Protocol for the Evaluation of Alternate Test Procedures for Organic and Inorganic Analytes in Drinking Water

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Foreword

This document provides guidelines for the submission and validation of analytical methods under the drinking water alternate test procedures (ATP) program. This 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 equally effective as an existing EPA-approved method. This protocol provides basic information on the criteria the Agency generally uses in deciding whether a method is suitable for evaluation under the 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 ATP method through sufficient multi-laboratory validation to support their use at a national level. The drinking water regulations are national standards and as such, single laboratory or regional approvals are not permitted.

EPA anticipates that the standardized procedures described herein will expedite the processing of ATPs, 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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1 Introduction

1.1 Background and Objectives

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

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. Accordingly, EPA assesses 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 Safe Drinking Water Act §1401(1)); that is, the 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. For those methods that demonstrate acceptable performance through their ATP evaluation, EPA will initiate an appropriate approval action.

1.2 Scope of ATP

The ATP evaluation process is based on demonstrating ruggedness of a method (that is the method yields reliable, accurate results over the range of field and lab conditions specified in the method) and the use of designated quality control acceptance criteria against which ATP methods are tested for equivalency relative to approved methods.

2 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 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. Find additional information on EPA's expedited method web page.

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. All required application information and any associated attachments should be submitted 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 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 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 Method Development and Validation Study

3.1 Introduction

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, that is, 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 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.

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 (for example, 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 (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 method validation study are provided in Appendix C. In general, the validation study plan will consist of the following sections.

3.2.1 Background

The Background section of the validation study plan should:

- Include a summary of the candidate method.
- List the analytes measured by the candidate method including corresponding Chemical Abstracts Service Registry identification.

3.2.2 Study Management

The Study Management section of the validation study plan should:

- Identify the organization responsible for managing the study.
- Identify the laboratories or other organizations that will participate in the study.
- Delineate the study schedule.

3.2.3 Sample Holding Time and Preservation

In general, candidate methods are expected to use the sample holding times, extract holding times (if applicable) and preservation agents specified in approved EPA methods for the analyte, unless these parameters are being explicitly modified in the candidate method. If no changes to holding times or preservation are proposed in a given candidate method and no additional analytes are being added to a method, then this part of the validation study plan is likely to require little discussion. If however, the proposed candidate method alters, or could affect holding times or the preservation of the sample, a holding time or preservation study or both will be required.

3.2.4 Method Procedures

This section of the validation study plan 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. 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 B of this document should be included for all candidate test methods. Recent drinking water methods published by EPA (for example, methods 524.3, 525.3) may also be consulted for format and the level of detail required.

3.2.5 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 make every attempt to identify those parts of the procedures that could be vulnerable to technician expertise or result in poorer performance with slight but realistic departures from ideal conditions. The Plan should identify, when possible, the steps that will be taken to control these critical steps.

3.2.6 Potential Interferences and Plans to Address Them

Many chemical methods are subject to chemical or physical interferences or both which, if left uncontrolled, result in inaccurate monitoring results. Through an understanding of the chemistry of the method, the applicant should identify potential interferences to the candidate method and plans to address and control these interferences.

3.2.7 Demonstration Data

In this section, the applicant will specify the data to be collected using the candidate method and the approved reference method. Generally, all candidate methods will determine precision and accuracy of the method using both fortified reagent water and different real or synthetic drinking water matrices. Synthetic drinking water matrices should be prepared to provide objective evidence of method capabilities in a "worst case" situation (for example, high hardness or ionic strength and high total organic carbon.)

3.2.8 Fortified Reagent Water Analyses

Generally, ATP candidate methods are required to determine precision, accuracy and sensitivity in reagent water fortified with the contaminant(s) of interest at relevant concentrations. Accordingly, multiple replicates at the relevant concentration levels will be needed. Concentration levels evaluated in the precision and accuracy studies are expected to extend both above and below the published regulatory Maximum Contaminant Level effectively demonstrating the candidate method will satisfy all regulatory measurement requirements.

