ mixed gamma source (Section 1.7.1.2b)i)). The initial efficiency calibration (Section 1.7.1.2b)ii)) was performed using a reference mixed gamma standard (Sections 1.7.1.2c) and 1.7.2.6c)). The calibration was verified (Section 1.7.1.3) and instrument performance checks were performed as scheduled (Section 1.7.1.4).

A specific project for measurement of fresh fission products required readjusting of conversion gain to 16384 channels for the same energy range (Section 1.7.1.1.c)). The laboratory recalibrated the energy using Sb/Eu source (Section 1.7.1.2b)i)). Subsequent performance checks did not indicate any change in efficiency or resolution.

Comment: No efficiency re-calibration is necessary because performance did not change. The limits for the new energy calibration will need to be regenerated.

Example 2 – Performance check failure

An analyst performed a daily instrument check on a solid-state scintillation detector (Section 1.7.1.4b)v)) and it had no counts. The analyst recognized that the high voltage was off. He turned it on and the repeated performance check passed (Section 1.7.1.4a)vi)).

Comment: Since zero counts did not enter the database, the analyst followed laboratory SOP (Section 1.7.1.4a)vii)) which did not require informing supervisor or write a corrective action in this case.

Example 3 – Performance check failure

An analyst performed an instrument check on a semiconductor gamma detector (Section 1.7.1.4b)i)1). The performance check was outside 95% tolerance (Section 1.7.1.4a)vi)). The analyst repeated the measurement (Note to Section 1.7.1.4) and it was outside tolerance again. The analyst informed the supervisor per laboratory SOP (Section 1.7.1.4a)vii)). The supervisor determined that the check source was measured at a wrong position. The source was repositioned and subsequent performance check passed.

Comment: Since the out of tolerance results were entered into the database, a dated record in the detector manual was entered, however, no written corrective action was necessary. The outliers do not affect past or future tolerance charts because they are rejected by a Grubbs test in calculations.

Example 4 – Performance check deviates from expected value

After initial calibration of a liquid scintillation counter for tritium analysis, the laboratory performs recalibrations on an annual basis (Section 1.7.1.2). Performance check is performed using a factory sealed tritium check source (Section 1.7.1.4a)iii)). The performance check results are plotted on a tolerance chart (Section 1.7.1.4a)vi)) and include fitting of exponential decay of tritium (Section 1.7.1.4a)v)). In between

Bob Shannon 2/28/2017 2:42 PM
Comment [22]: I get the example but will it open more questions than it answers since it involves a new energy calibration that continues using existing limits?

Bob Shannon 3/1/2017 1:15 PM
Deleted: performance

recalibrations, the supervisor observes a steadily increasing deviation from the fitted exponential curve up to 0.5%, in spite of satisfying statistical tolerance chart.

Comment: The supervisor determines that this discrepancy is caused by an ageing of the optical system in the liquid scintillation counter. However, since this deviation is much smaller than the uncertainty of the laboratory reported results (5% or more), supervisor decides that it is not necessary to either replace the detector system or initiate out of schedule recalibration. The next recalibration will accommodate this aging of the counter.

Example 5 – Exception to minimum frequency of performance check

An analyst performs daily performance check procedure for a gas proportional counter on Friday (Section 1.7.1.4b)iii)) and then submits another procedure containing a batch of 20 samples which will count till Sunday morning. The analyst prepares another daily performance check procedure to be counted automatically and immediately after the sample procedure on Sunday, skipping Saturday.

Comment: Skipping Saturday is allowed according to Section 1.7.1.4c)ii). Measuring of performance check on Monday instead of Sunday would also be acceptable.

Example 6 - Compromised check source

The laboratory uses a Marinelli beaker geometry for a performance check source on a Ge gamma spectrometer. In spite careful handling and sealing the source lid with a silicone caulk (Section 1.7.1.4a)iii)), the lid cracked from stress and some leak was observed. The detector was decontaminated per Section 1.7.1.7. A new performance check source was prepared. The detector calibration was verified with an old reference standard (Section 1.7.1.3).

Comment: In spite of some short-lived radionuclides decay in the old standard, ^{241}Am, ^{137}Cs, and ^{60}Co still contained useful reference gamma peaks. The initial calibration was verified with these and no recalibration was necessary.

Question on this example ???Since the performance check source was compromised and is no longer usable, would a new tolerance chart based on the replacement performance check standard be required?

"The laboratory shall use the same check source for ongoing performance checks as the one in the preparation of the tolerance or control chart limits at the point of the initial calibration."

Example 7 – Corrections to calibration

The laboratory performed a calibration of a Marinelli beaker geometry for Ge gamma spectrometer, using a physical source containing mixed gamma reference standard (Sections 1.7.1.2c) and 1.7.2.6c)). The source consists of an acidic solution of density 1.015 g cm^{-3}. Then two LCS samples were prepared by spiking and homogenizing vegetation (Section 1.7.2.3) with densities of 0.5 and 0.9 g cm^{-3}. The density and coincidence(cascade)-summing corrections were calculated for these two samples using Monte Carlo program (Section 1.7.1.2d)). In the calculations, nominal Ge detector parameters were used as given by the manufacturer, Marinelli beaker dimension were measured, and the chemical composition was taken for an average vegetation. The LCS samples were quantified, the calculated corrections were applied, and the results verified the known values.

Bob Shannon 2/28/2017 2:44 PM
Comment [23]: Suggest:

…and then begins counting another batch of 20…

Bob Shannon 3/1/2017 10:27 AM
Comment [24]: Comment from Terry Romanko

Just want to confirm that replacing a compromised check source with a new check source is OK without a complete new calibration.

The requirement (1.7.1.4.a.ii) is:
"The laboratory shall use the same check source for ongoing performance checks as the one in the preparation of the tolerance or control chart limits at the point of the initial calibration."

Here, only a verification with an old reference standard is performed. This is near to my heart, as we have some old sources that have "degraded", and now have to get new sources. I do believe that if a verification of the original calibration were performed, it should be sufficient to show the original calibration is still valid. Then, a new set of counts to generated points for limits could be performed with the new source.

Bob Shannon 2/28/2017 2:47 PM
Comment [25]: This is not supported in the standard. Verifying the calibration shows that the calibration is good but leaves us with bad set of check data.

How does the comment about decay pertain to the leak?

Bob Shannon 2/28/2017 2:48 PM
Comment [26]: This is not about performance check. Need this example to support mathematical calibrations above.

Comment: The nominal detector parameters as well as average vegetation composition are acceptable because the calculated corrections are not very dependent on uncertainties in these quantities. For analyzing real vegetation samples, the corrections were calculated between 0.5 and 0.9 g/ cm^3 in steps of 0.05. From these values, the corrections are interpolated for a given sample density in the range. This is much faster and nearly as accurate as calculating the corrections for every sample.

1.7.1.5 Subtraction Background Measurements

Subtraction background measurements are performed to assess and correct for contributions due to cosmic radiation, naturally-occurring radioactivity, electronic noise, impurities in the detector, shielding, and source mounting material, or other sources that are not affected by the analytical processes. Contributions from impurities in the reagents, reference standards, or other sources introduced during the analytical processes are assessed with the use of method blanks.

Numerous counting configurations may be used to determine subtraction background, depending on the detector and the method, including: counting an empty detector; counting an empty container or blank Test Source in a detector; or counting a container filled with a surrogate matrix material free of measureable levels of radioactivity.

Note: The frequency of subtraction background measurements may be increased from the above requirements when there is low tolerance for lost data due to failure of a subtraction background measurement.

