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

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FOREWORD

Within the U.S. Environmental Protection Agency (EPA), the Office of Water (OW) publishes test methods (analytical methods) for the analysis of drinking water. Listed at part 141 of Title 40 in the *Code of Federal Regulations* (CFR), these methods are authorized for use in data gathering and environmental monitoring under the Safe Drinking Water Act (SDWA). These methods have been developed by EPA, by consensus standards organizations and by others to satisfy the data quality mandates of the SDWA.

This document gives specific information to external organizations regarding the submission, validation and EPA evaluation of modifications or changes to an existing procedure or a new method for the measurement of radioactive contaminants in drinking water, herein called alternate test procedures (ATPs). EPA anticipates that the standardized procedures described herein should encourage the development of innovative technologies, expedite the evaluation of ATPs and enhance the overall utility of the EPA-approved methods for compliance monitoring under the National Primary Drinking Water Regulations (NPDWRs).

DISCLAIMER

The Office of Ground Water and Drinking Water (OGWDW) has reviewed and approved this document for publication. The Office of Ground Water and Drinking Water, with the assistance of NAREL, directed, managed and reviewed the work of CSC in preparing this report. Neither the U.S. government nor any of its employees, contractors, or their employees make any warranty, expressed or implied, or assumes any legal responsibility for any third party's use of, or the results of such use, of any information, apparatus, product, or process discussed in this protocol. The mention of company names, trade names, or commercial products does not constitute an endorsement or recommendation for use.

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.

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1.0 INTRODUCTION

1.1 Background and Objectives

Pursuant to the Safe Drinking Water Act (SDWA), the U.S. Environmental Protection Agency (EPA) promulgates test procedures (analytical methods) for data gathering and compliance monitoring under National Primary Drinking Water Regulations (NPDWRs).

Under the Agency's 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 methods will be referred to as "candidate" test methods through the remainder of this document. The organization or entity seeking the evaluation is responsible for validating the candidate test method.

EPA evaluates test methods used to measure regulated contaminants in drinking water for nationwide approval. This requires EPA to assess any candidate test 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 test method must be equally as effective as the approved method (see SDWA §1401(1)); i.e., 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 SDWA are comparable on a nationwide basis. For those methods that demonstrate acceptable performance through their ATP evaluation, EPA will initiate an appropriate approval action.

1.2 Scope and Application

The protocol design described in this document is consistent with candidate test 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 three ways: 1) the types of detection systems used are different, 2) the chemical yields for sample preparation steps are generally measured and corrected for and 3) the detection limits 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.

2.0 OVERVIEW OF THE ATP PROCESS

Agency staff reviews the application, including justification for the ATP provided by the applicant and determines whether an ATP evaluation is warranted. If the application is accepted for ATP consideration, the applicant then develops a validation study plan in consultation with ATP staff. Once the study plan is approved, the applicant performs the validation study and submits a validation study report to the ATP program. If EPA determines that the laboratory validation demonstrates performance equivalent to or better than that obtained with an approved method, EPA will generally recommend approval 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 at: http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_expedited.cfm.

2.1 Submission (initial application and subsequent documentation)

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

2.2 Application Information

Information required on the ATP application includes: the name and address of the applicant; the date of submission of the application; the title of the proposed candidate method; 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 in order for the application to be considered complete.

2.2.1 Justification for ATP

The applicant should provide a brief justification for why the ATP is being proposed. Because EPA review and evaluation of proposed ATPs can entail considerable effort, EPA strives to minimize the submission of impractical methods or method modifications that fall within the scope of flexible options 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 you submit information with the proposed ATP application, you may, if you desire, assert a business confidentiality claim covering part or all of the information. The method for submitting a claim is described in the regulations 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 methods to be proposed for approval in the *Federal Register* cannot themselves be claimed as confidential business information.

If a claim of business confidentiality is received after the information itself is received, 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 in light of the possibility of prior disclosure or widespread prior dissemination of the information, See §2.203(c).

3.0 METHOD DEVELOPMENT AND VALIDATION STUDY PLAN

Method development and validation is the process 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, i.e., yields acceptable method performance and data quality over the range of drinking water sample types and over the range of laboratory conditions specified in the method. In order to produce a method that is rugged and meets QC 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.

Critical points of a method can take a variety of forms depending on the method. For example, certain methods may require extraction of an analyte at a specific pH or narrow pH range. Thus, for the method to be truly rugged, pH control (e.g., use of buffers) may be required to ensure that other samples, laboratory conditions, or chemists obtain satisfactory results using the method. For candidate methods intended to be used in the field, ambient temperature may be a critical factor affecting performance of the method. The applicant should examine and control such factors, or limit the conditions under which the method can be used. Other examples of critical steps requiring ruggedness demonstration are:

- Determination of the breakthrough volume in solid phase extraction
- Effect of laboratory temperature on a purge and trap method
- Determination of a critical solvent to sample ratio in liquid-liquid extraction.

Many methods have procedural options in certain steps, for example, a choice of two sample preservation agents. If more than one preservation option is specified in a candidate method, the applicant must demonstrate acceptable method performance using both preservation options. Similarly, if a candidate method specifies either of two different solid phase sorbents for extraction, the applicant must demonstrate acceptable performance using both sorbents.