Fortified reagent water samples should incorporate the preservation agent(s) specified in the method and any other reagents or treatments specified in the method. Fortified reagent water samples should be prepared and analyzed for every option specified in the method. For example, if two or more preservation agents are specified as options in the method, reagent water analyses should be performed using each preservation agent given in the method.

3.2.9 Matrix Analyses

For ATP candidate methods, precision and accuracy should be examined using different drinking water matrices that may be encountered during routine sample analysis. These drinking water matrices may be actual or synthetic and the exact number and type needed will be determined when the validation study plan is constructed. Generally the matrices are a combination of the following types: (1) finished drinking water drawn from a hard ground water source (hardness > 250 mg/L as $CaCO_3$), (2) finished drinking water drawn from a surface water source and containing total organic carbon (TOC ≥ 2 mg/L), (3) artificial drinking water matrix high in ionic strength and (4) artificial drinking water matrix high in organic content. Additional matrices may need to be examined to document adequate performance of the method as appropriate. For example, if chloride is known or suspected to interfere with a given method, the validation study plan may need to include a public water supply sample or artificial matrix having the maximum, tolerable chloride concentration that the applicant has determined for the candidate method. If a method is designed to measure a particular disinfection byproduct it may be necessary to examine various finished drinking waters to adequately test the method. ATP staff will work with the applicant to determine appropriate matrices to include in the validation study plan.

Analysts should review an applicable approved or published method for indications of matrix effects that are unique to the analyte separation and measurement technologies used in the ATP. Water quality characteristics that can affect analysis of drinking water samples include, but are not limited to, pH, total organic carbon content, turbidity, total organic halogen content, ionic strength, sulfate, metal contamination and trihalomethane contamination of the drinking water sample.

For each drinking water matrix specified in the validation study plan, replicates are fortified at a concentration sufficiently below the Maximum Contaminant Level, along with a midrange and a high level spike. Precision and accuracy are determined for each set of replicates. As noted above for reagent

water analyses, additional replicates or fortified concentration levels may be required depending on the method. Also, as noted previously, each sample is tested using any and all options specified in the candidate method.

3.2.10 Quality Control

Quality control is an important aspect of method performance. Quality control needs to be incorporated within each ATP candidate method and the applicant should address the quality control specified in the method. Common quality control parameters include:

- Initial calibration and calibration verification.
- Blanks.
- Ongoing precision and accuracy.
- Surrogate recovery.
- Internal standard response.
- Fortified matrix precision and accuracy.

Appendix C, Table 1 summarizes the above quality control parameters as they are addressed for organic and inorganic contaminants in EPA drinking water methods.

3.3 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 support an equivalent method performance determination, relative to an approved method.

Consistent with 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 approved 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 validation study plan that were made in implementing the study along with problems encountered and corrective actions.

3.3.1 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.

3.3.2 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.

3.3.3 Detailed Method Procedure and Demonstration Data

This section of the validation study report presents a detailed version of the method. Format should follow that specified in Appendix B. Following the detailed method, the 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.

3.3.4 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.

3.3.5 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).

3.3.6 Validation Study Plan

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

4 EPA Review and Approval

4.1 EPA Review of Candidate ATP Method

EPA's ATP program reviews the drinking water ATP candidate methods and the validation data. If a candidate method is determined to provide equivalent method performance relative to an approved reference method, it will be recommended for approval.

4.2 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 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 expedited method 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 separately by the Drinking Water ATP program and the Wastewater ATP program.

Appendix A: 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 test method title:
Reference method number or name or both:

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

EPA use only
Case number:

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 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 at least address the quality control specifications listed in Appendix C, Table 1 of this document.]