Bob Shannon 2/28/2017 2:50 PM

Comment [27]: MBs assess the entire process including biased background measurements. Why do we talk about MBs here when backgrounds are the issue?

It might be worth mentioning that "Even a small amount of bias in background measurements may result in significant bias of results close to background.

Bob Shannon 3/1/2017 10:30 AM

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Key Points:

- Background counting time must be at least as long as the associated sample counting time and be representative of the background count rate.

- The subtraction background measurement shall be accomplished in one of the following ways:

  i) Paired measurements in which the subtraction background measurement is counted before or after the Test Source measurement or batch of Test Source measurements.

  ii) Measurements performed at a fixed frequency, in which Test Sources may be measured between successive background subtraction measurements. In this case, the laboratory shall perform background subtraction measurements at the following minimum frequencies:
  1. Gamma-ray spectrometry systems: Monthly.
  2. Alpha-particle spectrometry systems: Monthly.
  3. Gas-proportional and semiconductor alpha/beta detectors: Quarterly.
  4. Liquid scintillation detectors.
     - Individual quenched background: Once per Preparation Batch.
     - Quenched background curve: According to frequency specified in laboratory procedures.
  5. Solid-state scintillation detectors (e.g., zinc sulfide) used for non-spectrometric Measurements: Day of use.

Example:
The laboratory shall maintain written procedures for performing and evaluating subtraction background measurements.

1.7.1.6 Short-Term Background Checks

Short-term background checks, performed between subtraction background measurements, are quality control measures used to verify the integrity of subtraction background measurements, check for possible detector

contamination, electronics noise and to monitor each detector for trends and deviations from Poisson statistics. These background checks may be shorter in duration, yet more frequent than the subtraction background measurements, and therefore they may not always effectively identify every discrepancy that could compromise Test Source measurements (e.g., low-level contamination).

Key Points:

- The laboratory shall maintain written procedures for performing and evaluating short-term background checks.
- The laboratory shall establish exceptions to minimum frequencies for short-term background checks.
- When short-term background has changed since the previous determination such that significant background bias is imparted to intervening Test Source measurements, the laboratory shall initiate a corrective action. If the bias cannot be resolved, the laboratory shall qualify affected results.
- If subtraction background measurements are performed with sufficient frequency for a given method or detector type, such that they ensure background integrity and are capable of identifying detector contamination, the subtraction background measurements may be substituted for short-term background checks, in which case the short-term background checks shall not be required.
- For liquid scintillation detectors, the laboratory shall check short-term unquenched backgrounds each day of use.

1.7.1.7 Contamination Monitoring

The laboratory shall have written procedures that address cases where radiation detectors have been contaminated, as determined by the subtraction background measurements, short-term background checks, or method blanks. Detectors may not be brought back into service until corrective actions are completed.

Key Points:

- The laboratory shall maintain written procedures that address cases where radiation detectors have been contaminated as determined by the subtraction background measurements, short-term background checks or method blanks.
- Contaminated detectors may not be brought back into service until corrective actions are completed

1.7.2 Quality Control for Radiochemistry

The essential elements of quality control are the quality control tests and/or samples that must be utilized to properly document the quality and defensibility of the data being generated. These elements consist of positive and negative controls, detection capability, data reduction, quality of standards and reagents, selectivity, and constant and consistent test conditions. Negative controls are method blanks (laboratory reagent blank) and positive controls are laboratory control samples (laboratory fortified blank), while sample specific controls consists of matrix spikes and matrix spike duplicates, matrix duplicates, and surrogate spikes.

1.7.2.1 General

It is important to recognize that radiochemistry laboratories rely heavily on *non-mandated* methods. To this ends, they develop or modify (and validate) methods to address analytical needs. Since requirements are often not specified by a source external to the laboratory (e.g., regulation or contract) it may be incumbent on laboratories to establish additional QC. In such cases, this section states that QC requirements must be *consistent* with the TNI standard, guidelines in MARLAP or other consensus standard organizations. This provides flexibility while helping to ensure that the laboratory has a defensible basis for their QC requirements. It also allows assessors to ask about the basis for specific requirements, and to point to MARLAP or other standards in cases where their specific unaddressed needs for QC may be identified.

Bob Shannon 2/28/2017 2:53 PM
Comment [28]: Is it worth mentioning that if subtraction backgrounds change, even it the change is not detected by short backgrounds, all sample counts since the last long background check may be suspect and need to be recounted.

Bob Shannon 2/28/2017 2:55 PM
Comment [29]: Will labs know what the unquenched background is? Possibly say use an unquenched background vial such as one prepared by an instrument manufacturer similar to the process specified in ANSI N42.15, Section 4.3)

Carolyn Wong 11/28/2016 4:09 PM
Deleted: s

Bob Shannon 2/28/2017 2:57 PM
Comment [30]: It is important to recognize that radiochemistry laboratories rely heavily on *non-mandated* methods. Similarly, many reference methods do not provide requirements for quality control.

Also consider that this section does not say QC must be consistent with TNI. Rather it says that when applicable external requirements are more stringent than the standard, the more stringent requirements must be met.

Carolyn Wong 11/28/2016 4:09 PM
Deleted: there

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Key Points:

- The Laboratory shall follow a documented QC program that monitors and assesses the performance of the laboratory's analytical systems. At a minimum, the QC program shall incorporate requirements imposed by regulation, methods, and the TNI standard.
- The laboratory shall process batch and sample-specific quality control samples to obtain empirical evidence that demonstrates their analytical system is in control.
- The laboratory shall employ either a sample Preparation Batch or a Radiation Measurement Batch (RMB) to determine the grouping of samples and assignment of batch QC.
- A sample Preparation Batch shall be initiated where sample testing is performed that involves physical or chemical processing which affects the outcome of the test. Samples and associated QC assigned to a Preparation Batch shall be prepared together using the same processes, personnel, and lot(s) of reagents.
- Where testing is performed that does not involve physical or chemical processing which affects the outcome of the test (e.g., non-destructive gamma spectrometry, alpha/beta counting of air filters, or swipes on gas proportional detectors), an RMB may be initiated in lieu of a Preparation Batch. The samples and associated QC in the RMB shall share similar physical and chemical parameters, and analytical configurations (e.g., analytes, geometry, calibration, and background correction).
- Samples may be added to the RMB for fourteen (14) calendar days from the start of the first sample count, or until twenty (20) environmental samples have been counted, whichever occurs first.
- The laboratory may combine samples and associated QC within an RMB that share a range of physical and chemical parameters, and analytical configurations (e.g., analytes, geometry, calibration, density) that conform to the ranges of physical and chemical parameters, and analytical configurations demonstrated by method validation studies (see Section 1.5).
- The laboratory procedures must document how method validation was performed, and records must document any corrections (e.g., for efficiency, density, cascade summing, and background) applied to physical calibrations.
- The laboratory QC program shall document the frequency required for quality controls.
- The laboratory shall process all batch QC samples together with and under the same conditions as the associated samples, and shall use the same processes and procedures for preparation, analysis, data reduction and reporting of results.

Note: Although samples in a Preparation Batch must be prepared together, they need not be analyzed concurrently on a single detection system, rather they may be analyzed on different detection systems as long as the detection systems are calibrated for the technique in question and instrument quality controls indicate that the systems are in control. See also Appendix C. Radiation Measurements Batch.

