Protocol for the Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water

Office of Water (MS-140)

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Foreword

This document provides guidelines for the evaluation of radioactive contaminant analytical methods under EPA's Drinking Water Alternate Test Procedure (ATP) Program. The Drinking Water ATP Program only evaluates alternate methods for analytes regulated under the Safe Drinking Water Act (SDWA), the program will not evaluate methods for unregulated or secondary contaminants. Additionally, devices and equipment will only be evaluated as part of a complete method and not evaluated alone. This drinking water ATP protocol provides guidance for the modification or development of drinking water methods for compliance monitoring. It incorporates current recommendations for method validation that have been developed by the Forum on Environmental Measurements. Under the Drinking Water ATP Program, applicants are required to demonstrate that the alternate method being proposed is an equally effective procedure, relative to an existing EPA-approved method. That demonstration then provides basis for EPA's Office of Ground Water and Drinking Water to consider, independent of the ATP *evaluation*, the *approval* a particular method.

This protocol provides basic information on the criteria the Agency generally uses in deciding whether a method is suitable for evaluation under the Drinking Water ATP Program and the analyses that are generally needed to demonstrate method equivalency. In this protocol, applicants are also directed to demonstrate adequate ruggedness of the drinking water ATP through sufficient multi-laboratory validation to support EPA's consideration of their use at a national level.

EPA anticipates that the standardized procedures described herein will expedite the processing of drinking water ATP reviews, encourage the development of innovative technologies, and enhance the overall utility of the EPA- approved methods for compliance monitoring under the National Primary Drinking Water Regulations.

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This document does not alter, substitute for, establish or affect legal obligations under Federal regulations. This document is not a rule, is not legally enforceable, and does not confer legal rights or impose legal obligations on any federal or state agency or on any member of the public. Interested parties are welcome to suggest procedures that are different from what's recommended in this document. EPA reserves the right to change this protocol without prior notice.

Contents

1 Introduction

1.1 Background and Objectives

Pursuant to the Safe Drinking Water Act, EPA promulgates, via publication in the *Federal Register*, test procedures (analytical methods) for data gathering and compliance monitoring under National Primary Drinking Water Regulations.

Under the Agency's Drinking Water Alternate Test Procedure (ATP) Program, an organization may request evaluation of a method as an alternate test procedure to a method already approved in the drinking water regulations. These alternate drinking water methods, or ATPs, will be referred to as "candidate" methods through the remainder of this document. Devices and equipment will only be evaluated as part of a complete method and not evaluated alone. The organization or entity seeking the candidate method evaluation is responsible for validating the candidate method. EPA evaluates test methods used to measure regulated contaminants in drinking water for nationwide approval. This requires EPA to assess any candidate method in such a manner that its interlaboratory range in accuracy, precision and detection capability can be compared to EPA-approved test methods measuring the same target analyte(s). To be considered for approval, the candidate method must be an equally effective procedure as the approved method (see Safe Drinking Water Act §1401(1)); that is, a method's performance characteristics in general must be equivalent to, or better than, those of existing approved methods for the contaminant of interest. This allows EPA to ensure that data gathered under the Safe Drinking Water Act are comparable on a nationwide basis. Those methods that demonstrate acceptable performance through their ATP evaluation, become candidates for an EPA approval action.

1.2 Scope of Radiochemical Drinking Water ATP Process

The protocol design described in this document is consistent with candidate method validation requirements in other areas of chemistry but has been modified to adjust for the technical differences between chemical and radiochemical test methods. Radiochemical test methods differ from the other areas of analytical chemistry in several ways, including: 1) the types of detection systems used, 2) the chemical yields for sample preparation steps are generally measured and corrected for and 3) the detection limits (DLs) for radiochemical test methods for finished drinking water analyses are specifically defined by Federal regulation. This validation protocol is designed to address these differences with special attention to the manner in which accuracy, precision and detection capability are assessed for method approval.

2 Overview of the Drinking Water ATP Process

Agency staff reviews the application, including justification for the candidate method provided by the applicant, and determine whether a drinking water ATP evaluation is warranted. If the candidate method application is accepted for consideration, the applicant then develops a validation study plan in consultation with EPA's drinking water ATP staff. Once the study plan is approved, the applicant performs the validation study and submits a validation study report and candidate method to the Drinking Water ATP Program. If EPA determines that the laboratory validation demonstrates performance equivalent to or better than that obtained with an approved method, EPA Drinking Water ATP Program representatives will generally recommend approval by EPA senior leadership using one of two options: 1) approval through the conventional "notice and comment" rulemaking process, or 2) approval through the expedited method approval process. Additional information on the expedited method approval process can be found on EPA's drinking water analytical methods web page. A general checklist of the ATP process can be found in Appendix A.

2.1 Submission (initial application and subsequent documentation)

Applicants should submit drinking water ATP applications (see Appendix B) to the Drinking Water ATP Coordinator. Upon receipt and acknowledgment of the application, EPA staff will assign an identification number or name to the application. The applicant should use the identification number or name and Appendix B as a cover sheet for all future communications and any supplemental documentation concerning the application.

2.2 Application Information

Information required on the drinking water ATP application includes: the name and address of the applicant; the date of submission of the application; the title of the proposed candidate method including a shortened method name or number to use in the regulation and for reference; the analyte(s) for which the ATP is proposed; a brief summary of the proposed method and the justification for proposing the ATP. The applicant should provide all required application information and any associated attachments for the application to be considered complete.

2.2.1 Justification for Drinking Water ATP

The applicant should provide a brief justification for why the drinking water ATP is being proposed. Because EPA review and evaluation of proposed ATPs can entail considerable effort, EPA does not expect to entertain evaluation of impractical methods or method modifications that fall within the scope of flexibility already allowed in an approved method or in EPA's "Technical Notes on Drinking Water Methods" (EPA Document No. EPA-600-R-94-173, October 1994). Examples of appropriate justifications include but are not limited to: the candidate method successfully overcomes some or all of the interferences associated with the approved method; the candidate method reduces the amount of hazardous wastes generated by the laboratory; the cost of analyses or the time required for analysis is reduced; or, the quality of the data is improved. It is highly recommended that the method developer consult with ATP staff concerning the proposed candidate method and its justification prior to extensive method development.

2.3 Confidential Information in Applications

When submitting information with the proposed drinking water ATP application, the applicant may assert a business confidentiality claim covering part or all of the information. The method for submitting a claim is described in the Code of Federal Regulations (CFR) at 40 CFR 2.203(b). EPA staff will handle such information according to the regulations in subparts A and B of 40 CFR Part 2. Information covered by such a claim will be disclosed by EPA only to the extent, and by means of the procedures, set forth in 40 CFR Part 2, Subpart B. If no such claim accompanies the information when it is received by EPA, it may be made available to the public by EPA without further notice to the business.

Specifically, in accordance with 40 CFR §2.203(b), a business may assert a business confidentiality claim covering the information by placing on (or attaching to) the information at the time it is submitted to EPA, a cover sheet, stamped or typed legend, or other suitable form of notice employing language such as *trade secret, proprietary, or company confidential*. Confidential portions of otherwise non-confidential documents should be clearly identified and may be submitted separately to facilitate identification and handling by EPA. If confidential treatment is only required until a certain date, the notice should state so accordingly. It should be noted, however, that any analytical method being considered for approval in the Federal Register cannot itself be claimed as confidential business information; the vendor must be prepared for the method to be published and made widely available.

If a claim of business confidentiality is later received after the information is initially conveyed as part of an ATP application, EPA will make such efforts as are administratively practicable to associate the late claim with copies of the previously submitted information in EPA files. However, EPA cannot ensure that such efforts will be effective considering the possibility of prior disclosure or widespread prior

dissemination of the information, See §2.203(c).

3 Method Development and Validation Study Plan

3.1 Introduction

Method development and validation are the processes by which a laboratory substantiates the performance of a method by demonstrating that the method can meet EPA's acceptance criteria and that the method is rugged, that is, yields acceptable method performance and data quality over the range of drinking water sample types and of laboratory conditions specified in the method. In order to produce a method that is rugged and meets quality control acceptance criteria, the method developer needs to have a firm understanding of the chemistry involved in the method. Because methods vary widely in their chemistry and procedures, no definitive global guidance can be provided on how to develop a rugged method. In general, though, all candidate methods should: (a) identify critical points of each step in the procedure, (b) demonstrate that these critical points are satisfactorily addressed or controlled in the method and (c) demonstrate that acceptable method performance is attained using all procedural options specified in the method. Generally, there is an expectation that multiple, independent laboratories or sites be used in the validation process to ensure method ruggedness.

Critical points of a method can take a variety of forms depending on the method. For example, certain methods may require separation of an analyte at a specific pH or a narrow pH range. Thus, for the method to be truly rugged, pH control may be required to ensure that other samples, laboratory conditions, or chemists obtain satisfactory results using the method.

Once an application has been accepted by the Drinking Water ATP Program, the applicant should discuss their plans to address method ruggedness with drinking water ATP staff prior to formulating the validation study plan. Such consultation will help avoid both inadequate study plans (for example, not enough analyses addressing critical points of the method) and study plans with unnecessary analyses. The following sections summarize the major components of the validation study plan.

3.2 Development of a Validation Study Plan

Prior to conducting the candidate method validation study, the applicant should prepare and submit a detailed study plan for EPA approval. Guidelines describing the parameters that should be addressed in a radiochemical method validation study are provided in Appendix C. Sections specific to radiochemical methods are also identified.

3.2.1 Background

The Background section of the validation study plan should:

- Identify the candidate method.
- Include a summary of the candidate method.
- Describe the reasons for development, the logic behind the technical approach and the advantages of the method in comparison to existing technology or methodology.
- List the analytes measured by the candidate method including corresponding Chemical Abstract Services Registry Number (if applicable).