Once an application has been accepted by the ATP program, the applicant should discuss their plans to address method ruggedness with ATP staff prior to formulating the validation study plan. Such consultation will help avoid both inadequate study plans (e.g., 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.

3.1 Validation Study Plan Elements

Prior to conducting the candidate method validation study, the applicant should prepare and submit a detailed study plan for EPA approval. The technical details for the validation study design are found in Section 4.0. The validation study plan should contain the elements described in Sections 3.2.1 through 3.2.5 of this document.

3.1.1 Background

The Background section of the validation study plan should do the following:

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

3.1.2 Study Management

The Study Management section of the validation study plan should do the following:

- Identify the organization responsible for managing the study
- Identify laboratories, facilities and other organizations that will participate in the study
- Delineate the study schedule following approval of the study plan

3.1.3 Technical Approach

The Technical Approach section of the validation study plan should do the following:

- 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

3.1.4 Data Reporting and Evaluation

The Data Reporting and Evaluation section of the validation study plan should explain the procedures that will be followed for reporting and validating study data and should address statistical analysis of study results.

3.1.5 Limitations

The Limitations section of the validation study plan should explain any limiting factors related to the scope of the study.

3.2 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.

4.0 METHOD VALIDATION STUDY

4.1 Introduction

Method validation is the process by which a method developer substantiates the performance of a candidate test method. Candidate test 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 be evaluated.

Recently, the NELAC Institute (TNI) published radiochemistry Performance Testing (PT) study acceptability criteria that are based on the results of past radiochemistry PT studies (Reference 2 in Section 8.0). These acceptability limits 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 test methods validated using the procedures detailed in this protocol on the current NELAC PT acceptability criteria. This approach will provide limits for performance characteristics that are representative of the current proficiency for all the test methods currently in use.

4.2 Candidate Radiochemistry Test Method Validation Study Design

The candidate test method validation study design described in this protocol is intended to provide sufficient data to determine the performance characteristics of candidate test 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 test method's performance in obtaining measurements for the test matrix and determine if the candidate test 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 D for definition and discussion of the SDWA detection limit) and the method performance study.

Because the RB and DL studies assess the candidate test 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 test 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 test method's intra-laboratory and inter-laboratory performance. Each study (RB, DL and method performance) is discussed in more detail in Section 4.4.

Under the validation study, the sample test matrix (as identified) should be analyzed at four different matrix/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/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 in **Table 2**.

Table 2. Types and Numbers of Samples Required for the Candidate Test Method Validation Study

Study	**Sample Type[1]**	**Number of Samples per Participating Laboratory**	**Total Number of Samples in a 3 Lab Study**
Reagent Blank	RB	6	18
Detection Limit[2]	DL	7	21
Study	**Sample Type[1]**	**Number of Samples per Participating Laboratory**	**Total Number of Samples in a 3 Lab Study**
Method performance	Reagent Water Fortified at MCL	7	21
	Test Matrix at MCL	7	21
	Test Matrix at ½ MCL	7	21
	Test Matrix at 2 x MCL	7	21
Totals		**41**	**123**

[1] RB = Reagent Blanks
DL = Replicates spiked at or below the target radioanalyte's required detection limit

[2] In some cases the DL study may not be needed if the DL test is passed (see Section 4.4 for details)

4.3 General Study

4.3.1 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 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 test method SOP, 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.

4.3.2 Validation Study Test Matrix

Finished drinking water matrices could potentially have levels of regulated and unregulated chemical and radioactive constituents (i.e. 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 Suppliers (PWSs) are approved for nationwide use, any method validation study for candidate test 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 single 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 C.

The applicant should provide EPA with documentation that the test matrix was preserved and stored according to the approved procedures for the candidate test 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.

4.3.3 Significant Figures, Rounding Data Results and Data Reporting Conventions

The value of a measurement result should: (1) be reported directly as obtained with appropriate units, (2) all values should be reported even if they are 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.

4.3.4 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 (ISO) 1995 (Reference 3 in Section 8.0). 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.

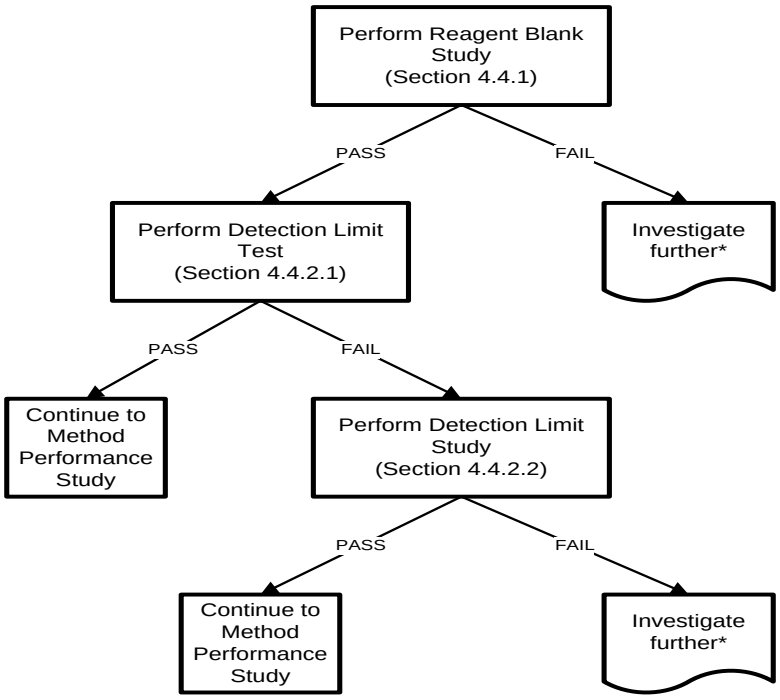
Additional information about the evaluation and expression of uncertainty can be found in National Institute of Standards and Technology (NIST) Technical Note 1297: *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (Reference 4 in Section 8.0) and the *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (Reference 5 in Section 8.0).