- The laboratory shall not systematically or preferentially use specific detectors, equipment or glassware for the analysis of QC samples. This should not preclude laboratories from segregating detectors, equipment, or glassware to minimize the risk of cross-contamination of samples or equipment as long as the criteria for segregation applies equally to batch QC samples and samples.
- The laboratory's QC program shall document acceptance criteria for batch QC samples, sample-specific QCs, and for the evaluation of long-term trends and the methods used to establish these criteria.
- The laboratory shall assess the results of the QC samples against acceptance criteria documented in the QC program. Where there are no established criteria in regulations, the method, or contract, the laboratory shall develop its acceptance criteria consistent with guidelines in MARLAP[3] or other consensus standards, or other criteria such as statistical control charts developed by the laboratory.

- The laboratory shall track and trend the results of batch QC samples using statistical or tolerance control charts.

- The laboratory shall investigate the cause when results do not meet acceptance criteria and take corrective actions to eliminate the source or minimize the magnitude of the problem. The laboratory shall consider samples associated with a failed QC parameter as suspect and shall, wherever possible, reprocess such samples. Where reprocessing is not possible, the laboratory shall report results with appropriate data qualifiers. The laboratory shall note the occurrence of a failed QC sample and any associated actions in the laboratory report.

Examples:

1. A typical preparation batch consists of up to 20 samples prepared together along with a matrix blank (MB), laboratory control sample (LCS), matrix spike (MS), a matrix duplicate (MD) or matrix spike duplicate (MSD). All samples in the preparation batch along with the quality control samples are prepared together using the same processes, personnel, and lot(s) of reagents. This ensures that all samples and quality control samples are prepared similarly. Examples of analyses requiring preparation batches are: gross alpha/gross beta in water; tritium in water; or total strontium in air filters. All samples within a preparation batch must be started within a 24-hour period. All samples in a preparation batch need not be counted on the same detection system. Thus, the samples in a preparation batch maybe counted using multiple detector systems. The included quality control samples should be randomly counted on different detector systems.
2. For samples which do not involve physical or chemical processing which affects the outcome of the test sample preparation a Radiation Measurement Batch (RMB) may be used. For example, given a situation where one air filter is collected on a daily basis requiring gamma analyses, the laboratory may create a RMB beginning with the first sample and add up to 20 samples to the RMB as long as analyses are completed within 14 days (in this case, since samples are collected daily, there is a maximum of 14 samples in the RMB). In addition to the samples in the RMB, one must also intersperse quality control samples (MB, LCS, MS, MD or MSD) during the 14-day period (this will require count times of less than 24 hours if only one detector is used). If multiple detectors are used, the quality control samples must be randomly placed on the detectors.
3. If a laboratory is applying mathematical or statistical corrections based on mathematical techniques such as Monte Carlo to establish calibrations for varying soil densities and has verified these calibrations over the range of soil densities in the samples, the laboratory may include in a RMB soils of different densities.
4. The laboratory shall not systematically or preferentially use specific detectors, equipment or glassware for the analysis of QC samples. For example, given a bank of alpha spectrometers the quality control samples (MB, LCS, MS, MD or MSD) should be randomly placed on the detectors. This does not preclude designating a group of detectors for a specified analysis such as thorium analyses. It also does not preclude designating specific glassware for samples known to contain higher levels of activity which may include LCS, MS an MSD.
5. Results for quality control samples are typically plotted on statistical or tolerance control charts. Statistical control charts are used when the acceptance criteria are based on the statistical variation of a measurement result. Acceptance criteria are typically established by regulations, the method, or contract. Warning limits are typically set at +/- 2 standard deviations from the mean. Control limits are typically set at +/-3 standard deviations from the mean. Statistical control charts are typically used for LCS and MS. Tolerance charts are established when exceeding the established tolerance limit would have adverse effects on the analytical results. Tolerance charts may be used for background measurements (RB MB). All control charts should be reviewed for trends in the analytical data.

1.7.2.2 Negative Control – Method Performance: Method Blank (MB)

The MB assesses the process of handling, preparation and analysis for cross-contamination and for low-level analytical bias. For methods with minimal physical treatment or no chemical processing (e.g., drying, grinding and homogenization of

Bob Shannon 3/1/2017 10:31 AM
Comment [31]: Comment from Terry Romanko
Should be method not matrix blank

Bob Shannon 2/28/2017 3:04 PM
Comment [32]: Suggest that we say the typical batch includes MB, LCS, and a duplicate, and not include MS/MSD. Then say that the MS/MSD are added when…

Bob Shannon 2/28/2017 3:04 PM
Comment [33]: may be

Bob Shannon 2/28/2017 3:05 PM
Comment [34]: The requirement says that "Samples may be added to the RMB for fourteen (14) calendar days from the start of the first sample count." Thus the analysis need not be completed within 14 days, only started.

Bob Shannon 2/28/2017 3:06 PM
Comment [35]: This is not consistent with the standard. There is nothing about interspersing. Also not sure what is added by mentioning count times here.

Bob Shannon 2/28/2017 3:03 PM
Comment [36]: While this may be nice practice, it is not part of the standard. There is a requirement that RMBs share a range of physical and chemical parameters, and analytical configurations (e.g., analytes, geometry, calibration, density) that conform to the ranges of physical and chemical parameters, and analytical configurations demonstrated by method validation studies (see Section 1.5).

This, however, has nothing to do with calibrations and corrections. Suggest reverting to original language and then provide a ... [2]

Bob Shannon 2/28/2017 3:07 PM
Comment [37]: Suggest possible edit ... [3]

Bob Shannon 2/28/2017 3:09 PM
Comment [38]: This whole section is treading on thin ice. There is nothing in the standard that says use stats or toleran ... [4]

Bob Shannon 2/28/2017 3:09 PM
Comment [39]: Often?

Bob Shannon 2/28/2017 3:09 PM
Comment [40]: Often?

Bob Shannon 2/28/2017 3:11 PM
Comment [41]: Good examples for tolerance charts might include for a project that specifies a specific acceptance ran ... [5]

Bob Shannon 2/28/2017 3:12 PM
Comment [42]: There is nothing here about ... [6]

solid samples, or preparation of sample Test Sources for swipe or air filter samples for non-destructive gamma spectrometry or alpha-beta counting), the MB assesses sample handling and the analytical process. Absolute bias may result from contamination, changes in reagents or media, instability of the instrument background, or issues with subtraction backgrounds.

Key Points:

- The laboratory shall have procedures that determine when the MB is significantly different than zero, or impacts the analytical results, e.g., compare the result to the combined standard deviation.
- The laboratory shall analyze a MB at a minimum of 1 per Preparation Batch or RMB.
- The laboratory shall evaluate results of MBs for long-term trends, absolute bias, possible contamination or interferences that may affect sample results.
- The laboratory shall not subtract the batch MB from sample results in the associated Preparation Batch or RMB. The laboratory may subtract the average historical activity of MB measurements to address a demonstrated bias.
- The laboratory shall account for the uncertainty of the subtracted value in its estimate of uncertainty for the final result.