3.2.2 Study Management

The Study Management section of the validation study plan should:

- Identify the organization responsible for managing the study.
- Identify certified (if applicable), independent laboratories, facilities, and other organizations that will participate in the study.

- Delineate the study schedule following approval of the study plan.

3.2.3 Technical Approach

The Technical Approach section of the validation study plan should:

- Describe how participating laboratories will be selected.
- Explain who will prepare the test matrix and how it will be distributed.
- Specify the numbers and types of analyses to be performed by the participating laboratories in accordance with this protocol.
- Identify specific reagents, materials, instrumentation or software required.

3.2.4 Identification of Critical Steps and Plans for Addressing Critical Steps

As mentioned previously, a properly developed and validated method recognizes and controls critical steps in terms of the chemistry or ruggedness, or both, of the method. The applicant should identify those parts of the procedures that could be vulnerable to technician expertise or result in poorer performance with foreseeable departures from ideal conditions. The Plan should identify the steps that will be taken to control these critical steps.

3.2.5 Draft Candidate Method

A draft of the candidate method should be included as a separate attachment to the validation study plan. The draft details the step-by-step procedures of the candidate method. This includes all equipment, reagents and materials required and data evaluation or calculation procedures. Unless the applicant is a consensus standards organization or government organization that has their own method format requirements, all applicants should submit the candidate method written in the standard EPA method format (Appendix D). Applicants from organizations having their own format requirements should compare their specific method format with the EPA method format to ensure that all sections of the EPA method format are addressed. The 17 sections listed in Appendix D of this document should be included for all candidate methods. Recent drinking water methods published by EPA (for example, Methods 150.3, 533, 546) may also be consulted for format and the level of detail required.

3.2.6 Radiochemical Method Validation Study

Radiochemical methods follow different procedures for validation than those methods analyzing for organic and inorganic contaminants. Procedures specific to radiochemical methods can be found in Appendix C.

3.3 Approval of Validation Study Plan

Once EPA is satisfied that the written method and the proposed study plan meet the criteria described in this document, the applicant will be instructed to proceed with the method validation study.

3.4 Method Validation Study Report

The applicant should document the results of the validation study in a formal validation study report containing the elements described in this section. In all cases, a copy of all required validation data should be maintained at the laboratory or other organization responsible for developing the method. The information and supporting data in the validation study report must be sufficient to enable EPA to determine whether the candidate method performs as well as or better than the approved reference method.

The validation study report should contain background information and describe the study design. In addition, the validation study report should detail the process and results of the study, provide an analysis and discussion of the results, and present study conclusions. The approved validation study plan should be appended to the validation study report and referenced as appropriate.

The validation study report should identify and discuss any deviations from the validation study plan that were made in implementing the study along with problems encountered and corrective actions. To the extent possible, deviations should be discussed with EPA in advance of being implemented to ensure that the deviations are appropriate.

See Appendix E for the validation study report template.

3.4.1 Background

The Background section of the validation study report describes the candidate method. The Background section of the validation study report should:

- Include a method summary.
- Summarize the justification for the ATP evaluation and the proposed benefits the candidate method offers to drinking water monitoring.
- List the analytes measured by the candidate method, including corresponding Chemical Abstracts Service Registry identification.

3.4.2 Study Implementation

The Study Implementation section of the validation study report describes the methodology and approach undertaken in the study. This section should:

- Identify the laboratories or other organizations or both that participated in the study.
- Delineate the study schedule that was followed.
- Explain how samples were collected and handled.
- Specify the numbers and types of analyses performed by the laboratory.
- Identify any problems encountered or deviations from the study plan and their resolution or impact on study performance or results or both.

3.4.3 Demonstration Data

This section of the validation study report should include the demonstration data for the analyzed samples. For each sample, the report should compare method performance data obtained with the candidate method to the approved reference method performance data. Demonstration data should be provided for samples using all procedural options specified in the method.

3.4.4 Calculations, Data Analysis and Discussion

This section of the validation study report should provide sufficient documentation of the data obtained with the candidate method to permit an independent reviewer to verify the study results. Example calculations are required as part of the results and should be included in the validation study report. The test data and calculations should be electronically reported in a format compatible with Microsoft© Office applications. The discussion should address any discrepancies between the results and the quality control acceptance criteria.

3.4.5 Conclusions

The Conclusions section of the validation study report describes the conclusions drawn from the study based on the data analysis discussion. The Conclusions section should contain a statement(s) regarding achievement of the study objective(s).

3.4.6 Candidate Method

The candidate method should be appended to the validation study report. Format should follow that specified in Appendix D.

3.4.7 Validation Study Plan

The validation study plan should be appended to the validation study report.

4 EPA Review and Approval

4.1 EPA Review of Candidate Method

EPA's Drinking Water ATP Program reviews the candidate methods and the validation data. If a candidate method is determined to provide equivalent method performance relative to the reference method, it becomes a candidate for approval by EPA senior leadership.

4.2 Approval Recommendation

EPA will complete its review and notify the applicant of EPA's recommendation. If the candidate method is recommended for approval, EPA will pursue formal approval using one of two options: 1) approval via the conventional "notice and comment" rulemaking process or 2) approval via the expedited method approval process. Find additional information on EPA's drinking water analytical methods web page .

4.3 Joint Drinking Water Wastewater Applications

Candidate methods can be submitted for ATP evaluation for both drinking water and wastewater applications. However, the requirements for compliance monitoring under the National Primary Drinking Water Regulations differ from those under the National Pollutant Discharge Elimination System permit program. Review and evaluation of ATP candidate methods that are submitted for dual applications are thus handled by both the Drinking Water ATP Program and the Wastewater ATP Program.

5 References

1. The NELAC Institute. (n.d.). *Radiochemistry Performance Testing Scoring Criteria*. Retrieved from The NELAC Institute: http://www.nelac-institute.org/
2. International Organization for Standardization. (1995). *Guide to the Expression of Uncertainty in Measurement.* Geneva, Switzerland.
3. U.S. Department of Commerce. (1994). *Guidelines for Evaluating and Expressing the Uncertainty of National Institute of Standards and Technology Measurement Results. Technical Note 1297*. Retrieved from National Institute of Standards and Technology: http://www.nist.gov/
4. U.S. Environmental Protection Agency. (2004). *Multi-Agency Radiological Laboratory Analytical Protocols Manual.* NUREG - 1576, EPA 402-B-04-001C.
5. U.S. Environmental Protection Agency. (2005). Chapter VI, Critical Elements for Radiochemistry. *The Manual for the Certification of Laboratories Analyzing Drinking Water*. Washington, D.C. EPA 815-R-05-004.
6. U.S. Environmental Protection Agency. (2017). *Procedure for Safe Drinking Water Act Program Detection Limits for Radionuclides*. EPA 815-B-17-003.

Appendix A: ATP Applicant Process: General Checklist

Step 1: Initial Inquiry	Y	N	N/A	Notes
The application includes name, address, date, and title of the proposed method.				
The proposed method is for drinking water and the analysis of regulated contaminants or water quality parameters.				
The EPA has assigned a unique identifier to the submitted method.				
The applicant has included method data with their request (optional).				
The EPA has determined the request is allowed within the method-specified flexibility.				
The EPA has determined an evaluation of the proposed method as an ATP candidate method is warranted.				

Step 2: ATP Initial Application	Y	N	N/A	Notes
The applicant has provided the Application and Document Submission Form with all requested information.				
The application includes the analyte to be studied.				
The application lists the approved EPA reference method(s) used for comparison with the candidate method.				
The applicant has submitted justification for the candidate method to the Drinking Water ATP Coordinator.				
The applicant is asserting a claim the candidate method contains confidential business information (CBI).				
The applicant has attached paperwork pursuant to 40 CFR 2.203(b) regarding CBI.				
The applicant has submitted and separated the CBI and indicated with an appropriate coversheet marked "confidential."				
The EPA has handled CBI pursuant to subparts A and B of 40 CFR Part 2.				

Step 3: Submission of Study Plan	Y	N	N/A	Notes
The study plan cover sheet includes name, address, date, case number, and title of the proposed method.				
A draft of the candidate method has been provided.				
The applicant has identified the critical points of the study proposal.				
The applicant has discussed methods to control the critical points of the proposal.				
The applicant has included experiments to verify all procedural options specified in the method.				
The applicant has included in their validation study plan a discussion to address method ruggedness.				
The applicant has submitted a complete validation study plan to EPA for review following the ATP protocol guidelines.				
The background of the study plan includes a summary of the candidate method.				
The background of the validation study plan includes a list of the analytes				

Step 3: Submission of Study Plan	Y	N	N/A	Notes
and corresponding Chemical Abstracts Service (CAS) Registry identifications.				
The validation study plan identifies the organization responsible for managing the study.				
The validation study plan identifies the laboratories/organizations that will participate in the study.				
The validation study plan contains and assigns a study schedule to the laboratories/organizations participating in the study.				
The validation study plan uses the same holding times, extract holding times, and preservation agents specified in the candidate method.				
The validation study plan lists all the equipment that will be used in the candidate method.				
The validation study plan lists all the reagents that will be used in the candidate method.				
The validation study plan includes all 17 sections of the EPA method format.				
The validation study plan identifies critical steps and the plan to monitor and account for departures from method performance.				
The validation study plan identifies interferences (chemical, physical) that may affect the results and the plans to mitigate the interferences.				
The validation study plan includes a method to determine precision and accuracy using fortified reagent water.				
The validation study plan includes a method to determine effectiveness above and below the Maximum Contaminant Level (MCL).				
The validation study plan includes a method to incorporate the preservative agent(s) into fortified reagent water as identified in the method.				
The validation study plan includes analysis of drinking water from a hard water source. (Optional)				
The validation study plan includes analysis of drinking water from a source that contains total organic carbon ≥ 2mg/L. (Optional)				
The validation study plan includes analysis of artificial drinking water with a high ionic strength. (Optional)				
The validation study plan includes analysis of artificial drinking water with a high organic content. (Optional)				
The validation study plan includes analysis of artificial drinking water with a high chloride content. (Optional)				
The validation study plan includes analysis of artificial drinking water with a disinfection byproduct. (Optional)				
The validation study plan includes an analysis of the Quality Control Targets used in the candidate method.				