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 test method that is independent of matrix interferences. These data assess laboratory baseline proficiency with the candidate test method prior to assessing matrix interferences with a candidate test method performance study.

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

In some cases, applicants may only need to do the RB study and forgo the DL study if the candidate test method can successfully pass the DL test in Section 4.4.2.1.



*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.

4.4.1 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 test method can meet the required detection limit 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 test method's baseline performance as it is used by the participating laboratories. Each participating laboratory should use the candidate test 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 test method for routine sample analysis. They should be measured using the detection system specified in the candidate test method using the count times calculated as necessary for routine sample measurements in order to meet the required detection limits. 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 Detection Limit (RDL) for each radioactive contaminant measured using the candidate test 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 RDL, 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.

4.4.2 Detection Limit Test and Detection Limit Study

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

4.4.2.1 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 detection limits for radiochemical measurements see Appendix D. In this case, the calculated DL must not exceed the RDL. As an additional check, the results of the reagent blank analyses will be evaluated statistically to test whether the observed variability significantly exceeds the standard deviation expected at the RDL, as shown below.

Statistical Evaluation of the Reagent Blanks

Let $B_1, B_2, \ldots, B_n$ denote the results of all the reagent blank analyses (e.g., $n = 18$ if there are 3 labs and 6 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 test method should NOT be deemed to pass the DL test if $W > W_C$ and the applicant should conduct a detection limit study. If EPA determines that the data appear suspect (e.g., if all the blank results are exactly zero) the applicant may be requested to perform a DL study.

4.4.2.2 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 SDWA detection limit 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 D 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 RDL, an experimental DL study should be performed as described below. However, if the theoretical estimate of the DL exceeds the RDL, 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 (e.g., 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 II reagent water, at a minimum, using the sample volume prescribed in the method. The sample should be spiked with NIST traceable source(s) of the method

target radionuclide(s) to an activity concentration at or below their RDL. The sample should be mixed and then processed through sample preparation, processing and analysis per the candidate test method. The measurements of the DL study samples will then be assessed by calculating a precision statistic. See Section 4.6.1 for further information.

4.5 Method Performance Study

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

1) Reagent water, spiked at the MCL

2) The test matrix, spiked at the MCL

3) The test matrix, spiked at ½ the MCL

4) The test matrix, spiked at 2 times the MCL

The results of the bias and precision evaluations are subject to the criteria as described in Sections 4.6.3 and 4.6.4, respectively, at each matrix/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/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.

4.6 Acceptability Criteria for Radiochemical Study Results

TNI has published and maintained a table of radiochemical Performance Testing (PT) study acceptability criteria (http://www.nelac-institute.org/) (Reference 2 in Section 8.0). The calculations discussed in this section were developed to account for the presence of variability between multiple laboratories. The precision evaluation in Section 4.6.4 is based on the single-laboratory standard deviations (presented in **Table 3**) that were used to develop the National Environmental Laboratory Accreditation Conference (NELAC) PT 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.

4.6.1 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 RDL.

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

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

Where:

m	is the number of laboratories (3 or more).
n	is the number of replicate measurements (n = 7)
μ	is the spike concentration (not to exceed the RDL)
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:

$$\chi^2 = \sum_{i=1}^{m} \chi_i^2 \qquad (4)$$

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 E - Sample Calculations Section 1.0 for an example calculation.

4.6.2 Method Performance Study Criteria

Sections 4.6.3 and 4.6.4 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 TNI updates their PT 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 3. Means and Standard Deviations (from NELAC PT Criteria)

Analyte	Spike Level Range (µ*)	Standard Deviation (σ_{NELAC})
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*)	Standard Deviation (σ_{NELAC})
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

*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 Ba-133 and Cs-134:

Ba-133 – 50 pCi/L equivalent to slightly greater than 1/2 the MCL of Ba-140 (90 pCi/L)
Cs-134 – 40 pCi/L equivalent to 1/2 the actual determined MCL

4.6.3 Bias Evaluation for the Method Performance Study

In order to assess whether the average concentration of the replicates for a given spike level/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.