Examples:

1. Method Blanks (MB) are samples in the same media known not to contain the contaminant of interest. For aqueous samples this may be deionized water, for air filter samples this may be an unused air filter, and for soil and vegetation a sample of soil and vegetation collected in an uncontaminated area may be used. The method blank must be treated like a sample and taken through the entire analytical process. Except as noted below, analytical results are not corrected for the MB.
2. A statistical evaluation should be made to determine if the result of the MB is different from background. For example, if the result of the MB is greater than three times the standard uncertainty, there is a 99% confidence that the result is greater than background. Alternately if the results for MBs are plotted on a control chart, a result exceeding the control limit of 3 standard deviations has a 99% confidence that it is different from background. Note to Tom when would censor a method blank??
3. There may be circumstances where the MB is different from background. An example of this is the analysis of low-levels of uranium in water. Uranium is naturally occurring and is present in the reagents used during the analyses. This will result in MB results which are different from background introducing a bias in the analytical results. If a laboratory wishes to correct for this bias, they may determine the average and standard deviation of the historical MB data and use these values to correct for this bias. The standard deviation of the average MB must be incorporated in the combined standard deviation of the analytical results.

1.7.2.3 Positive Control – Method Performance: Laboratory Control Sample (LCS)

Bob Shannon 2/28/2017 3:14 PM
Comment [43]: …there is more than 99% that..

Bob Shannon 2/28/2017 3:13 PM
Comment [44]: If anything, we did not address censoring – and if anything discourage it.

Censoring is never really addressed in the standard. Would it be safer to say that it is always technically incorrect to censor against an MDA or SDWA DL? If we do this, wouldn't we don't have to introduce new concepts such as the upper 95th%ile value?

Bob Shannon 2/28/2017 3:14 PM
Comment [45]: may

The LCS is used to evaluate the performance of the analytical system, including all preparation and analysis steps. For methods with minimal physical treatment and no chemical processing (e.g., drying, grinding and homogenization of solid samples, or preparation of sample Test Sources for swipe or air filter samples for non-destructive gamma spectrometry or alpha-beta counting), the LCS assesses the analytical process for bias.

For RMBs, a calibration verification standard may be analyzed in lieu of the LCS. Since there is no preparation, a standard may be substituted for the LCS. Note that laboratories may use a standard prepared by an external vendor since there is no requirement for them to prepare the standard parallel to associated samples. A frequent practice would be to use an older calibration standard since this will also comply with Positive Control QC requirements.

Key Points:

- The laboratory shall analyze a LCS at a minimum of one (1) per Preparation Batch or RMB. The minimum spike concentration should be based on the relative uncertainty of the acceptance criteria. For methods with minimal physical treatment and no chemical processing, the laboratory may reuse the prepared standard in subsequent sample batches.
- The laboratory shall use material for the LCS that is free of analytes of interest at levels that will interfere with evaluation of results. If material is not available the laboratory may be characterized and documented for the analyte(s) of concern and then accounted in the evaluation of the LCS.
- The laboratory shall spike the LCS at a level of such that the uncertainty of the analytical result is less than one-third of the acceptance criteria. This links the uncertainty of the measurement to the acceptance criteria used for the LCS.
- When available, the standard used to prepare the LCS shall meet the requirements for reference standards provided in the Reagent Quality, Water Quality and Checks section. The final prepared LCS need not be traceable to a national standard organization. The LCS shall include all of the radionuclide(s) being determined with the following exceptions:
    - For methods that measure gross activity (e.g., gross alpha, gross beta), an appropriate surrogate analyte shall be used. This will generally be the radionuclide(s) used to calibrate the detector. Examples of such methods commonly encountered at laboratories and the reference nuclides most frequently used:
        a. Gross alpha – ^{230}Th or ^{241}Am
        b. Gross beta – ^{90}Sr/Y, or ^{137}Cs
        c. Total alpha emitting radium – ^{226}Ra
        d. Total uranium (^{238}U+^{235}U+^{234}U in the natural ratios observed in undisturbed samples
        e. Total Radiostrontium (^{90}Sr)
    - For alpha spectrometry measurements, when multiple individual radionuclides with similar chemical characteristics are determined simultaneously with a single measurement and calibration, only one of the analytes/isotopes needs to be included in the LCS at the activity level indicated in this section previously.
    - Where a non-destructive gamma-ray spectrometry measurement is made using a multi-point energy/efficiency calibration curve which covers the energy range of the analyte(s) of interest:
        - a radionuclide with similar gamma energies as those of the analyte(s) of interest may be used (e.g., ^{133}Ba may be used in place of ^{131}I), or
        - the LCS shall contain gamma-emitting radionuclides that, at a minimum, represent the low (e.g., ^{241}Am) and high (e.g., ^{60}Co) energy range of the analyzed gamma-ray spectra. Commonly a medium energy radionuclide is also included in the LCS (e.g., ^{137}Cs). As indicated by these

examples, the nuclides need not exactly bracket the calibration energy range or the range over which radionuclides are identified and quantified.

- The laboratory shall evaluate results of the batch LCS using a statistical technique such as the percent recovery or z-score that allows comparison to acceptance criteria documented in the laboratory QC program.

Examples:

1. The media used for the MB (i.e. deionized water for aqueous samples, unused air filters, soil and vegetation from an uncontaminated area) may be used for the LCS. Alternately well-characterized performance test samples, or purchased spiked samples in an appropriate activity range may be used as LCS.
2. For RMBs a calibration source in the same media and geometry as the samples may be used. If a calibration source is used it should be from a different lot as the standard used for calibration. This may be accomplished by calibrating with a new calibration source and using an old calibration source as continuing calibration verification sample. Alternately two separate calibration sources from two separate lots/vendors may be purchased.
3. The LCS should be spiked at an activity level which ensures the precision of the measurement is sufficient to determine if the results meet the acceptance criteria. For example, if the results for the LCS must be within +/- 15% of the known value, the LCS must be spiked such that the uncertainty of the measurement is less than 5**%** (1/3 of the acceptance criteria).

1.7.2.4 Sample-Specific QC Measures

The laboratory shall document procedures for determining the effect of the sample matrix on the analytical results. These procedures relate to the analyses of specific QC samples and are designed as data quality indicators for a specific sample using the designated method. Examples of sample-specific QC include: Matrix Spike (MS); Matrix Spike Duplicate (MSD), Matrix Duplicate (MD), Tracers, and Carriers. The laboratory shall have procedures in place for tracking, managing, and handling sample-specific QC criteria including spiking radionuclides at appropriate activities, calculating recoveries, determining variability (e.g., relative percent difference and/or z-score), and evaluating and reporting results based on the performance of the QC samples.

Key Points:

Matrix Spike (MS)

- MS recoveries are an indication of effects of the matrix on sample result accuracy for the selected method.
- MSs are not typically employed for non-destructive methods or or for methods that utilize a chemical yield tracer or carrier for each sample.
- The frequency of the analysis of MSs shall be specified by the method, a regulation or determined as part of the contract review process.
- The analytes in the MS should parallel those in the LCS. Additional radionuclides may be required by the mandated method, regulation or as determined as part of the contract review process.
- The activity of the MS analyte(s) shall be greater than 5 times the MDA.
- The MS shall be prepared by adding a known activity of target analyte prior to any processes that affect the analyte of interest.

Matrix Duplicates (MD)/Matrix Spike Duplicates(MSD)

- Duplicate analyses provide a measure of precision when the target analyte is present in the sample.
- Acceptance criteria for duplicates shall be documented or referenced in the laboratory's quality manual.

Carolyn Wong 12/26/2016 5:27 PM
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- At a minimum, the laboratory shall analyze one MD per Preparation Batch or RMB. For RMBs, the MD shall consist of a second measurement of one sample. If the batch is counted on more than one detector, the MD shall be performed on a second detector.

- When samples have low-levels of activity (less than approximately three (3) times the MDA) the laboratory, at its discretion, may analyze MS/MSD to determine reproducibility within a Preparation Batch in place of a MD.