Step 4: Submission and Review of Method Validation Study Report (MVSR)	Y	N	N/A	Notes
The background of the MVSR contains a method summary, justification for the ATP evaluation, and a list of the analytes.				
The MVSR study implementation section identifies the laboratories/organizations that participated in the study.				
The MVSR implementation report lists the study schedule that was followed.				
The MVSR study implementation section explains how the samples were				

Step 4: Submission and Review of Method Validation Study Report (MVSR)	Y	N	N/A	Notes
collected and handled.				
The MVSR implementation section specifies the types and numbers of analyses to be performed in the lab.				
The MVSR implementation report identifies and describes any deviations or problems that impacted the study performance.				
The MVSR presents a sufficiently detailed version of the candidate method in the correct EMMC format.				
The MVSR contains sample calculations.				
The test data is reported in a format compatible with Microsoft© Office applications.				
The MVSR contains a discussion of discrepancies between results and quality control acceptance criteria.				
The MVSR contains a conclusion section discussing achievement of the study objective(s).				
The MVSR contains the approved validation study plan in the appendix.				
Developed in collaboration with EPA, the MVSR contains data from multiple matrices to identify interferences or matrix effects.				

Step 5: Data Review of MVSR by EPA	Y	N	N/A	Notes
Applicant has completed the Application and Document Submission Form.				
The applicant has submitted evidence of instrument calibration.				
The applicant has submitted a rigorous evaluation of bias in their analytical method.				
The applicant has submitted an evaluation of precision, using the extremes of the quantitation range, regulatory levels, and multiple matrices.				
The method blank meets the minimum reporting level (MRL) described in the reference method (if applicable).				
The results from the initial demonstration of capability (IDC) passes the Quality Control Targets used in the candidate method.				
The method demonstrates chemical and microbiological storage and stability.				
The method has utilized a minimum number of sites/laboratories for data collection, as determined by the EPA.				

Step 6: Final Evaluation by EPA	Y	N	N/A	Notes
The applicant has demonstrated through design, experiment, and data collection that their candidate method is rugged.				
The applicant has submitted any additional paperwork and data requested by the EPA.				
The EPA has satisfactorily protected the CBI of the applicant.				
The EPA has determined the candidate method as ab ATP submission is equally effective as the reference method.				

Appendix B: Application and Document Submission Form

EPA Office of Ground Water and Drinking Water Alternate Test Procedure Candidate Method Application

☐ Initial Application
☐ Supplemental Documentation
☐ Final Application

Applicant Information
Applicant Name:
Address:
State:
Zip Code:
Contact name:
Phone number:
Email address:
Submission Date:
Candidate method:
Analyte(s):
Candidate method title:
Reference method number or name or both:

Attachments

☐ Justification for Candidate Method
☐ Validation Study Plan
☐ Validation Study Report
☐ Raw Data Package (spreadsheets, calibrations, etc.)
☐ Data Collection Certification
☐ Other Documentation:

EPA use only Case number:

Appendix C: Radiochemical Method Validation

1 Introduction

Method validation is the process by which a method developer substantiates the performance of a candidate method. Candidate methods should be validated to demonstrate they have acceptable performance characteristics such as accuracy, precision and detection capability for the measurement of their target radioanalyte(s). Although this is generally achieved by comparing the performance of the candidate method to that of existing approved methods, additional metrics such as robustness or ruggedness may also warrant evaluation.

Recently, the NELAC Institute (TNI) published radiochemistry Performance Testing study acceptability criteria that are based on the results of past radiochemistry Performance Testing studies (*Radiochemistry Performance Testing Scoring Criteria*, (1)). These scoring criteria are not test method-specific, but instead reflect the average performance of all test methods for a specific radioanalyte. EPA may base the acceptability criteria for candidate methods validated using the procedures detailed in this protocol on the current NELAC Performance Testing scoring criteria. This approach will provide limits for performance characteristics that are representative of the current proficiency for all the test methods currently in use.

2 Candidate Radiochemistry Test Method Validation Study Design

The candidate method validation study design described in this protocol is intended to provide sufficient data to determine the performance characteristics of candidate methods and provide data to determine whether constituents typically found in finished drinking water matrices will adversely affect method performance. The study design will evaluate the candidate method's performance in obtaining measurements for the test matrix and determine if the candidate method is comparable to test methods already approved by EPA to measure the same target radioanalytes in drinking water. The validation study is broken down into the Reagent Blank (RB) study, the Detection Limit (DL) study (see Appendix F for definition and discussion of the Safe Drinking Water Act DL) and the method performance study.

Because the RB and DL studies assess the candidate method's performance independent of matrix effects, these studies should employ water equivalent to or better in quality than ASTM Type II water. The method performance study will gather data to assess the candidate method's performance in the test matrix, which is representative of the types of samples that the method may be used to measure on a routine basis. The method performance study's design is intended to provide sufficient data to characterize the candidate method's intra-laboratory and inter-laboratory performance. Each study (RB, DL and method performance) is discussed in more detail in App. C, Sect. 4.

Under the validation study, the sample test matrix (as identified) should be analyzed at four different matrix and spike level combinations by three certified laboratories and their results employed in the validation study report. The applicant may elect to employ more than three laboratories or more than four matrix and spike level combinations. However, in such cases, the applicant is responsible for adjusting the calculations for the study appropriately. The number of study samples and the total number of samples in a three-lab study are listed below in Table 1.

Table 1. Types and Numbers of Samples Required for the Candidate Method Validation Study

Study	Sample Type	Number of Samples per Participating Laboratory[1]	Total Number of Samples in a Three Lab Study[2]
Reagent Blank	RB	6	18
Detection Limit[3]	DL (replicates spiked at or below the target radioanalyte's required DL)	7	21
Method performance	Reagent Water Fortified at Maximum Contaminant Level	7	21
Method performance	Test Matrix at Maximum Contaminant Level	7	21
Method performance	Test Matrix at ½ Maximum Contaminant Level	7	21
Method performance	Test Matrix at 2 x Maximum Contaminant Level	7	21

[1] The total number of samples required per participating laboratory is 41.
[2] The grand total number of samples required in a three-lab study is 123.
[3] In some cases the DL study may not be needed if the DL test is passed (see App. C, Sect. 4).

3 General Study

3.1 Selecting and Supporting the Participating Laboratories

A minimum of three laboratories should participate, in order to characterize inter-laboratory method performance. The laboratories employed should be certified by EPA or a State to test for radioanalytes in drinking water. If the applicant is a certified laboratory, the applicant should locate at least two other certified radiochemistry laboratories to participate in the method validation study with them. If the applicant is not a certified laboratory, the applicant should obtain the services of at least three certified radiochemistry labs. The applicant should provide the participating laboratories with the candidate method standard operating procedure, any technical assistance requested by them and with sufficient volume of the test matrix to run the method performance study. The applicant should collect the necessary data from the participating laboratories to produce a single validation study report and data package for submission to EPA.

3.2 Validation Study Test Matrix

Finished drinking water matrices could potentially have levels of regulated and unregulated chemical and radioactive constituents (that is, organics, solvents, cations, anions, metals, etc.) at concentration levels by themselves or in summation with others that may interfere with the sample preparative steps in a radiochemical test procedure. Since test methods used to monitor the compliance status of public water systems are approved for nationwide use, any method validation study for candidate methods for drinking water should be conducted using a test matrix that is representative of the diversity in both unregulated and regulated constituents that may be found in finished drinking water.

A test matrix has been developed for use in the method performance study. This test matrix was tested

by EPA, is within the bounds of the types of finished drinking water that are found nationally and is reasonable to test the method performance of a high ionic strength water matrix. The matrix sample components and directions for preparing the test matrix are identified in Appendix G.

The applicant should provide EPA with documentation that the test matrix was preserved and stored according to the approved procedures for the candidate method and that all analyses took place within the required holding times. The applicant laboratory should ensure sufficient quantities of the test matrix are available for all the test batches needed by all the participating laboratories.

3.3 Significant Figures, Rounding Data Results and Data Reporting Conventions

All measurement results should: (1) be reported directly as obtained with appropriate units, (2) be reported even if it is negative, (3) be expressed in an appropriate number of significant figures and (4) include an unambiguous statement of the uncertainty. The appropriate number of significant figures is determined by the magnitude of uncertainty in the reported value.

The value, as measured (including zero and negative numbers) and the measurement uncertainty (either expanded uncertainty or the combined standard uncertainty) should be reported in the same units. For presentation of data in the method validation report the measurement uncertainty should be rounded to two significant figures and both the value and uncertainty should be reported to the same number of decimal places. For example, a value of 0.8961 pCi/L with an associated combined standard measurement uncertainty of 0.0234 should be reported as 0.896 ± 0.023 pCi/L with a coverage factor of one.

Note: Rounding should only be used in determining the final results.

3.4 Uncertainty Evaluation and Reporting

The submitted method should describe the equations or procedures used to evaluate the uncertainty of each result. When describing uncertainties, the method should use the terminology and symbols of the *Guide to the Expression of Uncertainty in Measurement; International Standards Organization 1995* (2). Each measurement result should be reported with its associated counting uncertainty in accordance with the applicable regulations; however, EPA also encourages labs to perform a complete uncertainty evaluation and report the overall measurement uncertainty of each result as well.

Since laboratories may calculate uncertainties using different methods and report them using different coverage factors, uncertainties should be reported with an explanation of what they represent. In particular, reports should clearly distinguish between counting uncertainties and total uncertainties.