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

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

Where:

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

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

Where:

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

$\overline{\overline{X}}$ is the grand mean of the 21 results over all 3 laboratories

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

2) Calculate the ratio *r*:

$$r = \frac{s_b}{s_w} \qquad (7)$$

3) Using σ_{NELAC} (Table 3), calculate the acceptable combined standard deviation for the lab averages, σ_c,:

$$\sigma_c = \sigma_{NELAC} \times \sqrt{\frac{r^2 + \frac{1}{7}}{r^2 + 1}} \quad (\mathbf{8})$$

Please note that the appropriate value of σ_{NELAC} may differ for different spike levels.

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

$$\mu \pm \frac{\sigma_c \times 2.58}{\sqrt{3}} \quad (\mathbf{9})$$

Where:

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

Refer to Appendix E – Sample Calculations Section 2.1 for an example calculation.

4.6.4 Precision Evaluation for the Method Performance Study

Calculate a statistic for total precision using the equation below.

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

Where:

σ^2_{NELAC} is determined from Table 3

$\overline{\overline{X}}$ is the grand mean of the 21 tests over 3 laboratories for the given spike level/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 E – Sample Calculations Section 2.2 for an example calculation.

4.7 Acceptability Criteria for QC Tests

Candidate test method SOPs should reference Chapter VI, Critical Elements for Radiochemistry, in *The Manual for the Certification of Laboratories Analyzing Drinking Water* (EPA 815-R-05-004) for the required instrument stability checks and preparation batch QC samples, their frequencies and acceptability limits (Reference 6 in Section 8.0).

4.8 Validation Studies Review

After completing the validation studies of candidate test methods, the organization responsible for developing the method should document the study results and submit them to EPA. EPA will review the results and contact the responsible organization to answer any question or concerns raised based upon the provided results. If necessary, EPA may require further testing or clarification prior to the originator proceeding with final application.

5.0 FINAL APPLICATION

5.1 Introduction

After completion of the validation study, the applicant should submit a final application. The final application will be combined with the initial application materials to constitute the complete application. If the results of the validation study indicate that the candidate test method should be approved, EPA will generally pursue 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. Information about this process can be found at (http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_expedited.cfm). If based on its review of the method, EPA concludes that the method is not sufficiently rugged or reliable for its intended use, EPA may require further method development and further testing to define the stability and reliability of the method. The tests and studies that should be performed in this case are dependent upon the analyte(s) and the analytical system and will be determined on a case-by-case basis as these situations arise.

Section 5.2 describes the materials and information needed for the final application. Applications should be made in triplicate and should include a completed application form (provided in Appendix A of this document) with required attachments. All applications for EPA evaluation of radiochemistry candidate test methods to be used for the SDWA compliance monitoring should be sent along with all application materials to the following address:

Steven C. Wendelken, PhD.
U.S. EPA, OGWDW-TSC
26 W. Martin Luther King Dr.
ML 140
Cincinnati, Ohio 45219
Phone: (513) 569-7491
Fax: (513) 569-7837
wendelken.steve@epa.gov

5.2 Final Application and Supporting Materials

As shown in **Table 4**, the final application should include an application form filled out as described in Section 2.2.1 (but identified as a final application), the method validation study report, the raw study data and any additional pertinent method development information.

Table 4. Final Application

• Completed final application form • Data Certification Form • Validation study report including the raw study data • Method development information and documentation

5.2.1 Validation Study Report

Laboratories or other organizations responsible for developing new candidate radiochemical test methods for drinking water monitoring should document the results of the validation study in a formal validation study report that is organized and contains 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 candidate test method.

The information and supporting data required in the validation study report should be sufficient to enable EPA to evaluate the performance of a candidate test method. The applicant is responsible for ensuring that all method-specified requirements are met by the participating laboratories and that the validation study report contains all necessary data.

Like the validation study plan, the validation study report contains background information and describes the study design. In addition, the validation study report details the process and results of the study, provides an analysis and discussion of the results and presents study conclusions. The validation study plan should be appended to and referenced in the validation study report. The validation study report should identify and discuss any deviations from the study plan that were made. The validation study report should contain the elements described in sections 5.2.1.1 through 5.2.1.9.

5.2.1.1 Background. The Background section of the validation study report should describe the candidate test method that was validated and identify the organization responsible for developing the method. This Background section of the validation study report should:

- Include a method summary
- Describe the reasons for developing the candidate test method, the logic behind the technical approach to the candidate test method and the result of the candidate test method
- List the analytes measured by the method including corresponding CAS RN (if applicable)

- State the purpose of the study
- Cite any studies of the method or papers whose studies use data collected using the candidate test method that have been published in peer reviewed literature

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

- Identify the person or organization that was responsible for managing the study
- Identify the laboratories, facilities and other organizations that participated in the study
- Describe how participating laboratories were selected and explain the role of each organization involved in the study
- Include initial performance data from each of the participating laboratories using the candidate test method
- Delineate the study schedule that was followed
- Describe how the test matrix was prepared and how samples were distributed
- Specify the numbers and types of analyses performed by the participating laboratories
- Identify any problems encountered or deviations from the study plan and their resolution/impact on study performance and/or results

5.2.1.3 Data Reporting and Validation. This section of the validation study report should describe the procedures that were used to report and validate study data. EPA has not established a standard format for analytical data submission because of the large variety of formats currently in use.