- Based on specific project or program requirements or when there is insufficient sample available, the laboratory may choose to analyze a LCS in duplicate in place of a MD. The LCS and its duplicate will provide a measure of analytical precision. However, they will not provide information on matrix effects.

Chemical Yield Tracers and Carriers

- For those methods that employ a radioactive Tracer or a stable Carrier as a chemical yield monitor in the analysis, each sample shall have an associated chemical yield calculated and reported. The chemical yield is one of the quality control measures to be used to assess the associated sample result acceptance.

- The selection of a Tracer or Carrier shall not significantly interfere with the analyte(s) of interest nor cause bias in its measurements. When such a Tracer or Carrier is unavailable, the interference or bias caused shall be quantifiable and appropriate correction applied to the sample results.

- The Tracer or Carrier used to monitor chemical yield shall be added to the sample prior to performing any processes that affect the analyte of interest (e.g., chemical digestion, dissolution, ashing, separation, etc.) unless otherwise specified by the method.

- The chemical yield shall be assessed against acceptance criteria specified in the method, regulation, contract or laboratory SOP. The laboratory shall develop its criteria for data acceptance based on guidelines established in the MARLAP or other criteria such control charting developed by the laboratory. This assessment shall meet established project or program measurement quality objectives.

- When the established chemical yield acceptance criteria are not met, the specified corrective action and contingencies shall be followed. The occurrence of a failed chemical yield and the actions taken shall be noted in the laboratory report.

Examples:

Matrix Spikes

1. The laboratory shall document procedures for determining the effect of the sample matrix on the analytical results. This may be done by incorporating a MS in the preparation batch and/or a chemical yield tracer or carrier to every sample.
2. MSs, chemical yield tracers and carriers are not required for non-destructive methods.
3. For procedures which include a chemical yield tracers or carriers, the chemical yield tracer or carrier serves to determine if the matrix is interfering with the analytical processes, thus MSs are not required for these types of analyses.
4. The analytes in the MS should parallel those in the LCS. For example, if ^{230}Th is used to spike the LCS for gross alpha analyses, ^{230}Th should also be used for the MS.
5. MSs should be spiked at a level at least five times the MDA in order to provide sufficient counting statistics to determine if there is any matrix interference.

6. The sample matrix must be spiked prior to any processes that affect the analyte of interest. For example, soil samples must be spiked prior to any chemical leaching or decomposition procedures.

Duplicates

1. Two examples of acceptance criteria may for duplicate analyses are the Relative Percent Difference (RPD) or Duplicate Error Ratio (DER) methods:

$$RPD = \frac{|S - D|}{((S + D)/2)} \cdot 100$$

$$DER = \frac{|S - D|}{\sqrt{(CSU_S)^2 + (CSU_D)^2}}$$

The requirement for duplicate analyses may be met in one of the following ways:

- For non-destructive analyses where a RMB is used, a single sample may be counted twice. For low-activity samples (less than three times the MDA) the LCS may be counted twice. If multiple detectors are use the duplicate must be counted on a different detector than the original count.
- A second aliquot of a sample taken through the total analytical process.
- When the sample activity levels are expected to be low (less than three times the MDA) a MSD may be used at the discretion of the laboratory.
- If there is insufficient sample to perform a duplicate or matrix spike duplicate a LCS may be processed in duplicate.

Chemical Tracers or Carriers

1. The selected chemical tracer or carrier should have identical chemical properties as the analyte of interest. This is typically a different isotope of the analyte of interest. For example ^{242}Pu for the analysis of ^{238}Pu/^{239}Pu or stable strontium for the analysis of ^{89}Sr/^{90}Sr. The selected chemical tracer or carrier should not interfere with the analyses. If it is not possible to select a chemical tracer or carrier which does not interfere with the analyses the interference should be quantifiable and appropriate correction applied to the sample results. For example, ^{242}Pu may contain sufficient quantities of ^{241}Am to interfere with a sequential plutonium/americium analyses. In this case the ^{241}Am contaminant in the ^{242}Pu tracer should be quantified and the ^{241}Am results corrected for the contaminant in the tracer.
2. The tracer/carrier must be added to the samples prior to any processes that affect the analyte of interest. For example, soil samples must be traced prior to any chemical leaching or decomposition procedures.

1.7.2.5 Data Reduction

The procedures for data reduction shall be documented. All calculations used to determine results shall be included or referenced under the laboratory's quality system. Detection capability (e.g., MDA or Critical Level) and measurement uncertainties shall be calculated as per procedure.

1.7.2.6 Reagent Quality, Water Quality and Checks

In methods where the purity of reagents is not specified, reagents shall be analytical reagent grade or better. The quality of water sources shall be monitored and documented and shall meet method specified requirements. The QC program shall establish and maintain provisions for radionuclide standards.

Key Points:

- Reference standards shall be obtained from a national metrology institute (NMI), e.g. NIST in the USA or NPL in Great Britain, or from suppliers of NMI reference standards. Alternatively, reference standards

Bob Shannon 3/1/2017 10:32 AM
Comment [46]: Comment from Terry Romanko

The wording in the TNI document is "at its discretion" (1.7.2.4.b.iv).. It would probably be better to use the word "may" instead of "should"

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Bob Shannon 3/1/2017 10:34 AM
Comment [47]: Comment from Terry Romanko

Is this really a requirement based upon the wording in TNI? Some labs have the calculations in a common document, such as the Quality Assurance Manual. Also, some labs have separate preparation and analysis procedures. What would be meant by "the test method SOP"? The TNI requirement is "The procedures for data reduction shall be documented." It is not defined where it "shall" be located.

Bob Shannon 3/1/2017 10:34 AM
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may be obtained from an ISO/IEC Guide 34 accredited reference material provider, or an ANSI N42.22 reference material manufacturer.

- Reference standards shall be accompanied with a certificate of calibration that meets the requirements of either ISO Guide 31, or ANSI N42.22, Section 8, Certificates and shall include at least the following information: manufacturer, radionuclides calibrated, identification number, calibration method, activities or emission rates with associated uncertainties and the confidence limits, standard quantity, activity reference time (date or time as appropriate to the half-life of the radionuclide), physical and/or chemical description of the source, and radionuclide impurities.

- The laboratory shall account for radioactive decay/ingrowth whenever decay/ingrowth has occurred between the Activity Reference Date and use that could impact use of the results.

- The laboratory shall have written procedures for handling, storing and establishing expiration dates for reference standards.

- If there is no known provider of a particular standard (e.g., non-routine radionuclide or non-standard matrix), the laboratory may have no alternative but to use a standard with less rigorously established traceability. In this event, the laboratory shall obtain from the provider the minimum information described the standards listed earlier. The laboratory shall independently verify the activity of such standards prior to use and document the verification.

- If the laboratory's verification indicates a significant deviation from the original information from the provider, the standard should not be used unless the discrepancy can be resolved. If the standard is used for analysis of sample unknowns, the source and any other known limitations of the standard shall be disclosed in the final report.

Example:

1. Because the half-life of tritium is only 12.32 years, the laboratory must decay correct the activity of the tritium standard when it is used to prepare an LCS so that the true activity of the LCS can be calculated.

1.7.2.7 Constant and Consistent Test Conditions

The laboratory shall assure that test instruments consistently operate within the specifications required of the application for which the equipment is used. Labware shall be cleaned to meet the sensitivity requirements of the method. Any cleaning and storage procedures that are not specified by the method shall be documented in the laboratory's quality system and records. Note that some applications may require single-use glassware.