Furthermore, any analytical report, even one consisting of only a table of results, should state whether the uncertainty is a standard uncertainty ("one sigma") or an expanded uncertainty ("*k* sigma") and in the latter case it should also state the coverage factor (*k*) and, if possible, the approximate coverage probability. If the laboratory uses a shorthand format for the uncertainty, the report should include an explanation of the format.

Additional information about the evaluation and expression of uncertainty can be found in National Institute of Standards and Technology Technical Note 1297: *Guidelines for Evaluating and Expressing the Uncertainty of National Institute of Standards and Technology Measurement Results* (3) and the *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (4).

4 Performing the Reagent Blank and Detection Limit Studies

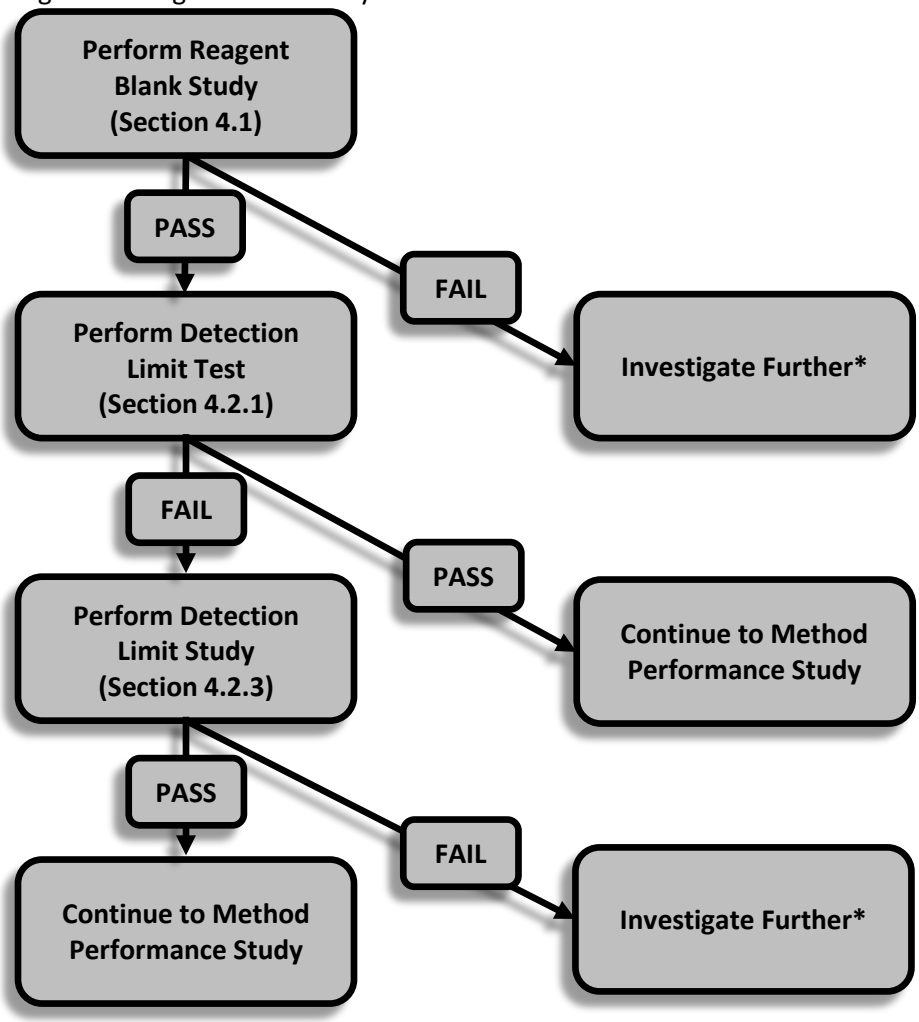
Participant laboratories should initially produce RB and DL data quantifying their performance with the candidate method that is independent of matrix interferences. These data assess laboratory baseline proficiency with the candidate method prior to assessing matrix interferences with a candidate method

performance study.

The data generated by these initial demonstrations of performance are designed to determine if the laboratory can perform the candidate method and generate results comparable to those generated using the approved test methods for a specific regulated radioactive contaminant or contaminants. The candidate method's detection capability is assessed with a RB study and DL study.

In some cases, applicants may only need to do the RB study and forgo the DL study if the candidate method can successfully pass the DL test in App. C, Sect. 4.2.1.

Figure 1. Reagent Blank Study Process



*If the RB or DL study fail, the applicant may wish to modify the method and repeat the calculation. If a method modification is necessary, the applicant should notify EPA of the modification before proceeding.

4.1 Reagent Blank Study

Each participating laboratory should demonstrate that it is capable of measuring the analyte at sufficiently low levels to determine if the candidate method can meet the required DL for the target radioanalyte(s). An RB analysis is performed to measure the effect of possible contamination of the reagents and lab ware. The RB study should use deionized water that meets or exceeds the ASTM Type II standard for reagent water. This sample should be free of matrix interferences and will allow an initial assessment to be made for the candidate method's baseline performance as it is used by the participating laboratories. Each participating laboratory should use the candidate method to prepare

and measure two RBs on three non-consecutive days for a total of six RBs. The RBs should be assumed to be a normal sample that is dispensed, prepared and processed with the reagents and procedures specified in the candidate method for routine sample analysis. They should be measured using the detection system specified in the candidate method using the count times calculated as necessary for routine sample measurements in order to meet the required DLs. The average net activity for these RB measurements should then be calculated. For each participating laboratory, the absolute value of the average net activity found in the study's RBs should not exceed one-half of the required DL for each radioactive contaminant measured using the candidate method as they are listed in Table B at 40 CFR part 141.25(c)(1) and Table C at 40 CFR part 141.25(c)(2). If the absolute value of the average net activity found in the study's RBs exceeds one-half of the required DL, the applicant may wish to modify the method and have each participating laboratory repeat the RB study. If a method modification is necessary, the applicant should notify EPA of the modification before proceeding.

4.2 Detection Limit Test and Detection Limit Study

The candidate method should be evaluated against the DL test criteria to determine if an additional DL study should be done. If the candidate method can pass the DL test, applicants can forgo the DL study and begin the method performance study.

4.2.1 Detection Limit Test

If the method always produces a result (positive, negative or zero) and if there are theoretically defensible equations for calculating the DL, then the applicant may determine the DL by a documented calculation without performing a DL study. For more information on calculating theoretical DLs for radiochemical measurements see Appendix F. In this case, the calculated DL must not exceed the required DL. As an additional check, the results of the RB analyses will be evaluated statistically to test whether the observed variability significantly exceeds the standard deviation expected at the required DL, as shown below.

4.2.2 Statistical Evaluation of the Reagent Blanks

Let B_1, B_2, …, B_n denote the results of all the RB analyses (for example, n = 18 if there are three labs and six blanks per lab). Calculate the following statistic W:

$$W = \frac{1.96^2}{RDL^2} \sum_{i=1}^{n} B_i^2 \qquad (1)$$

The critical value for W is the 99th percentile of the chi-squared distribution with n degrees of freedom.

$$W_c = \chi^2_{0.99}(n) \qquad (2)$$

For example, if n = 18, the critical value is W_C = 34.81.

The candidate method should NOT be deemed to pass the DL test if $W > W_C$ and the applicant should conduct a DL study. If EPA determines that the data appear suspect (for example, if all the blank results are exactly zero) the applicant may be requested to perform a DL study.

4.2.3 Detection Limit Study

The DL study will verify that the method is capable of routinely achieving the required detection

capability for the method. Whenever practical, the first step of the DL study should be a theoretical estimation of the Safe Drinking Water Act DL based on the definition in 40 CFR 141.25(c) and all relevant data obtained in the method background study, such as instrument background levels, chemical yields, etc. Appendix F of this document describes how to calculate such a theoretical estimate in the simplest cases. If the theoretical estimate of the DL does not exceed the required DL, an experimental DL study should be performed as described below. However, if the theoretical estimate of the DL exceeds the required DL, the performance of the method will be considered inadequate and there will be little value in completing the experimental DL study. In this case, the applicant may wish to modify the method (for example, increase counting time or increasing the sample volume) and repeat the calculation of the theoretical estimate of the DL. If a method modification is necessary, the applicant should notify EPA of the modification before proceeding. If a theoretical estimation of the DL is found to be impractical, the experimental DL study is required.

The experimental DL study consists of seven replicate samples. Each sample should be made with ASTM Type II reagent water, at a minimum, using the sample volume prescribed in the method. The sample should be spiked with National Institute of Standards and Technology traceable source(s) of the method target radionuclide(s) to an activity concentration at or below their required DL. The sample should be mixed and then processed through sample preparation, processing and analysis per the candidate method. The measurements of the DL study samples will then be assessed by calculating a precision statistic. See App. C, Sect. 6.1 for further information.

5 Method Performance Study

The method performance assessment study is to be performed by three laboratories, each analyzing seven replicates at four different matrix and spike level combinations, as listed below:

1) Reagent water, spiked at the Maximum Contaminant Level.
2) The test matrix, spiked at the Maximum Contaminant Level.
3) The test matrix, spiked at ½ the Maximum Contaminant Level.
4) The test matrix, spiked at 2 times the Maximum Contaminant Level.

The results of the bias and precision evaluations are subject to the criteria as described in App. C, Sect. 6.3 and App. C, Sect. 6.4, respectively, at each matrix and spike level for the study to be acceptable. Therefore, it is recommended that the analyses be performed in reagent water first, then in the order of increasing concentration in the matrix. There is no need to complete all four sets of analyses if one has failed.

If either the results of the bias or precision evaluations fails the criteria for any spike level or matrix, then the applicant should investigate why the method failed the criteria and possibly modify the method and repeat the calculation. If a method modification is necessary, the applicant should notify EPA of the modification before proceeding.