5.2.1.4 Results. This section of the validation study report should present the study results in summary form. Raw data and example calculations are required to support the results and should be included in Appendix C to the validation study report (see Section 5.2.1.9).

5.2.1.5 Data Analysis/Discussion. This section of the validation study report should provide a statistical analysis and discussion of the study results. Discussions of the candidate test method's observed accuracy, precision and detection capability should be presented.

5.2.1.6 Conclusions. This section of the validation study report should describe 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).

5.2.1.7 Appendix A - The Method. Include a copy of the candidate test method SOP as Appendix A to verify no changes in the procedure occurred since its submission with the initial application. If any changes to the method occurred after its submission in the initial application (such as the result of unforeseen factors discovered during the method validation study) a track edits copy (in Microsoft Word or Excel format) along with a description of the changes and an explanation why they were necessary should be included. The updated SOP should also adhere to the standard EPA format or if the method is sponsored by another government agency or consensus standards organization, their preapproved required format.

5.2.1.8 Appendix B - Validation Study Plan. Attach a copy of the EPA approved validation study plan as Appendix B.

5.2.1.9 Appendix C - Supporting Data. The validation study report should be accompanied by raw data and example calculations that support the results presented in the report. These data and calculations should be included in the report as Appendix C.

5.2.1.9.1 Raw Data. This section of the validation study report should include raw data as generated (i.e., without rounding) that will allow an independent reviewer to verify each determination and calculation performed by the laboratory. EPA will perform a detailed audit of the candidate test method validation study data. The evaluation of data submitted in support of applications can be accomplished more quickly if machine-readable files of test data (spreadsheets) are provided. This data verification consists of tracing the instrument output (e.g., instrument background counting rates, gross sample counting rates, for spectrometric methods the peak height or area or other indicators of signal intensity) to the final result reported. The raw data are method specific and may include any of the following:

- Sample measurement operating conditions, including detailed information on:
  - Type of detector used
  - Sample count times
  - Volume of samples
- Spectrum printouts should be submitted for each sample (if the candidate test method collects spectra) with any library search result used to quantitate data from the spectrum
- Control charts and data from the instrument used to establish its stability with regard to calibration including background during the time period of the analyses
- Identification of any analyte-specific efficiency standards used or prepared for the ATP
- Sample numbers or other identifiers used by the both the regulated entity and the laboratory
- Sample preparation (precipitation/column separations) dates
- Analysis dates and times

- Sequence of analyses or run logs
- Quantitation reports, direct instrument readouts and/or data system outputs sufficient to allow a third party to regenerate/reconstruct the calculations.
- Laboratory bench sheets and copies of all pertinent logbook pages for all sample preparation, cleanup steps and for all other parts of the determination

Raw data should be provided for all samples, calibrations, verifications, blanks, matrix spikes and duplicates and other QC analyses required by the candidate test method. Data should be organized so that an analytical chemist can clearly understand how the analyses were performed. The names and titles of the analysts who performed the analyses and of the quality assurance officer who verified the analyses should be provided.

5.2.1.9.2 Example Calculations. The validation study report should provide example calculations that will allow the data reviewer to determine how the laboratory used the raw data to arrive at the final results. All formulas for sample activity concentration, uncertainty of the measurement and the detection limit calculation used to set the count times and volumes should be included in the Example Calculations section. Examples of other method specific calculations, such as those for assessing method detection efficiency or chemical recovery of a carrier or tracer, should also be included. All constants and variables used in the calculations should be specifically defined. An example calculation should have the general formula on the first line, sample specific data then included in the formula on the second line, then an appropriate number of lines demonstrating the mathematical simplification and derivation of the final result.

6.0 APPROVAL RECOMMENDATION

EPA will complete its review and notify the applicant of EPA's recommendation. If the candidate test method is recommended for approval, EPA will generally pursue 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 (http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_expedited.cfm).

7.0 QUALITY CONTROL

Laboratories measuring radiochemical compliance monitoring samples in support of the SDWA should follow the requirements found in Chapter VI, Critical Elements for Radiochemistry, in "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). Section 7.4 in Chapter VI of this manual requires laboratories to participate in at least one Performance Testing (PT) study per year for each regulated radioactive contaminant using a specific method for certification. Section 7.7 in the same chapter specifies QC tests and their acceptance criteria to assess sample preparation batch accuracy, precision, detection capability and interferences. Section 7.7 also requires instrument QC 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 QC data and order them by QC 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 QC requirements found in currently approved methods.

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

8.0 REFERENCES

1. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. 1996. Guidelines and Format for Methods to Be Proposed at 40 CFR Part 136 or Part 141 (Guidelines and Format document). Washington, D.C. EPA- 821-B-96-003.

2. TNI NELAC Radiochemistry PT Scoring Criteria http://www.nelac-institute.org/.

3. International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement*. Geneva, Switzerland.

4. National Institute of Standards and Technology (NIST). 1994. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*. Technical Note 1297. Available at the NIST Web site.