Key Points:

- The laboratory shall maintain a radiological control program that addresses analytical radiological control.
- The radiological control program shall explicitly define how low-level and high-level samples will be identified, segregated and processed to identify and minimize sample cross-contamination.
- The radiological control program shall include the measures taken to monitor and evaluate background activity or contamination on an ongoing basis.

Example:

1. Laboratories should monitor trends in instrument background each day of use with the use of control charts.

1.7.3 Data Evaluation and Reporting

Data acceptance and corrective actions requirements must be established for data review. The criteria may be established by the method, regulation, or by the laboratory. The laboratory should have specific protocol established for evaluating quality control samples that includes re-analysis of the samples, reporting sample data with qualification, or rejection of data. Corrective actions must be documented.

1.7.3.1 Negative Control – Method Performance: Method Blank

MB results shall be evaluated for long term trends, absolute bias, possible contamination, or interferences that may affect results for samples in the batch.

Key Points:

- If acceptance limits are not met, corrective actions shall be taken to investigate the source of contamination or other bias. If sample activity levels are greater than five (5) times the activity found in the MB, lacking other requirements, it is acceptable to report qualified results for the samples associated with the blank. Otherwise, reprocessing and reanalysis of the associated samples shall be required.
- When sample results associated with a failed MB are reported, the failure and associated corrective actions, or inability to complete corrective actions, shall be noted in the laboratory report.

Examples:

1. Method Blank – Shall be performed at a frequency of one per preparation batch. The results of this analysis shall be one of the quality control measures to be used to assess batch acceptance. For the method blank to be valid, gross alpha result must be below the method detection limit. When the specified method blank acceptance criteria are not met, the entire batch must be re-prepared and reanalyzed. The occurrence of a failed method blank acceptance criterion and the actions taken shall be noted in the laboratory report.
2. There shall be no subtraction of the required method blank result from the sample results in the associated preparation or analytical batch. This does not preclude the application of any correction factor (e.g. instrument background) to all analyzed samples, both program/project submitted and internal quality control samples. However, these correction factors shall not depend on the required method blank result in the associated analytical batch.
3. The method blank acceptance criteria shall address the presumed aliquot size on which the method blank result is calculated and the manner in which the method blank result is compared to sample results of differing aliquot size.

1.7.3.2 Positive Control – Method Performance: LCS

LCS recoveries shall be evaluated to assess the performance of the entire analytical system independent of the sample matrix. LCS results shall be calculated in percent recovery or other appropriate statistical measure that allows comparison to established acceptance criteria. The laboratory shall document the calculation.

Key Points:

- An LCS that is determined to be within established acceptance limits effectively demonstrates that the analytical system is in control and validates system performance for the samples in the associated batch.
- Samples associated with an LCS that fails to meet acceptance limits are considered suspect and the samples shall be reprocessed and reanalyzed.
- If samples cannot be reprocessed and reanalyzed, the failure and associated corrective actions or inability to complete corrective actions shall be noted in the laboratory report.

Examples:

1. Laboratory Control Samples - Shall be performed at a frequency of one per preparation batch. The results of this analysis shall be one of the quality control measures to be used to assess batch acceptance. The acceptance criteria for the LCSs are 80-120% recoveries of the theoretical value. When the specified laboratory control sample acceptance criteria are not met, analyze the LCS in a different detector. If the LCS still fails, the batch must be re-prepared and reanalyzed. If the LCS meets criteria, then the detector where the failure occurred cannot be used to analyze the batch. Troubleshoot the cause of failure, including the possibility that a new calibration curve may be required. The occurrence of a failed laboratory control sample acceptance criteria and the actions taken shall be noted in the laboratory report.
2. The activity of the LCS must be between 2 to 10 times the detection limit. The volume of sample used for the LCS must be equivalent to the volume used for sample analysis.
3. The laboratory standards used to prepare the laboratory control sample shall be from a source independent of the laboratory standards used for instrument calibration.

1.7.3.3 Sample-Specific Controls

Key Points:

Matrix Spike, Matrix Duplicates, Matrix Spike Duplicates

- MSs and MDs allow evaluation of the effect of matrix on the accuracy and precision of results.
- When results fall outside established criteria, corrective actions must be documented and the data reported with appropriate data qualifying codes. QC results outside acceptance limits must be noted in the laboratory report.

Tracers and Carriers

- Tracers or stable carriers monitor chemical yield in the sample with the results expressed as percent yield or other appropriate statistical measure that allows comparison to established method acceptance criteria.
- For alpha spectrometry, evaluation of Tracer acceptability shall include evaluation of chemical yield (e.g., uncertainty, variability) and peak resolution.

- Samples associated with Tracers or Carriers that fail to meet acceptance limits are considered suspect, and the samples shall be reprocessed and/or reanalyzed. If samples cannot be reprocessed and/or reanalyzed, the failure and associated corrective actions or inability to complete corrective actions shall be noted in the laboratory report.

Examples:

1. Matrix Spike - Shall be performed at a frequency of one per preparation batch for those methods which do not utilize an internal standard or carrier and for which there is a physical or chemical separation process and where there is sufficient sample to do so. The results of this analysis shall be one of the quality control measures to be used to assess batch acceptance. The matrix spike result shall be assessed against the specific acceptance criteria of 70-130% recoveries of the theoretical value. When the specified matrix spike acceptance criteria are not met the specified corrective action and contingencies will be followed. The occurrence of a failed matrix spike acceptance criteria and the actions taken shall be noted in the laboratory report. The lack of sufficient sample aliquot size to perform a replicate analysis should be noted in the laboratory report.
2. The activity of the matrix spike analyte(s) shall be greater than ten times and less than one hundred times the prior detection limit. The volume of sample used for the LCS and matrix spike must be equivalent to the volume used for sample analysis.

3. The laboratory standards used to prepare the matrix spike shall be from a source independent of the laboratory standards used for instrument calibration.

1.7.3.4 Evaluation of Sample Results

Instrument raw data from energy spectral analysis shall be evaluated to ensure that the target radionuclides are quantified consistent with laboratory procedures and applicable measurement quality objectives, and that target radionuclides in the spectra are evaluated for possible interferences. Results shall be reviewed for internal consistency, such as the presence of radionuclides consistent with known parent-progeny relationships and expected or likely decay series.

Key Points:

- Sample-specific estimates of uncertainty and MDA shall be evaluated to ensure that MQOs have been met.
- If objectives have not been met, then samples shall be reprocessed and/or reanalyzed.
- If samples cannot be reprocessed and/or reanalyzed, the failure and associated corrective actions, or inability to complete corrective actions, shall be noted in the laboratory report.

1.7.3.5 Reporting Results

Results should be reported with an appropriate number of significant figures and an estimate of uncertainty. The result shall also include the Activity Reference Date. The date listing may be a simple comment in the case narrative as long as it unambiguously defines the date for the reported results.

Note: Although the above criteria have a solid technical basis and rationale, specific regulations and programs may have requirements that would supersede them.

1.7.4 Sample Handling

While it may not be possible to physically verify all methods of preservation (e.g., addition of oxidizing or reducing agents), wherever practicable the laboratory shall verify that samples have been preserved in compliance with all applicable requirements specified by regulation, method, or contract, or as established in the laboratory's quality system (if there are no established mandatory criteria).