6 Acceptability Criteria for Radiochemical Study Results

The NELAC Institute has published and maintained a table of radiochemical Performance Testing study acceptability criteria (1). The calculations discussed in this section were developed to account for the presence of variability between multiple laboratories. The precision evaluation in App. C, Sect. 6.4 is based on the single-laboratory standard deviations (presented in Table 2) that were used to develop the NELAC performance testing criteria. Assessing method performance using these criteria will help ensure compliance monitoring measurements for regulated contaminants that meet or exceed a minimum acceptable level of performance for laboratories nationally.

6.1 Experimental Detection Limit Studies

The assessment of the replicate results for one analyte at all of the participating laboratories uses a chi-square statistic to test whether the pooled relative standard deviation of the results exceeds the maximum value allowed at the required DL.

Calculate the mean, $\bar{X}_i$ and a chi-square statistic, χ^2 for each of the participating laboratories, $m(\chi_1^2, \chi_2^2, \ldots \chi_m^2)$:

$$\bar{X}_i = \frac{1}{n}\sum_{j=1}^{n} X_{ij} \qquad \text{and} \qquad \chi_i^2 = \frac{1.96^2}{\mu^2}\sum_{j=1}^{n}(X_{ij} - \bar{X}_i)^2 \tag{3}$$

Where:

m is the number of laboratories (three or more).
n is the number of replicate measurements (n = 7).
μ is the spike concentration (not to exceed the required DL).
X_{ij} is the result of the j^{th} replicate measurement (j = 1, 2, …, n) at the i^{th} laboratory (i = 1,2,…, m).

Then calculate the overall chi-square statistic:

$$\chi^2 = \sum_{i=1}^{m} \chi_i^2 \tag{4}$$

To be deemed acceptable, the value of χ^2 should be less than or equal to the 99th percentile of the χ^2 distribution with m x (n-1) degrees of freedom. When n = 7 and m = 3, the value of this percentile is 34.81.

Note: Refer to Appendix H – Sample Calculations Section 1.0 for an example calculation.

6.2 Method Performance Study Criteria

App. C, Sect. 6.3 and App. C, Sect. 6.4 present the step-by-step processes by which the bias and precision of the method performance study data should be assessed. In the event that the NELAC Institute updates their performance testing acceptability criteria in the future, the updated table should be used to reference these limits until an addendum to or revision of this document is published.

Table 2. Means and Standard Deviations (from NELAC Performance Testing Criteria)

Analyte	**Spike Level Range (μ[1])**	**Standard Deviation (σNELAC)**
Gross Alpha	7 to 75	(0.1610 μ) + 1.1366
Gross Beta	8 to 75	(0.0571 μ) + 2.9372
Barium-133	10 to 100	(0.0503 μ) + 1.0737
Cesium-134	10 to 100	(0.0482 μ) + 0.9306
Cesium-137	20 to 240	(0.0347 μ) + 1.5185
Cobalt-60	10 to 120	(0.0335 μ) + 1.3315
Iodine-131	3 to 30	(0.0624 μ) + 0.6455
Radium-226	1 to 20	(0.0942 μ) + 0.0988
Radium-228	2 to 20	(0.1105 μ) + 0.3788

Analyte	Spike Level Range (μ[1])	Standard Deviation (σNELAC)
Strontium-89	10 to 70	(0.0379 μ) + 2.6203
Strontium-90	3 to 45	(0.0902 μ) + 0.5390
Tritium	1000 to 24000	(0.0532 μ) + 38.8382
Natural Uranium	2 to 70	(0.0700 μ) + 0.2490
Uranium (mass)	3 to 104 μg/L	(0.0700 μ) + 0.3700
Zinc-65	30 to 360	(0.0530 μ) + 1.8271

[1] μ = spike level (pCi/L or μg/L)

Based on an EPA study using the test matrix, the following spike levels should be used for Barium-133 and Cesium-134:

Barium-133 – 50 pCi/L equivalent to slightly greater than 1/2 the Maximum Contaminant Level of Barium-140 (90 pCi/L).

Cesium-134 – 40 pCi/L equivalent to 1/2 the actual determined Maximum Contaminant Level.

6.3 Bias Evaluation for the Method Performance Study

In order to assess whether the average concentration of the replicates for a given spike level and matrix is significantly different from the spike level, it is first necessary to calculate *r*, the ratio of the between-laboratory standard deviation to the within-laboratory standard deviation.

The within-laboratory standard deviation (s_w) and the between-laboratory standard deviation (s_b) are calculated as follows:

$$s_w = \sqrt{\frac{1}{3}\sum_{i=1}^{3} s_i^2} \tag{5}$$

Where:

s_i is the standard deviation of the 7 replicate results for laboratory *i.*

$$s_b = \sqrt{\frac{1}{2}\sum_{i=1}^{3} (\bar{X}_i - \bar{\bar{X}})^2 - \frac{s_w^2}{7}} \tag{6}$$

Where:

$\bar{X}_i$ is the mean of the 7 results for laboratory *i.*

$\bar{\bar{X}}$ is the grand mean of the 21 results over all three laboratories.

Note: If the radicand is negative, s_b should be set to zero.

Calculate the ratio *r*:

$$r = \frac{s_b}{s_w} \tag{7}$$

Using σNELAC (Table 2), calculate the acceptable combined standard deviation for lab averages,

$$\sigma_c = \sigma_{NELAC} \times \sqrt{\frac{r^2 + \frac{1}{7}}{r^2 + 1}} \tag{8}$$

Note: The appropriate value of σNELAC may differ for different spike levels.

For the method to be acceptable, the grand mean, $\bar{\bar{X}}$, should be within the following range:

$$\mu \pm \frac{\sigma_c \times 2.58}{\sqrt{3}} \tag{9}$$

Where:

μ is the spike level.
2.58 is the 99.5th percentile of a standard normal deviation distribution.

Refer to Appendix H – Sample Calculations (App. H., Sect. 2.1) for an example calculation.

6.4 Precision Evaluation for the Method Performance Study

Calculate a statistic for total precision using the equation below.

$$\chi^2 = \frac{1}{\sigma^2_{NELAC}} \sum_{i=1}^{3} \sum_{j=1}^{7} (X_{ij} - \bar{\bar{X}})^2 \tag{10}$$

Where:

σ^2_{NELAC} is determined from Table 2.
$\bar{\bar{X}}$ is the grand mean of the 21 tests over three laboratories for the given spike level and matrix.

For the method to be acceptable χ^2 should be below the 99th percentile of the chi-square distribution with 20 degrees of freedom (37.57). Refer to Appendix H – Sample Calculations (App. H., Sect. 2.2) for an example calculation.

7 Acceptability Criteria for Quality Control Tests

Candidate method Standard Operating Procedures should reference Chapter VI, Critical Elements for

Radiochemistry, in *The Manual for the Certification of Laboratories Analyzing Drinking Water* (5) for the required instrument stability checks and preparation batch quality control samples, their frequencies and acceptability limits.

8 Quality Control

Laboratories measuring radiochemical compliance monitoring samples in support of the Safe Drinking Water Act should follow the requirements found in Chapter VI, Critical Elements for Radiochemistry, in *The Manual for the Certification of Laboratories Analyzing Drinking Water* (5). Section 7.4 in Chapter VI of this manual requires laboratories to participate in at least one Performance Testing study per year for each regulated radioactive contaminant using a specific method for certification. Section 7.7 in the same chapter specifies quality control tests and their acceptance criteria to assess sample preparation batch accuracy, precision, detection capability and interferences. Section 7.7 also requires instrument quality control checks be made in order to monitor their stability. Instrument specific calibration requirements and stability checks are described in Section 3.1. Section 7.8 in Chapter VI states that laboratories should collect quality control data and order them by quality control test in a control chart in order to document each method's performance and the stability of counting instrumentation. In order to ensure data consistency and reliability nationally, the requirements found in Chapter VI should be followed along with any quality control requirements found in currently approved methods.

The contents of the quality control section (Section 9) in candidate method standard operating procedures should be consistent with the requirements found in Chapter VI. The candidate method standard operating procedure should specify either the sample preparation batch quality control tests, the instrument stability checks and their acceptance criteria as they are found in Chapter VI or explicitly reference where the quality control test requirements appropriate to the candidate method may be found in Chapter VI.

Appendix D: Standard EPA Method Format

[Note: Each method should be a free-standing document, providing all information necessary for the method user to perform the analysis. References within a method should be restricted to associated or source material. Procedural steps or instructions should not be referenced as being found elsewhere but should be included in totality within the method. The following section numbering scheme is typical with the Environmental Monitoring Management Council (EMMC) format.]

1 Scope and Application

[This section outlines the purpose, range, limitations, and intended use of the method and identifies target analytes.]

2 Summary of Method

[This section provides an overview of the method procedure and quality assurance.]

3 Definitions

[This section includes definitions of terms, acronyms and abbreviations used in the method. If preferred, definitions may be provided in a glossary at the end of the method or manual. In this case, the definitions section should still appear in the method, with a notation that definitions are provided in a glossary (refer to the specific section number of the glossary) at the end of the method.]

4 Interferences

[This section identifies known or potential interferences that may occur during use of the method and describes ways to reduce or eliminate these interferences.]

5 Safety

[This section describes special precautions needed to ensure personnel safety during the performance of the method. Procedures described here should be limited to those which are above and beyond good laboratory practices. The section should contain information regarding specific toxicity of analytes or reagents.]

6 Equipment and Supplies

[This section lists and describes all non-consumable supplies and equipment needed to perform the method.]

7 Reagents and Standards

[This section lists and describes all reagents and standards required to perform the method and provides preparation instructions or suggested suppliers or both as appropriate.]

8 Sample Collection, Preservation and Storage

[This section provides requirements and instructions for collecting, preserving and storing samples.]