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

6. Chapter VI, Critical Elements for Radiochemistry, in "The Manual for the Certification of Laboratories Analyzing Drinking Water" (EPA/815-R-05-004). Copies of the Manual can be obtained at http://water.epa.gov/scitech/drinkingwater/labcert/methods_index.cfm.

APPENDIX A: APPLICATION FORM

EPA Office of Ground Water and Drinking water

Alternate Test Procedure Candidate Method Application

☐ **Initial Application** ☐ **Supplemental Documentation** ☐ **Final Application**

Applicant Name		**EPA use only**
Address		**Case No.**
	State	
	Zip Code	
Applicant Contact Information	**Contact Name**	
	Phone Number	
	E-mail address	
Submission date		

CANDIDATE METHOD:

Analyte(s)	
Candidate Test Method Title	
Reference Method Number/Name	

ATTACHMENTS:

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

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 was collected under the conditions outlined in the validation study plan.

_____

Applicant (print name)

_____ _____

Applicant (signature) **(Date)**

APPENDIX B: STANDARD EPA METHOD FORMAT

NOTE: Each method should be a free-standing document, providing all information necessary for the method user to perform the method. 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.

1.0 Scope and Application

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

2.0 Summary of Method

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

3.0 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.

4.0 Interferences

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

5.0 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.

6.0 Equipment and Supplies

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

7.0 Reagents and Standards

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

8.0 Sample Collection, Preservation and Storage

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

9.0 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 (QA) program and specific quality control (QC) 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" (Reference 6 in Section 8.0) for the required QC tests and the specific QC acceptance criteria for each of them.

10.0 Calibration and Standardization

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

11.0 Procedure

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

12.0 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. For more information please refer to Section 4.3.3 of this document.

13.0 Method Performance

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

14.0 Pollution Prevention

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

15.0 Waste Management

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

16.0 References

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

17.0 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 C: SOP FOR THE PREPARATION OF RADIOCHEMISTRY ATP DRINKING WATER TEST MATRIX

1.0 Purpose and Scope

This SOP 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.

2.0 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 liter 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 –Criteria and Procedures Quality Assurance – 5th Edition, EPA 815/R-05-004, January 2005 (Reference 16.4).

3.0 Health and Safety Warnings

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

4.0 Definitions

None

5.0 Equipment and Supplies

5.1 1-L and 4-L containers to meet sample container requirements for specified drinking water analysis, glass or plastic

5.2 Top loading balance, maximum allowed mass at least 10,000 grams readability to 0.01 grams (10 mg)

5.3 ASTM Class 2 or equivalent calibration weight set with masses of 1, 2, 5, 10, 20 and 50 grams

5.4 Pipette – volumetric, to deliver, 1 mL and 4 mL

5.5 Spatula

5.6 Stir plate – magnetic

5.7 Stir bar – 40 mm magnetic

5.8 250 mL volumetric flask, glass or plastic, to contain, Class A

5.9 Weighing dish, polystyrene, minimal 40 x 40 x 8 mm

6.0 Reagents

6.1 All reagents used are to be ACS 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 1** (see Section 15.1).

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

6.2 Aluminum Chloride Hexahydrate – ACS Grade

6.3 Barium Chloride Dihydrate – ACS Grade

6.4 Calcium Nitrate Tetrahydrate – ACS Grade

6.5 Iron (III) Chloride – ACS Grade

6.6 Magnesium Sulfate Heptahydrate – ACS Grade

6.7 Potassium Chloride – ACS Grade

6.8 Sodium Phosphate Dibasic – ACS Grade

6.9 Sodium Bicarbonate – ACS Grade

6.10 Sodium Sulfate, Anhydrous – ACS Grade

6.11 Reagent Water – ASTM Type I or Type II

7.0 Interferences

None

8.0 Calibrations

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

9.0 Sample Handling and Preservation

9.1 Once prepared let the solution stand for at least 16 hours prior to filtration.

9.2 The solution is not to be preserved until it has been spiked.

10.0 Procedure

10.1 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 gram addition may be allowed in tolerance from 0.9 to 1.1 grams. The determined total dissolved solids of the *solution* and

the concentration of the contaminant will change accordingly. All weights used are to be documented.

10.1.1 Aluminum Chloride Hexahydrate 4 mg/mL: Dissolve 1.0 g of $AlCl_3 \cdot 6H_2O$, dilute to 250 mL with reagent water

10.1.2 Barium Chloride Dihydrate 4 mg/mL: Dissolve 1.0 g of $BaCl_2 \cdot 2H_2O$, dilute to 250 mL with reagent water

10.1.3 Calcium Nitrate Tetrahydrate, 40 mg/mL: Dissolve 10 g of $Ca(NO_3)_2 \cdot 4H_2O$, dilute to 250 mL with reagent water

10.1.4 Iron (III) Chloride, 4 mg/mL: Dissolve 1.0 g of $FeCl_3$, dilute to 250 mL with water

10.1.5 Magnesium Sulfate Heptahydrate, 100.0 mg/mL: Dissolve 25 g of $MgSO_4 \cdot 7H_2O$, dilute to 250 mL with reagent water

10.1.6 Potassium Chloride, 60 mg/mL: Dissolve 15 g of KCl, dilute to 250 mL with reagent water

10.1.7 Sodium Bicarbonate 80 mg/mL: Dissolve 20 g of $NaHCO_3$, dilute to 250 mL with reagent water

10.1.8 Sodium Phosphate Dibasic Anhydrous, 14 mg/mL: Dissolve 3.5 g of Na_2HPO_4, dilute to 250 mL with reagent water

10.1.9 Sodium Sulfate Anhydrous, 60 mg/mL: Dissolve 15 g of $NaSO_4$, dilute to 250 mL with reagent water

10.2 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.