Key Points:

- The laboratory shall document the required timing, methods for performing measurements to verify preservation, the acceptance range, or any other conditions indicating acceptable preservation.
- Where thermal preservation of samples is required, the laboratory shall verify the temperature of samples upon receipt.
- Where chemical preservation of samples is required, the laboratory shall verify that samples have been preserved using readily available techniques such as pH measurement prior to sample preparation or analysis.
- If the results of the preservation verification do not satisfy established criteria, the laboratory shall initiate corrective actions (i.e., notification of the client, preservation of the sample at the time of discovery), and qualify all impacted test results in the report to the client.

Examples:

1. The laboratory's written procedure for sample receiving shall include a list of requirements for acceptable types of sample containers, minimum sample volumes, thermal and chemical preservatives, and maximum holding times for each radiochemical analysis the lab performs. The

Bob Shannon 3/1/2017 10:39 AM

Comment [48]: b) . Following evaluation according to Section 1.7.3.4, results shall be reported directly as obtained, with appropriate units, even if the results are negative.

c) . Results shall be expressed with an appropriate number of significant figures.

d) . All radiochemical results shall be reported with an estimate of uncertainty, as discussed in Section 1.5.4.

e) . Laboratories shall report the Activity Reference Date in association with all radiochemical measurement results.

f) . Project- or client-specified reporting requirements can take precedence over the requirements of this Standard.

procedure should also indicate analytical parameters for which chemical preservatives should not be added to samples (e.g., carbon-14 in water).

2. The sample receiving procedure shall detail how pH measurements are to be conducted and documented.

3. The sample receiving procedure shall also describe the steps to be taken when sample acceptance criteria are not met, such as documentation of discussions with the client to either reject samples or proceed with analysis and qualify results on the final report.

APPENDIX:

A. MINIMUM DETECTABLE ACTIVITY

Radiochemical data is often reported to include minimum detectable activity (MDA) with sample results. The MDA is a sample specific detection limit.

A number of factors can adversely affect the MDA. Inadequate sample volume, short counting time, low detection efficiency all can affect the MDA individually or together. The laboratory must have procedures in place for meeting and reporting MDA. The 2009 TNI Standard requires that a laboratory establish criteria for reporting MDA when such criteria are not found in the method or a regulation. Additionally, projects involving cleanup of contaminated sites often include MDAs in the contract specifications. The laboratory shall comply with the contract specifications.

There is no single formula for MDA. Several variants of nearly the same formula are in use in the industry. Following is an example of an MDA calculation.

A lab received a 1 L wastewater sample from one of its customers. The chain of custody indicated that it was a ground water sample from site near an operating nuclear power plant. The analysis required on the sample is Cs-137.

With the above information, the lab analyzed the wastewater sample using EPA 901.0 method. The method involved adding stable cesium carrier followed precipitation of Cesium-137 and gamma spectrometry using HPGE detection system. The identification of Cesium-137 and quantitation was via 662 keV gamma-ray emission. The planchet geometry helped to achieve excellent results. The following data was gathered.

Sample volume: 1 L

Chemical Yield: 80%

Counting Efficiency, Cs-137: 25%

Sample counting time: 100 Min.

Reagent Blank (for Background) counting time: 100 Min.

Reagent Blank counts: 196 counts in 100 Min. MDA is calculated using paired measurements equation.

$$\mathrm{MDA} = \frac{2.71 + 4.65\sigma_B}{CY \cdot EFF \cdot V \cdot 100 \cdot 2.22}.$$

B. METHOD VALIDATION STUDY

A lab is an accredited NELAP laboratory. The Laboratory is seeking accreditation for Gross Alpha analysis in drinking water by co-precipitation method. The laboratory performed a method validation study and documented the results. Following is an excerpt from the study for illustrative purposes.

Method: Determination of for Gross Alpha Radioactivity in Drinking Water by
Reference Method: SM 7110 C, Co-precipitation Method
Applicable Matrix: DW

This study includes the following:

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

A) DETECTION LIMIT STUDY:

When analyzing drinking water samples for compliance monitoring purposes under Safe Drinking Water Act (SDWA). The ATP requires the DL for the method to be determined to ensure it meets the requirements of the SDWA.

[Note: Some laboratories continue to report minimum detectable activity concentration, (MDA or MDC) for all analysis including drinking water. Those laboratories must implement SDWA DL to be in compliance.]

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)'.

The equation for SDWA DL[1] is as given below.

$$\text{SDWA DL}\left(\frac{\text{pCi}}{\text{L}}\right) = \frac{1.96^2}{2t_G} \cdot \frac{1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} R_B \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}}{2.22(\text{Efficiency})(\text{Volume})(\text{Chemical Recovery})}$$

Where,

- Volume of the sample is in L. It is recommended to use 1.0 L for co-precipitation method.
- Chemical recovery refers to gravimetric recovery of the co-precipitate (radium-barium sulfate). We will assume 100% recovery for this example. In reality, a recovery of 90 – 95% is routinely achieved.
- 2.22 is conversion factor for DPM to pCi.
- Detection efficiency for alpha particles is 0.187. This value is known to laboratory and is specific to the detector being used for counting.
- R_B = mean background count rate is 0.11 CPM. This value is known for the same detector above, being used for counting samples, and
- t_G and t_B are counting times for sample and background, each 200 min.
- Note: the DL equation should be modified to reflect factors used in the calculation of activity for the method in question.

Substituting these values in the above equation, the SDWA DL for Gross Alpha activity is 0.18 pCi/ L. This value is far below the RDL, 3 pCi/L. Therefore, the detection limit study for the co-precipitation method is acceptable.

How does the DL affected with limited sample volume or shorter counting intervals?

Too often, all laboratories find themselves having less than 1 L volume of sample, or that one of the instrument suddenly 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 this test. We assumed 1 L in our example. How will the reduced volume impact our DL? Again, by substituting 0.5 L in the above equation, we will find the DL is now 0.36 pCi/ L. The DL has just doubled, even though it is still very low in this example.

What happens if we count the sample and background for only 1 hour? All other things being the same, the DL will now be at 1.13 pCi/ L; still very low compared to RDL. Thus, it is possible to calculate DL in advance for optimum counting time or sample volume or both. This is especially advantageous for all laboratories with limited resources of equipment and manpower, and when additional challenge of higher than normal workload to be met at the laboratory.

B) PRECISION & BIAS (ACCURACY) STUDY:

BIAS EVALUATION:

The laboratory conducted replicate analysis to evaluate bias and precision for the method. The laboratory analyzed seven replicates at two concentration levels, one at RDL (3 pCi/ L) for and the other at MCL (15 pCi/ L) for gross alpha in drinking water.

TNI Standard V1M6 1.5.3 requires that the laboratory establish acceptance criteria for bias assessment, when such criteria do not exist in either the regulation or method. In general, such criteria are not included both regulations and the methods necessitating laboratories to establish the criteria. The lab has established the procedures outlined below.

Method performance will be established by analyzing seven replicates, in the quality systems matrix, spiked at least at two different concentration levels for the analyte. These concentrations shall be at or close to the RDL and MCL for the analyte, if only two levels are included.

Method bias is determined by calculating the mean recovery of the seven replicates and using the formula,

Bias = $\frac{\overline{X}}{\mu}$ x 100% where,

$\overline{X}$ is the mean recovery of the seven replicates, and
μ = true value if the spike

The criteria for validation of results for bias evaluation shall be ±25% (75%-125% range) of the true value at the RDL level; and ±20% (80%-120% range) of the true value at MCL concentration and beyond. If the calculated bias falls within the specified range, it will be acceptable. These criteria are most commonly found in the industry and stringent for the method validation.

The results of the replicate analysis at the RDL are summarized in the table below.