9 Quality Control

[This section cites the procedures and analyses required to fully document the quality of data generated by the method. The required components of the laboratory's quality assurance program and specific quality control analyses appropriate to the method are described in this section. It should reference Chapter VI, Critical Elements for Radiochemistry in The Manual for the Certification of Laboratories Analyzing Drinking Water (5) for the required quality control tests and the specific quality control acceptance criteria for each of them.]

10 Calibration and Standardization

[This section describes the method or instrument calibration and standardization process and the required calibration verification. Corrective actions are described for cases when performance specifications are not met.]

11 Procedure

[This section describes the sample processing and instrumental analysis steps of the method and provides detailed instructions to analysts.]

12 Data Analysis and Calculations

[This section provides instructions for analyzing data, equations, and definitions of constants used to calculate final sample analysis results and their uncertainties.]

13 Method Performance

[This section provides method performance criteria for the method, including precision or bias statements regarding detection limits and sources or limitations of data produced using the method.]

14 Pollution Prevention

[This section describes aspects of the method that minimize or prevent pollution known to be or potentially attributable to the method.]

15 Waste Management

[This section describes minimization and proper disposal of waste and samples.]

16 References

[This section lists references for source documents and publications that contain ancillary information.]

17 Tables, Diagrams, Forms, Flowcharts and Validation Data

[This section contains all the method, tables, figures, diagrams, example forms for data recording and flowcharts. This section may also contain validation data referenced in the body of the method.]

Appendix E: Validation Report Template

Microsoft© Word

This template is to be used to prepare final validation study reports for ATPs. The template sets up the primary validation study report sections along with brief instructions for each section. The template is prepared using an Adobe®-supported font for proper .pdf conversion. Please do not make any changes to fonts or styles. The following section numbering scheme is typical with the EMMC format.

If the alternate test method demonstrates equivalency to an approved method, EPA may subsequently approve the method for compliance monitoring through either conventional notice-and-comment rulemaking or through the expedited methods approval process. In either case, this validation report will be incorporated in the public docket associated with the approval action.

If typing the validation study report directly into the template, replace the text of the template and begin typing the report (that is, select the Title section and replace it with the method title). This page of instructions can be deleted upon completion of the validation study report.

Insert graphics within the text in TIFF, JPEG or Microsoft© Office compatible file format (*.wmf or *.emf).

Save the file with the graphics in place as a document file (.doc).

Alternate Test Procedure (ATP) Validation Study Report

Title

[The title should clearly and concisely specify the name of the method, the scope of the measurement (for example, “measurement of turbidity”, “nitrate analysis”, etc.) and the instrumentation (if applicable). The title should also include a shortened method name or number to use in the regulation and for reference]

Date

Name and address of organization

Author name(s)

[Include individual(s) with responsibility for overseeing development of the alternate test method and verifying accuracy of the data presented in the validation study report. Designate the appropriate point of contact in the event questions arise after review of the report.]

Phone number and email address

[Author or point of contact phone number and email address.]

1 Background

[Provide a method summary discussing the experimental technique.]

1.1 Method Justification

[Specifically cite the approved method that the candidate method is being compared to, the organization where the approved method originated (for example, ASTM, Standard Methods, EPA, etc.), and the method number. Summarize justification for the candidate method and describe the advantages relative to the approved method, especially in terms of improved sample throughput, reduction of hazardous waste, cost reduction, elimination of interferences, etc.]

1.2 Method Equivalency

[Summarize the quality control acceptance criteria as defined in the approved method and describe how the candidate method meets these specifications. Clearly indicate in the final sentence whether the candidate method is "equally effective" in meeting quality acceptance criteria as the approved method.]

1.3 Analytes

[Identify the analytes that are determined using the candidate method and list the corresponding Chemical Abstracts Service registry numbers.]

2 Study Implementation

[Clearly identify the managing organization responsible for development of the candidate method validation study plan and all of the laboratories participating in the study. Explain why specific laboratories were selected to participate and address any potential for conflict of interest.]

2.1 Study Schedule

[Delineate the study schedule.]

2.2 Sample Collection

[Describe how samples were collected and handled. Specify whether required holding times were met.]

2.3 Types of Analyses Performed

[Describe the number and types of analyses performed by each laboratory (for example, specify how many replicate analytical runs were performed to evaluate precision and accuracy in each drinking water matrix, incorporation of blanks, etc.]

2.4 Study Plan Deviations

[Fully describe any problems encountered or deviations from the study plan and the resolution or impact of these issues on the study plan performance results.]

3 Method Procedure and Data

[The candidate method should be prepared in standard EPA EMMC-method format and submitted with the initial validation study plan. In this final validation report, the method should be attached as an addendum and referenced as such in this section. Compare and contrast procedural differences between the candidate method and the approved method.]

3.1 Validation Study Demonstration Data

[Submit complete demonstration data for both reagent water and drinking water matrix analyses in tables, graphs or figures, as appropriate. The data should clearly present the candidate method data in comparison with the required reference method quality control criteria. Address the items in the following subsections, as appropriate.]

3.1.1 Calibration

[Demonstrate acceptable calibration performance as defined in the validation study plan. Include calibration verification through incorporation of calibration checks.]

3.1.2 Initial Demonstration of Capability

[Demonstrate acceptable low system background, precision and accuracy and detection limit or minimum reporting level confirmation (as specified in the validation study plan).]

3.1.3 Quality Controls

[Include verification of method performance using blanks, fortified blanks, matrix spikes, and other quality controls as specified in the validation study plan.]

3.1.4 Precision and Accuracy

[Include all precision and accuracy data for reagent water and drinking water matrix samples.]

3.2 Holding Time or Storage Stability

[If specified in the validation study plan, submit storage stability data. Otherwise, indicate that a holding time study was not required.]

4 Data Analysis and Discussion

[Provide a comparison of the candidate method data to the approved method to confirm equivalency of performance. Discuss in detail any discrepancies between the results and quality control acceptance criteria. Discuss method ruggedness based on overall performance as specified in the validation study plan (for example, multi-laboratory studies, analyses performed on multiple instruments, assessments of various drinking water matrices, etc.)]

5 Conclusions

[Discuss achievement of validation study objectives.]

Validation Report Appendix A: Validation Study Plan

[Append the approved validation study plan.]

Validation Report Appendix B: Supporting Data

Raw Data

[Submit raw data in an excel spreadsheet. Identify instruments used and operating conditions, detectors, and separation procedures.]

Example Calculations

[Provide sample calculations to verify that the laboratory has used the raw data to correctly arrive at the final results.]

Validation Report Data Collection Certification

It is the expectation of the ATP program that all data will be collected as outlined in the validation study plan. Applicants must attest on the application that the data collection was performed as outlined in the validation study plan.

The applicant hereby certifies that the data included with this application were collected as outlined in the validation study plan.

_____

Applicant (print name)

_____

Applicant (signature) and (Date)

[Questions, comments, or applications should be directed to:

William A. Adams, PhD.

U.S. EPA, OGWDW, TSC

26 W. Martin Luther King Dr. Cincinnati, OH 45268

Phone: (513) 569-7656

adams.william@epa.gov

Appendix F: Calculating Theoretical Detection Limits for Radiochemical Measurements (6)

1 Definition of the Detection Limit for the Safe Drinking Water Act Radiochemical Measurements

The detection capability of radiochemical measurements used for the Safe Drinking Water Act drinking water compliance monitoring is specifically defined at 40 CFR part 141.25(c) as a DL. It further defines a DL with the following conditions:

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

The Safe Drinking Water Act DL according to this definition differs from other "detection limits," such as the method detection limit or DL, (defined in 40 CFR part 136, Appendix B) and the minimum detectable activity or Minimum Detectable Activity, which is commonly used by radiochemists. Required DLs for the Safe Drinking Water Act drinking water compliance monitoring for radioactivity concentrations are expressed in terms of the definition given in 40 CFR 141.25(c).

For measurements involving simple nuclear counting with Poisson counting statistics, the procedure given in Section 2.0 below may be used to obtain a preliminary estimate of the Safe Drinking Water Act DL.

Note: Many radiochemical measurements involve simple Poisson counting. However, since it is possible that a submitted candidate method may involve measurement techniques with different statistics (for example, gamma-ray spectrometry), laboratories should contact EPA before submitting their study plan to determine if the equations in this appendix may be used to calculate the DL for the candidate method they wish to propose for approval.

2 Simple Poisson Counting

The definition of the Safe Drinking Water Act DL may be expressed mathematically as follows:

$$R_{DL} = 1.96 \times \sigma_{DL} \quad (11)$$

Where:

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

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

$$R_{DL} = R_G - R_B \quad (12)$$

Where:

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

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

$$R_G = \frac{C_G}{t_G} \quad \text{and} \quad R_B = \frac{C_B}{t_B} \tag{13}$$

Where:

R_G is the mean gross count rate for a sample (with concentration at the DL).
R_B is the mean background count rate for a sample measurement.
C_G is the mean total (gross) sample count.
C_B is the mean total background count.
t_G is the time of the measurement used to accumulate the sample count.
t_B is the time of the measurement used to accumulate the background count.

The standard deviation of a count rate is inversely proportional to the square root of the mean of a measurement. Assuming Poisson counting statistics, the standard deviation of *R*G and *R*B are given by:

$$\sigma_G = \frac{\sqrt{C_G}}{t_G} = \sqrt{\frac{R_G}{t_G}} \quad \text{and} \quad \sigma_B = \frac{\sqrt{C_B}}{t_B} = \sqrt{\frac{R_B}{t_B}} \tag{14}$$

Where:

σ_G is the standard deviation of the gross count rate.
σ_B is the standard deviation of the background count rate.