10.3 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.

10.4 Transfer to an appropriate glass or plastic container with label for storage.

10.5 Allow solution to stand for at least 16 hours, then filter.

10.6 Determine the Total Dissolved Solids (TDS) of the sample using an appropriate procedure.

10.7 Record the results of the TDS analysis for submittal with the Alternate Test Procedure application package.

10.8 Spike the Test Matrix with a known concentration of the radioisotope of interest as required based on proposed Alternate Test Method protocol. Swirl to mix.

10.9 Record the date, time and spike isotope(s) and level(s).

10.10 Preserve the Test Matrix with acid as required based on proposed Alternate Test Method 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.

10.11 Record the preservative used, concentration, amount added and pH of the Test Matrix.

10.12 Allow the Test Matrix to stand for at least 16 hours prior to sample analysis.

11.0 Data Acquisitions, Calculations and Data Reduction Requirements

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

12.0 Quality Control

12.1 Quality Control is to be maintained in accordance with testing laboratory's Quality Assurance Project Plan (QAPP).

12.2 Test Matrix TDS should be within ± 20 ppm of the target value of 300 ppm.

13.0 Waste Management and Pollution Prevention

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

13.2 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.

14.0 Records Management

14.1 All records are to be reviewed and approved in accordance with laboratory approved procedures and the laboratory's QAPP.

14.2 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 Alternate Test Procedure application.

15.0 Forms, Attachments, Flow Charts

Table 1. Test Matrix Solution Composition Chart

Chemical Compound Utilized (CU)	Analyte of Interest	Analyte to Compound Mass Ratio	Mass Added of Compound in grams	ppm of CU in Test Matrix	ppm of Analyte in Test Matrix
Aluminum Chloride Hexahydrate	Aluminum	0.11	1	4.00	0.45
Aluminum Chloride Hexahydrate	Chloride	0.44	1		1.76
Barium Chloride Dihydrate	Barium	0.56	1	4.00	2.25
Barium Chloride Dihydrate	Chloride	0.17	1		0.68
Calcium Nitrate Tetrahydrate	Calcium	0.17	10	40.00	6.79
Calcium Nitrate Tetrahydrate	Nitrate	0.53	10		21.03
Disodium Phosphate Anhydrous	Sodium	0.32	3.5		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		2.62
Magnesium Sulfate Heptahydrate	Magnesium	0.10	25	100.00	9.86
Magnesium Sulfate Heptahydrate	Sulfate	0.39	25		38.97
Potassium Chloride	Potassium	0.52	15	60.00	31.47
Potassium Chloride	Chloride	0.48	15		28.52
Sodium Bicarbonate	Sodium	0.27	20		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		40.58
		Total Dissolved Solids			298.70

16.0 References

16.1 40 CFR 141 National Primary Drinking Water Regulations

16.2 Protocol for the Approval of Alternate Test Procedures for Radiochemical Analytes

16.3 ASTM D1193-99$^{\epsilon 1}$; Standard Specifications for Reagent Water; American Society for Testing and Materials, March 1999 with editorial change made in October 2001

16.4 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 D: CALCULATING THEORETICAL DETECTION LIMITS FOR RADIOCHEMICAL MEASUREMENTS

1.0 Definition of the Detection Limit for the SDWA Radiochemical Measurements

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

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

The SDWA detection limit according to this definition differs from other "detection limits," such as the method detection limit or DL, (defined in 40 CFR part 136, Appendix B) and the minimum detectable activity or Minimum Detectable Activity (MDA), which is commonly used by radiochemists. Required detection limits (RDLs) for the SDWA 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 SDWA detection limit.

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 (e.g., 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 detection limit for the candidate method they wish to propose for approval.

2.0 Simple Poisson Counting

The definition of the SDWA detection limit may be expressed mathematically as follows:

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

Where:

R_{DL} is the mean net count rate for a sample with concentration at the detection limit

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

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

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

Where:

R_G is the mean gross count rate for a sample (with concentration at the detection limit)

R_B is the mean background count rate for a sample measurement

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 detection limit)

R_B is the mean background count rate for a sample measurement

C_G is the mean total (gross) sample count

C_B is the mean total background count

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

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

The standard deviation of a count rate is 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

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

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:

$$R_{DL} = 1.96 \times \sqrt{\frac{R_{DL} + R_B}{t_G} + \frac{R_B}{t_B}} \quad \textbf{(18)}$$

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

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

Square each side of the equation.

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

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

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

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.