Repl. #	Sample Results							Mean $\overline{X}$
	1	2	3	4	5	6	7	
X	2.45±0.19	2.38±0.19	2.15±0.18	2.41±0.19	2.61±0.2	2.62±0.2	2.30±0.19	2.42 add propagated uncertainty

Where, $\overline{X}$ is the mean concentration of the replicates spiked at the MCL/RDL(??).

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n = number (7) of replicates
μ = spike level at RDL, 3 pCi/ L

Using the above criteria, the bias for the seven replicates is 81%, falls within the acceptable range.

The laboratory analyzed seven replicates spiked at a concentration of 15 pCi/ L, at the MCL level for gross alpha activity in drinking water. Following table illustrates the sample results.

Sample Results in pCi/ L							
#	1	2	3	4	5	6	7
X	15.57± ??	14.11± ??	14.23± ??	14.90± ??	12.73± ??	13.36± ??	13.95± ??

The mean of the 7 replicates is: $\overline{X}$ = 14.12 pCi/ L.
The actual spike value is: μ = 14.8 pCi/ L
The Std. Deviation of the replicates: σ = 0.94 pCi/ L

Using the above criteria, the bias for the seven replicates is 95%. This is within the acceptable range and acceptable.

PRECISION OF THE METHOD:

The precision of the method is determined by calculating the relative percent standard deviation (%RSD) of the spiked analyte recoveries of the seven replicates.

Precision = $\frac{\sigma}{\overline{X}}$ x 100%, where

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

σ = Standard deviation for the seven replicates

The criteria for precision validation shall be <20% RSD which is stringent and an industry standard.

Using the above criteria, the precision demonstrated by the method is at 6.7% which is excellent.

C) Measurement Uncertainty:

Criteria: Per TNI Standard (2016) V1M6 1.5.4 (c), the experimatally observed standard deviation (σ)shall not be statistically greatrer than the maximum combined unecartinty (σ_c)of the measurement results. Using this criteria, the lab data is as shown below.

The observed standard deviation of 7 replicates, σ = 0.94 pCi/ L
The combined uncertainty of the measurements, σ_c = 1.33 pCi/ L

The observed $\sigma < \sigma_c$. Therefore, it is acceptable.

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. 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 sbstantially. 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.

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E) Analysis of an external QC Sample

The laboratory must successfully analyze at least one externally produced QC sample in accoradance with V1M6 1.5.1 f). Such an external QC sample could also be a PT Sample, if none is available. The lab has usccessfully anlayzed one PT Sample for this study.

[1]*Protocol for EPA Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water', February 2009.*

C. RADIATION MEASUREMENTS BATCH

The laboratory operates two germanium gamma spectrometers GE1 and GE2. They were initially setup according to Section 1.7.1.1. An initial calibration was performed for a 1-L Marinelli beaker geometry, according to Section 1.7.1.2, and verified according to Section 1.7.1.3. The laboratory does performance checks twice weekly (Section 1.7.1.4.b.i)1). The laboratory's subtraction background (Section 1.7.1.5) also serves as a short-term background check (Section 1.7.1.6.d). The laboratory starts a Radiation Measurements Batch (Sections 1.3.1 and 1.7.2.1). The laboratory does one MB (Section 1.7.2.2.a), LCS (Section 1.7.2.3.a), and MD (Section 1.7.2.4.b)iii) and does not do MS (Section 1.7.2.4.a)ii). The Quality control samples are done without preference for a detector (Section 1.7.2.1.f). The randomly arriving water samples need to be measured for 1000 minutes each, therefore, only two samples per day can be accommodated.

The laboratory's schedule is as follows:

Day	GE1	GE2
Monday	Performance check (CT the same as for samples??)	Performance check (CT the same as for samples??)
	Sample 1	Sample 2
Tuesday	LCS	MB
Wednesday	sample 3	sample 4
Thursday	Performance check	Performance check
	Sample 5	Sample 6
Friday	Subtraction background	Subtraction background
Monday	Performance check	Performance check
	MD	None[1]
Tuesday	Sample 7	
Wednesday	MB[2]	
Thursday	Performance check	
	Sample 8	
Friday	Sample 9	
Monday	End of RMB[3]	

Footnotes:

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1. GE2 was allocated to another urgent project, and removed from this RMB.

2. The laboratory re-measures MB on GE1 to maintain integrity of RMB, which could be jeopardized due to a loss of GE2.

3. The RMB reached 14 calendar days and had to be terminated, in spite of measuring less than maximum allowed 20 environmental samples (Section1.7.2.1.c)iii)).

Page 3: [1] Comment [6] **Bob Shannon** **2/28/17 2:11 PM**

Key Points:

- All methods must be validated and data on the detection capability, precision, bias, Measurement Uncertainty, and selectivity of the method (consistent with published guidelines such as MARLAP, FEM, EUROCHEM) available at the laboratory to document method performance at the laboratory.
- The validation must follow a pre-defined process that is consistent with Sections 1.5.2 through 1.5.5 of V1M2 of the TNI Standard.
- Generally, the activity range must include performance at zero activity since most radiochemical methods generate results that include zero activity.
- In the case of reference methods, performance data published in the method may be used in lieu of method validation at the laboratory. Where performance data is not available, or if the reference method is modified, the laboratory must generate this method performance data based on the final method used at the laboratory (e.g., by validating the method).
- Analysis of historical internal quality control data has been used to generate some or all of the performance validation data needed to satisfy validation requirements.
- The validation records must be maintained for the life of the method and be readily retrievable.

Page 14: [2] Comment [36] **Bob Shannon** **2/28/17 3:03 PM**

While this may be nice practice, it is not part of the standard. There is a requirement that RMBs share a range of physical and chemical parameters, and analytical configurations (e.g., analytes, geometry, calibration, density) that conform to the ranges of physical and chemical parameters, and analytical configurations demonstrated by method validation studies (see Section 1.5).

This, however, has nothing to do with calibrations and corrections. Suggest reverting to original language and then provide an example of what is meant by sharing a range…..

Page 14: [3] Comment [37] **Bob Shannon** **2/28/17 3:07 PM**

Suggest possible edit

The laboratory may not systematically or preferentially use specific detectors, equipment or glassware for the analysis of QC samples. This might entail using a specific beaker or detector for blanks or LCSs, or always counting duplicates on the same detector. For example, quality control samples should be placed on the detectors in a manner that would specifically use or avoid use of a detector. This does not preclude designating a group of detectors for a specified analysis such as thorium or plutonium analyses or designating specific glassware for batches of samples (and QC samples) that (may) contain higher levels of activity.

Page 14: [4] Comment [38] **Bob Shannon** **2/28/17 3:09 PM**

This whole section is treading on thin ice. There is nothing in the standard that says use stats or tolerance charts for specific types of samples. It would be reasonable to provide some examples, but it should focus on strategies that will help the lab make good choices.

Page 14: [5] Comment [41] **Bob Shannon** **2/28/17 3:11 PM**

Good examples for tolerance charts might include for a project that specifies a specific acceptance range, say ±15% for a QC sample recovery. Also, is there anything in the standard about MBs and tolerance charts?

Page 14: [6] Comment [42] **Bob Shannon** **2/28/17 3:12 PM**

There is nothing here about

simulate quality system matrix characteristics that significantly affect results, such as geometry, size, and other factors as appropriate

or that the blank matrix should be activity free

or that the aliquot size will be similar to that of routine samples or that alternate criteria be used that compensate for differing batch size.