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

$$\sigma_{DL} = \sqrt{\sigma_G^2 + \sigma_B^2} \tag{15}$$

Where:

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

Combine equation 14 and 15.

$$\sigma_{DL} = \sqrt{\frac{R_G}{t_G} + \frac{R_B}{t_B}} \tag{16}$$

When this expression for σ_{DL} is substituted into equation 11.

$$R_{DL} = 1.96 \times \sqrt{\frac{R_G}{t_G} + \frac{R_B}{t_B}} \tag{17}$$

Equation 12 may now be used to eliminate the variable R_G from the equation. Since $R_G = R_{DL} + R_B$, equation 17 may be rewritten as:

$$R_{DL} = 1.96 \times \sqrt{\frac{R_{DL} + R_B}{t_G} + \frac{R_B}{t_B}} \tag{18}$$

Equation 18 may now be solved algebraically for the value of R_{DL}. First rewrite the radicand.

$$R_{DL} = 1.96 \times \sqrt{\frac{R_{DL}}{t_G} + R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)} \tag{19}$$

Square each side of the equation.

$$R_{DL}^2 = \frac{1.96^2}{t_G} \times R_{DL} + 1.96^2 R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right) \tag{20}$$

Collect all terms on the left-hand side to put the equation in standard quadratic form.

$$R_{DL}^2 - \frac{1.96^2}{t_G} \times R_{DL} - 1.96^2 R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right) = 0 \tag{21}$$

The quadratic formula gives two solutions to equation 21, one of which is positive and one of which is negative. The positive solution is required, and it is given by the following equation.

$$R_{DL} = \frac{1.96^2}{2t_G} \times \left[1 + \sqrt{1 + \frac{4t_G^2}{1.96^2} \times R_B \times \left(\frac{1}{t_G} + \frac{1}{t_B}\right)}\right] \tag{22}$$

Equation (22) provides a reasonable estimate of the count rate at the DL for the net activity that is based on counting statistics alone. This count rate should then be divided by the product of the experimental factors, *H*, which can include the following items: the method of detection's counting efficiency, the sample volume, gravimetric or tracer recoveries, conversion factors to picocuries, etc. The result can be

used to derive a specific DL of the radioanalyte of interest for a radiochemical method of analysis that is used for the Safe Drinking Water Act compliance monitoring.

$$DL = \frac{R_{DL}}{H} \tag{23}$$

Where:

H is the product of the experimental factors.
DL is the Safe Drinking Water Act Detection Limit.

This DL is equivalent to the DL specified in 40 CFR part 141.25(c). It is expected that the experimental factors will vary with each specific method.

Appendix G: Procedure for Preparing the Radiochemistry ATP Drinking Water Test Matrix

1 Purpose and Scope

This standard operating procedure details the requirements for the preparation of the Test Matrix for use in performing tests associated with the development of candidate radiochemistry methods for application as an EPA ATP for Radiochemistry.

The Test Matrix applies only for use in developing Radiochemistry ATPs and should not be used as a basis for assessment of other drinking water procedures.

2 Summary of Method

Prescribed salt solutions are added to deionized water conforming to ASTM Type I or II requirements. The prepared Test Matrix is allowed to equilibrate for at least 16 hours. The result is a 1 L sample of approximately 350 ppm of total dissolved solids.

The Test Matrix is spiked as needed for the applicant's tests and acidified based on the radioanalyte of interest per the requirements for sampling preservation cited in *The Manual for the Certification of Laboratories Analyzing Drinking Water* (5).

3 Health and Safety Warnings

Laboratory safety procedures for handling reagents and chemicals are to be followed.

4 Definitions

None

5 Equipment and Supplies

- 1-L and 4-L containers to meet sample container requirements for specified drinking water analysis, glass or plastic.
- Top loading balance, maximum allowed mass at least 10,000 grams readability to 0.01 g (10 mg).
- ASTM Class 2 or equivalent calibration weight set with masses of 1, 2, 5, 10, 20 and 50 g.
- Pipette – volumetric, to deliver, 1 mL and 4 mL.
- Spatula.
- Stir plate – magnetic.
- Stir bar – 40 mm magnetic.
- 250 mL volumetric flask, glass or plastic, to contain, Class A.
- Weighing dish, polystyrene, minimal 40 x 40 x 8 mm.

6 Reagents

All reagents used are to be American Chemical Society grade or better.

Note: The following reagents may be substituted with equivalent salts of varying hydrated state. By example: Barium chloride anhydrous may be substituted for barium chloride dihydrate, provided the proper conversion has been made to adjust the water content of the salt for the elements of interest. The determined ppm content of each of the salts is presented in Table 3 (see Section 15).

Caution: ONLY the hydration state of the salts may be varied.

- Aluminum Chloride Hexahydrate – American Chemical Society Grade.
- Barium Chloride Dihydrate – American Chemical Society Grade.
- Calcium Nitrate Tetrahydrate – American Chemical Society Grade.
- Iron (III) Chloride – American Chemical Society Grade.
- Magnesium Sulfate Heptahydrate – American Chemical Society Grade.
- Potassium Chloride – American Chemical Society Grade.
- Sodium Phosphate Dibasic – American Chemical Society Grade.
- Sodium Bicarbonate – American Chemical Society Grade.
- Sodium Sulfate, Anhydrous – American Chemical Society Grade.
- Reagent Water – ASTM Type I or Type II.

7 Interferences

None

8 Calibrations

Ensure balance is calibrated and that daily or monthly performance checks are performed as required by the lab's standard operating procedures using acceptable weights for the masses to be measured (1 – 25 g).

9 Sample Handling and Preservation

Once prepared let the solution stand for at least 16 hours prior to filtration. The solution is not to be preserved until it has been spiked.

10 Procedure

a. Prepare each of the following stock standard reagents separately using reagent water and a 250 mL TC volumetric flask.

Note: The masses identified should be adhered to as closely as practical with no more than 10% variance in the mass of the salt added. Therefore, a 1.0 g addition may be allowed in tolerance from 0.9 to 1.1 g. The determined total dissolved solids of the solution and the concentration of the contaminant will change accordingly. All weights used are to be documented.

i. Aluminum Chloride Hexahydrate 4 mg/mL: Dissolve 1.0 g of $AlCl_3 \cdot 6H_2O$, dilute to 250 mL with reagent water.
ii. Barium Chloride Dihydrate 4 mg/mL: Dissolve 1.0 g of $BaCl_2 \cdot 2H_2O$, dilute to 250 mL with reagent water.
iii. Calcium Nitrate Tetrahydrate, 40 mg/mL: Dissolve 10 g of $Ca(NO_3)_2 \cdot 4H_2O$, dilute to 250 mL with reagent water.
iv. Iron (III) Chloride, 4 mg/mL: Dissolve 1.0 g of $FeCl_3$, dilute to 250 mL with water.
v. Magnesium Sulfate Heptahydrate, 100.0 mg/mL: Dissolve 25 g of $MgSO_4 \cdot 7H_2O$, dilute to 250 mL with reagent water.
vi. Potassium Chloride, 60 mg/mL: Dissolve 15 g of KCl, dilute to 250 mL with reagent water.
vii. Sodium Bicarbonate 80 mg/mL: Dissolve 20 g of $NaHCO_3$, dilute to 250 mL with reagent water.
viii. Sodium Phosphate Dibasic Anhydrous, 14 mg/mL: Dissolve 3.5 g of Na_2HPO_4, dilute to 250 mL with reagent water.
ix. Sodium Sulfate Anhydrous, 60 mg/mL: Dissolve 15 g of $NaSO_4$, dilute to 250 mL with reagent water.

b. To constitute 1 L of test matrix, add 1 mL of each reagent to a 1 L glass or plastic TC volumetric flask and dilute with reagent water to 1 Liter, swirling or stirring to mix.

c. To constitute 4 L of test matrix, add 4 mL of each reagent to a 4 L glass or plastic TC volumetric flask and dilute with reagent water to 4 Liters, swirling or stirring to mix.
d. Transfer to an appropriate glass or plastic container with label for storage.
e. Allow solution to stand for at least 16 hours, then filter.
f. Determine the Total Dissolved Solids of the sample using an appropriate procedure.
g. Record the results of the Total Dissolved Solids analysis for submittal with the ATP application package.
h. Spike the Test Matrix with a known concentration of the radioisotope of interest as required based on proposed ATP protocol. Swirl to mix.
i. Record the date, time and spike isotope(s) and level(s).
j. Preserve the Test Matrix with acid as required based on proposed ATP requirements. Test and adjust the pH of the Test Matrix to ensure that it meets drinking water sample requirements of less than 2.0. Swirl to mix.
k. Record the preservative used, concentration, amount added and pH of the Test Matrix.
l. Allow the Test Matrix to stand for at least 16 hours prior to sample analysis.

11 Data Acquisitions, Calculations and Data Reduction Requirements

All required recorded results of the preparation of the Test Matrix solution are to be reviewed and submitted with the ATP application package.

12 Quality Control

Quality control is to be maintained in accordance with testing laboratory's quality assurance project plan. Test Matrix Total Dissolved Solids should be within ±20 ppm of the target value of 300 ppm.

13 Waste Management and Pollution Prevention

The Test Matrix in an unspiked and unpreserved state contains no materials that are considered wastes of a regulatory concern for disposal.

Spiked or spiked and preserved Test Matrix solutions and Stock Standard Solutions are to be disposed of in accordance with the testing laboratory's procedures and State regulatory requirements.

14 Records Management

All records are to be reviewed and approved in accordance with laboratory approved procedures and the laboratory's quality assurance project plan.

Copies of the records developed in the preparation and quality control of the Test Matrix are to be provided with the records for supplied to EPA for the ATP application.