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

Equation (22) provides a reasonable estimate of the count rate at the detection limit 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 Detection Limit (DL) of the radioanalyte of interest for a radiochemical method of analysis that is used for the SDWA compliance monitoring.

$$DL = \frac{R_{DL}}{H} \quad \textbf{(23)}$$

Where:

H is the product of the experimental factors

DL is the SDWA Detection Limit

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

APPENDIX E: 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.

1.0 Example - Experimental Detection Limit Study

The instructions for performing the calculation in an experimental detection limit (DL) study are given in Section 4.6.1. 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 Section 4.4.2.2. (These are the minimum numbers of laboratories and samples permitted.). Assume that the required detection limit is 2.5 pCi/L and the 21 samples are spiked at 2.5 pCi/L. Then

$m = 3$

$n = 7$

$\mu = 2.5$ pCi/L

In Table 5 the analysis results for the Detection Limit study from the three laboratories have been compiled and the mean results determined.

Table 5. Example Detection Limit Study Results Spiked at 2.5 pCi/L

Detection Limit Study Sample (*j*) Results in 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

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 in Section 4.6.1. For example, the arithmetic mean for the first laboratory is:

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

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 3, as shown below.

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

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

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

Each of the individual chi-square statistics is presumed to have the χ^2 distribution with 6 degrees of freedom.

Next equation 4 of Section 4.6.1 is used to calculate the overall chi-square statistic.

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

This statistic has 18 degrees of freedom (3 times 6). 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.

2.0 Example – Method Performance Assessment Study

2.1 Bias

The instructions for performing the Method Performance Assessment study are given in Section 4.5. The evaluation criteria for the results are described in Sections 4.6.2 through 4.6.4. 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/spike level combinations, as listed below:

1) Reagent water, spiked at the MCL

2) The test matrix, spiked at the MCL

3) The test matrix, spiked at ½ the MCL

4) The test matrix, spiked at 2 times the MCL

The following example reflects the first set of data, reagent water spiked at the MCL. For Cesium-137, the MCL is 200 pCi/L. Therefore, 21 artificially spiked samples at 200 pCi/L of Cesium-137 are analyzed, seven per laboratory, as suggested in Section 4.5. (These are the minimum numbers of laboratories and samples permitted.). Therefore, $m = 3$, $n = 7$, $\mu = 200$ pCi/L

From Table 3 (Section 4.6.2), σ_{NELAC} equals 1.5185 + (0.0347 * 200) = 8.46 pCi/L.

Table 6 shows the analysis results of the method performance assessment study for the reagent water samples spiked at the MCL, including the mean and standard deviation determined for each laboratory.

Table 6. Example Method Performance Assessment Study Results Spiked at 200 pCi/L

Method Performance Assessment Study									
	Sample (j) Results in pCi/L								
Lab (*i*)	1	2	3	4	5	6	7	$\overline{X}_i$	s_i
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

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

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

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

$$\overline{\overline{X}} = \frac{1}{3}\left(203.2160 + 192.0841 + 192.6760\right) = 195.9921 \quad (\mathbf{30})$$

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

$$s_b = \sqrt{\frac{1}{2} \text{x} \left[\left(203.2160 - 195.9921\right)^2 + \left(192.0841 - 195.9921\right)^2 + \left(192.6760 - 195.9921\right)^2\right] - \frac{10.5989^2}{7}}$$

$$= 4.8145 \quad (\mathbf{31})$$

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

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

The combined standard deviation equals.

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

Finally, upper and lower acceptance limits are calculated as:

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

Therefore, the grand mean, $\overline{\overline{X}}$, 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 MCL for this method is acceptable.

2.2 Precision

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

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

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 MCL is acceptable.

Because both the bias and precision passed for the reagent water samples spiked at the MCL, separate analyses would then be performed in the test matrix, with each sample spiked at the MCL, ½*MCL and 2*MCL. 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.

APPENDIX F: ABBREVIATIONS AND ACRONYMS

ACS	American Chemical Society
ASTM	ASTM International
ATP	Alternate Test Procedure
CAS RN	Chemical Abstract Services Registry Number
CFR	*Code of Federal Regulations*
CSC	Computer Sciences Corporation
CSU	Combined Standard Uncertainty
CU	Chemical Compound Utilized
DL	Detection Limit
EPA	U.S. Environmental Protection Agency
ISO	International Standards Organization
MARLAP	*Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MCL	Maximum Contaminant Level
MDA	Minimum Detectable Activity
NAREL	National Air and Radiation Environmental Laboratory
NELAC	National Environmental Laboratory Accreditation Conference
NIST	National Institute of Standards and Technology
NPDWRs	National Primary Drinking Water Regulations
NW	Northwest
OGWDW	Office of Ground Water and Drinking Water
OW	Office of Water
PDF	Portable Document Format
PT	Performance Testing
PWS	Public Water Supply
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RB	Reagent Blank
RDL	Required Detection Limit
SDWA	Safe Drinking Water Act
SOP	Standard Operating Procedure
TDS	Total Dissolved Solids
TNI	The NELAC Institute
TSC	Technical Support Center
U.S.	United States