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 C: Method Validation

Method validation is the process of demonstrating that an analytical method is suitable for its intended use and involves conducting a variety of studies to evaluate method performance under defined conditions. Method validation studies may involve a single laboratory (intralaboratory) or multiple laboratories (interlaboratory). The goal is to demonstrate that analytical results produced by the application of a particular method are fit for an intended purpose. Properly designed and successful method validation studies create confidence in the reliability of a test method. Method validation is one of several important quality system components that are designed to ensure the production of scientifically valid and useful analytical data.

The information in this appendix is intended to serve as a guideline only. Because methods vary significantly in chemistry and technology it is not possible to define a single set of performance criteria that can be applied to all methods. This is due to the severe problems in translation of a complex domain of knowledge such as analytical chemistry into a mathematical statement. This appendix lists critical elements of the general method validation process that may not apply in all cases. The actual validation components that will be necessary will be determined during the creation of the method validation study plan.

Storage Stability

Before validating an analytical method, it is necessary to ensure that proper sample preservation and storage stability studies were performed during method development. Storage stability should investigate the stability of the analyte(s) from the time of sampling through the time of analysis. If an extraction is performed, the extract stability should also be investigated. Analytes may be lost through volatilization, sorption, chemical degradation (abiotic reactions) and microbial degradation. Traditionally, preservation to prevent chemical degradation is evaluated but preservation to prevent microbial degradation has been historically ignored. Microorganisms have the potential to degrade target analytes and represent a significant pathway for the fate and destruction of organic compounds.

Instrument Calibration

Instrument calibration refers to the procedures used for correlating instrument response to an amount of analyte (concentration or other quantity). The characteristics of a calibration function and justification for a selected calibration model should be demonstrated during a method validation study.

The performance of a calibration technique and the choice of calibration model (for example, first order, second order, weighting, etc.) are critical for minimizing sources of instrument bias and optimizing precision. The parameters of the model are usually estimated from the responses of known, pure analytes. Calibration errors can result from failure to identify the best calibration model; inaccurate estimates of the parameters of the model; or inadequately studied, systematic effects from matrix components.

During method development and validation, calibration models are typically evaluated by analyzing multiple levels of calibration standards over a selected working range. After a calibration curve is constructed from the responses, the concentrations of the standards are calculated from the curve. These values are then compared to the appropriate quality control criteria to determine the curve's adequacy. The calibration study results should be included in a method validation report. Access to

information about calibration performance characteristics assists the user in implementing new methods and verifying that a laboratory's instrument performance is acceptable.

Accuracy (Bias)

Bias refers to the overall magnitude of known systematic (determinate) errors associated with the use of an analytical method. The presence of systematic errors can only be determined by comparison of the average of many results with a reliable, accepted reference value. Method bias may be estimated by measuring materials whose composition is reasonably well known or by analyzing fortified materials. Rigorous evaluations of bias should be included in method validation studies. Minimally, bias should be evaluated at the extremes of the quantitation range, at regulatory levels and in representative matrices.

Precision

The general term "precision" is used to describe the magnitude of random (indeterminate) errors associated with the use of an analytical method. The sources of random error evaluated depend upon the range of conditions over which the data are collected.

Precision should be evaluated at the extremes of the quantitation range, at regulatory levels and in representative matrices. Common measures of dispersion are the standard deviation and the percent relative standard deviation of repeated measurements. The repeatability and reproducibility conditions should be clearly stated so that the measures of dispersion can be properly interpreted and evaluated.

Quantitation Limits and Range

The term "quantitation range" is used to describe the span of analyte levels, as contained in a sample matrix, for which method performance has been tested and data quality is deemed acceptable for its intended use. For compliance, a quantitation range includes either a regulatory or other type of action level for the compound being analyzed.

A lower limit and an upper limit bound a quantitation range. A quantitation range may be wider than an instrument's calibration range because of dilution or concentration steps performed during sample preparation. Dilution factors or concentration factors are used to relate the calibration range to the quantitation range. Analyte concentration will have an effect on most method performance characteristics, including bias and precision. At a minimum, method bias and precision should be evaluated at the extremes of the quantitation range.