15 Forms, Attachments, Flow Charts

Table 3. Test Matrix Solution Composition Chart

Chemical Compound Utilized	**Analyte of Interest**	**Analyte to Compound Mass Ratio**	**Mass Added of Compound in grams**	**ppm of Chemical Compound Utilized in Test Matrix**	**ppm of Analyte in Test Matrix[1]**
Aluminum Chloride Hexahydrate	Aluminum	0.11	1	4.00	0.45
Aluminum Chloride Hexahydrate	Chloride	0.44	1	Not applicable	1.76
Barium Chloride Dihydrate	Barium	0.56	1	4.00	2.25
Barium Chloride Dihydrate	Chloride	0.17	1	Not applicable	0.68
Calcium Nitrate Tetrahydrate	Calcium	0.17	10	40.00	6.79
Calcium Nitrate Tetrahydrate	Nitrate	0.53	10	Not applicable	21.03
Disodium Phosphate Anhydrous	Sodium	0.32	3.5	Not applicable	4.53
Disodium Phosphate Anhydrous	Ortho Phosphate	0.67	3.5	14.00	9.37
Iron (III) Chloride	Iron	0.34	1	4.00	1.38
Iron (III) Chloride	Chloride	0.66	1	Not applicable	2.62
Magnesium Sulfate Heptahydrate	Magnesium	0.10	25	100.00	9.86
Magnesium Sulfate Heptahydrate	Sulfate	0.39	25	Not applicable	38.97
Potassium Chloride	Potassium	0.52	15	60.00	31.47
Potassium Chloride	Chloride	0.48	15	Not applicable	28.52
Sodium Bicarbonate	Sodium	0.27	20	Not applicable	21.89
Sodium Bicarbonate	Carbonate	0.71	20	80.00	57.14
Sodium Sulfate Anhydrous	Sodium	0.32	15	60.00	19.42

Sodium Sulfate Anhydrous	Sulfate	0.68	15	Not applicable	40.58

[1] Total Dissolved Solids is 298.70.

16 References

40 CFR 141 National Primary Drinking Water Regulations Protocol for the Approval of ATPs for Radiochemical Analytes

ASTM D1193-99e1; Standard Specifications for Reagent Water; American Society for Testing and Materials, March 1999 with editorial change made in October 2001

The Manual for the Certification of Laboratories Analyzing Drinking Water (EPA 815-R-05-004) http://water.epa.gov/scitech/drinkingwater/labcert/methods_index.cfm.

Appendix H: Sample Calculations

The following section provides examples in performing the necessary calculations for the determination of sample data to meet the acceptance criteria established for the method.

1 Example – Experimental Detection Limit Study

The instructions for performing the calculation in an experimental DL study are given in App. C, Sect. 6.1. The following example illustrates how the evaluation criteria should be applied.

Suppose three laboratories participate in the DL study and that 21 artificially spiked samples at the same concentration (μ) are analyzed, seven per laboratory, as suggested in App. C, Sect. 4.2.3 (These are the minimum numbers of laboratories and samples permitted.). Assume that the required DL is 2.5 pCi/L and the 21 samples are spiked at 2.5 pCi/L. Then:

m = 3.
n = 7.
μ = 2.5 pCi/L.

In Table 4 the analysis results for the DL study from the three laboratories have been compiled and the mean results determined.

Table 4. Example Detection Limit Study Results Spiked at 2.5 pCi/L

Lab (*i*)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	$\overline{X}_i$
1	1.06	3.04	1.63	2.97	1.90	3.62	2.49	2.3871
2	1.77	0.419	2.22	2.65	0.878	5.93	3.03	2.4139
3	2.37	-1.12	2.56	2.12	2.35	2.08	2.71	1.8671

Sample (*j*) Results in pCi/L

The last column in the table shows the arithmetic mean of the seven results for each of the three laboratories, which is calculated using equation (3). For example, the arithmetic mean for the first laboratory is:

$$\bar{X}_1 = \frac{1}{7}\sum_{j=1}^{7} X_{1j} = \frac{1.06 + 3.04 + 1.63 + 2.97 + 1.90 + 3.62 + 2.49}{7} = \frac{16.71}{7} = 2.3871 \qquad (24)$$

Similar calculations are performed for the other two rows of the table.

After the three means are calculated a chi-square statistic is calculated for each laboratory using the second part of equation three, as shown below.

$$\bar{\chi}_1^2 = \frac{1.96^2}{2.5^2}\sum_{j=1}^{7}(X_{1j} - 2.3781)^2 = 2.9924 \qquad (25)$$

$$\bar{\chi}_2^2 = \frac{1.96^2}{2.5^2}\sum_{j=1}^{7}(X_{2j} - 2.4139)^2 = 12.0406 \quad (26)$$

$$\bar{\chi}_3^2 = \frac{1.96^2}{2.5^2}\sum_{j=1}^{7}(X_{3j} - 1.8671)^2 = 6.5822 \quad (27)$$

Each of the individual chi-square statistics is presumed to have the χ^2 distribution with six degrees of freedom.

Next equation (4) is used to calculate the overall chi-square statistic.

$$\chi^2 = \sum_{i=1}^{3}\chi_i^2 = 2.9924 + 12.0406 + 6.5822 = 21.6151 \quad (28)$$

This statistic has 18 degrees of freedom (three times six). So, the critical value for the statistic is the 99th percentile of the χ^2-distribution with 18 degrees of freedom, which equals 34.81. Since the calculated value of 21.6151 does not exceed 34.81, the method passes the experimental DL study.

2 Example – Method Performance Assessment Study

2.1 Bias

The instructions for performing the Method Performance Assessment study are given in App. C, Sect. 5. The evaluation criteria for the results are described in App. C, Sect. 6.2 through App. C, Sect. 6.4. The following example illustrates how the evaluation criteria should be applied.

Suppose that a method for the determination of Cesium-137 is being evaluated. For the method performance study, three laboratories each analyze seven replicates at four different matrix and spike level combinations, as listed below:

1) Reagent water, spiked at the Maximum Contaminant Level.
2) The test matrix, spiked at the Maximum Contaminant Level.
3) The test matrix, spiked at ½ the Maximum Contaminant Level.
4) The test matrix, spiked at 2 times the Maximum Contaminant Level.

The following example reflects the first set of data, reagent water spiked at the Maximum Contaminant Level. For Cesium-137, the Maximum Contaminant Level is 200 pCi/L. Therefore, 21 artificially spiked samples at 200 pCi/L of Cesium-137 are analyzed, seven per laboratory, as suggested in App. C, Sect. 5. (These are the minimum numbers of laboratories and samples permitted.). Therefore, m = 3, n = 7, μ = 200 pCi/L.

From Table 2 (Section 4.6.2), σ_{NELAC} equals 1.5185 + (0.0347 * 200) = 8.46 pCi/L.

Table 5 shows the analysis results of the method performance assessment study for the reagent water samples spiked at the Maximum Contaminant Level, including the mean and standard deviation determined for each laboratory.

Table 5. Example Method Performance Assessment Study Results Spiked at 200 pCi/L

Lab (*i*)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	$\overline{X}_i$	**si**
1	188.80	203.00	204.22	202.55	200.13	220.62	203.19	203.2160	9.3233
2	180.85	201.05	177.59	191.61	202.28	192.29	198.92	192.0841	9.7281
3	203.47	195.37	182.03	193.51	191.07	210.22	173.07	192.6760	12.4678

Sample (*j*) Results in pCi/L

The pooled within-laboratory standard deviation, s_w, is calculated as:

$$s_w = \sqrt{\frac{1}{3}(9.3233^2 + 9.7281^2 + 12.4678^2)} = \sqrt{112.3360} = 10.5989 \quad (29)$$

The grand mean, $\bar{\bar{X}}$, equals.

$$\bar{\bar{X}} = \frac{1}{3}(203.2160 + 192.0841 + 192.6760) = 195.9921 \quad (30)$$

The between-laboratory standard deviation, s_b is then calculated as:

$$s_b = \sqrt{\frac{1}{2} \times [(203.2160 - 195.9921)^2 + (192.0841 - 195.9921)^2 + (192.6760 - 195.9921)^2] - \frac{10.5989^2}{7}} = 4.8145 \quad (31)$$

The ratio of between-laboratory to within-laboratory standard deviation, then equals:

$$r = \frac{4.8145}{10.5989} = 0.4542 \quad (32)$$

The combined standard deviation equals.

$$\sigma_c = 8.46 \times \sqrt{\frac{0.4542^2 + \frac{1}{7}}{0.4542^2 + 1}} = 4.5509 \quad (33)$$

acceptance limits are calculated as:

$$200 \pm \frac{4.5509 \times 2.58}{\sqrt{3}} = 200 \pm \frac{11.7412}{1.7321} = 200 \pm 6.7788 = 193.22 \leftrightarrow 206.78 \quad (34)$$

Therefore, the grand mean, X, should fall between 193.22 and 206.78. Because the grand mean,

195.99 pCi/L falls between the lower acceptance limit, 193.22 and the higher acceptance limit, 206.78, the average concentration at the Maximum Contaminant Level for this method is acceptable.

2.2 Precision

The χ^2 statistic for total precision is calculated below:

$$\chi^2 = \frac{1}{\sigma^2_{NELAC}} \sum_{i=1}^{3} \sum_{j=1}^{7} \left(X_{ij} - \bar{\bar{X}}\right)^2 = \frac{1}{8.46^2} \sum_{i=1}^{3} \sum_{j=1}^{7} \left(X_{ij} - 195.9921\right)^2 = 35.94 \quad (35)$$

Because 35.94 is less than the 99th percentile of the chi-square distribution with 20 degrees of freedom (37.57), the precision for this method at the Maximum Contaminant Level is acceptable.

Because both the bias and precision passed for the reagent water samples spiked at the Maximum Contaminant Level, separate analyses would then be performed in the test matrix, with each sample spiked at the Maximum Contaminant Level, ½*Maximum Contaminant Level and 2*Maximum Contaminant Level. The bias and precision at each of these concentrations would then be assessed and if both tests pass at each spike level, the method would pass the method performance assessment study.