The lower limit of the quantitation range is commonly referred to as the "limit of quantitation." The method reporting limit should always be above the "limit of quantitation" and both should be at or above the lowest calibration standard.

Detection Limit(s)

The term "detection limit" is used to describe the lowest analyte level that can be confidently identified. There are many specific definitions for this term and it is used to describe the detection capabilities of detectors, instruments and analytical methods. Currently Office of Ground Water and Drinking Water is trying to phase out the use of detection limits and focus more on the application of method reporting limit. Where they are still required by regulation the procedure described at 40 CFR, Part 136, Appendix B is being used to determine them.

Ruggedness Testing

Ruggedness refers to the extent to which an analytical method remains unaffected by minor variations in operating conditions. Ruggedness testing involves experimental designs for examining method performance when minor changes are made in operating or environmental conditions. The changes should reflect expected, reasonable variations that are likely to be encountered in different laboratories.

Ruggedness testing is generally conducted at the end of method development but before an interlaboratory method validation study.

Quality Control Targets for Method Development

As previously mentioned, the necessary validation components will be determined during the creation of the method validation study plan. This includes the numeric limits for specific quality control parameters. These values will depend on the regulation, intended data use, the quality control parameters for existing reference methods and the individual technology that is being applied. Table 1 provides reference values that are generally used by Office of Ground Water and Drinking Water for method development.

Table 1. Reference Values generally used for Drinking Water Method Development

Parameter	**Organic Methods**	**Inorganic Methods (Ion Chromatography or wet)**	**Metals or Inductively Coupled Plasma**
Method Blank	< 1/3 MRL	< 1/3 MRL	< 1/3 MRL
Initial Demonstration of Capability Accuracy or bias, Continuing cal checks and Calibration curve checks (as % recovery)	> 2 x MRL ± 30%, ≤ 2x MRL ± 50%	> 2 x MRL ± 15%, ≤ 2x MRL ± 20%	> 2 x MRL ± 10%, ≤ 2x MRL ± 20%
Surrogate Recovery	± 30%	± 15%	Not Applicable
Initial Demonstration of Capability Precision and Duplicate Samples (% Relative Standard Deviation)	± 30%	± 20%	± 15%
Internal Standard	≥ 50% of the Internal Standard area or response in the active calibration	Same	60%-125%

Additionally, the general validation study would require the method to be evaluated by two independent certified laboratories in addition to the vendor's lab.

Appendix D: 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.

If the alternate test method demonstrates equivalency to an approved method, EPA may grant formal approval 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 your report (that is, select the Title section and replace it with your 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).]

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 alternate method is being compared to: cite the organization (for example, ASTM, Standard Methods, EPA, etc.) and the method number. Summarize justification for the ATP and describe the advantages the new method affords 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 alternate method meets these specifications. Clearly indicate in the final sentence whether the alternate method is "equally effective" in meeting quality acceptance criteria as the approved method.]

1.3 Analytes

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

2 Study Implementation

[Clearly identify the managing organization responsible for development of the alternate test method validation study plan and all of the laboratories participating in the study. Explain why specific laboratories were selected to participate and whether they received compensation for the work performed. Identify whether the study involved the use of different types of instrumentation (for example, gas chromatography–mass spectrometry analyses using ion trap detectors and triple quadrupole detectors).]

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 alternate method should be prepared in standard EPA 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 alternate 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 alternate 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 through the use of blanks, surrogates, internal standards 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 alternate 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.]

Appendix A: Validation Study Plan

[Append the approved validation study plan.]

Appendix B: Supporting Data

Raw Data

[Submit raw data in an excel spreadsheet. Identify instruments used and operating conditions, chromatographic column specifications, high-performance liquid chromatography gradients, gas chromatography temperature programs, detectors, injection volumes, solid phase extraction media and extraction procedures.]

Example Calculations

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

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:

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