United States Environmental Protection Agency

Office of Water

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Protocol for Review and Validation of Alternate Test Procedures for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program

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Office of Water
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Foreword

This document ("protocol") provides guidance on how the U.S. Environment Protection Agency (EPA) will evaluate certain test procedures under its National Alternate Test Procedure program for inclusion as an approved 40 Code of Federal Regulations (CFR) Part 136 method. The protocol applies to alternate test procedures (ATP) for measuring an organic or inorganic analyte for which there is already at least one existing Part 136 method to measure the analyte. The protocol outlines in substantial detail the kind of information and evidentiary showing EPA would expect is necessary to demonstrate the suitability of a method for approval and inclusion in Part 136. The protocol also includes guidance regarding obtaining approval of methods for measurement of method-defined analytes or parameters (MDPs) for which there is already at least one existing Part 136 method. This protocol applies to modifications of an EPA-approved method or a procedure that uses the *same* determinative technique and measures the same analyte(s) of interest as an approved method.

The protocol provides guidance for validation, submission, and EPA review of ATP applications under EPA's National ATP Program submitted for modifications of an EPA-approved method or a procedure that uses the same determinative technique and measures the same analyte(s) of interest as an approved method. Methods that use a *different* determinative technique to measure the same analyte(s) of interest or methods that measure a *different* form or species of an analyte or parameter than the approved method are considered new methods. The requirements for EPA approval of new methods are detailed in a separate protocol. The protocol provides supplementary information for complying with the ATP requirements at 40 CFR 136.4 and 136.5.

This protocol supersedes the 2016 version of the *Protocol for Review and Validation of Alternate Test Procedures for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program.* With respect to ATP applications for methods that measure MDPs, this guidance recommends side-by-side comparison studies to validate that there are no systematic differences in performance between the ATP and the EPA-approved methods. This protocol continues the recommended current practices for ATP applications involving other types of methods for measurement of organic and inorganic analytes (i.e., applicants should conduct validation studies in the recommended number of laboratories depending upon the type of approval being sought to demonstrate acceptable method performance by meeting or exceeding the quality control (QC) acceptance criteria associated with EPA-approved reference methods for the corresponding combination of analyte(s) and determinative technique).

Under EPA's ATP program, in certain circumstances, a method developer may apply for approval for the use of an ATP to test for a specific regulated constituent. The recommended procedures described herein will likely expedite the approval of these methods for organic and inorganic analytes, encourage the development of innovative technologies, and enhance the overall utility of the EPA-approved methods for compliance monitoring under the National Pollution Discharge Elimination System (NPDES) permit program.

Disclaimer

This guidance generally describes the approval process for EPA's program for establishing test procedures for organic and inorganic analytes that are used in Clean Water Act programs and codified at 40 CFR Part 136. It describes EPA's conclusions about the types of data and information EPA will need in order to evaluate whether to approve any particular ATP for such analytes. It includes a model application form for use when requesting EPA approval for ATPs for such analytes. Although the guidance provides additional explanation of EPA's requirements, it does not alter or substitute for any of the regulations at 40 CFR Part 136. The guidance, including the model application form, is not a rule and

is not legally enforceable. It does not confer legal rights or impose legal obligations on any federal, state agency or any member of the public. It does not create any rights, substantive or procedural, enforceable at law by a party to litigation with EPA or the United States. In the event there is an apparent conflict between the guidance and any statute or regulation, the guidance is not controlling. EPA has made every effort to ensure the accuracy of information in the guidance, but the requirements for EPA approval of test procedures for use in its CWA programs are determined by the relevant statutes, regulations or other legally binding requirements.

This protocol represents EPA's "best thinking" about the information that is useful in making the determination of whether or not to approve use of any ATP for organic and inorganic analytes. This guidance document reflects EPA views about what data and information sound scientific practice would require for approval of an ATP for such analytes. Where the guidance uses the word "should," or in some cases "must," this is only intended to apprise the applicant of the kind of information that, in EPA's view, will demonstrate the adequacy of a given method for use under the CWA and thus its suitability for EPA approval. Applicants may provide other data or information for use in EPA's determination and remain free to deviate from the recommendations EPA has provided here. EPA will make the decision to approve or disapprove any ATP for such analytes based on the record before it, and that decision is subject to challenge and judicial review.

40 CFR 136.4 and 136.5 establish the procedures and regulatory requirements for applying for and for EPA approval of alternate test procedures for nationwide use and for limited use. The regulations require submission of an application that, among other things, provides comparability data for the performance of the alternate test procedure as compared to the performance of the approved Part 136 method for which it is a proposed alternative (40 CFR 136.4(a)(4) and 40 CFR 136.5(a)(5)). This guidance explains in more detail the information that EPA expects will be necessary for EPA to determine comparability or justify using the alternate test procedures instead of the approved Part 136 method for organic and inorganic analytes.

EPA may decide to revise the guidance without public notice. The public may offer suggestions to EPA for clarifications at any time.

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1.0 INTRODUCTION

1.1 Background and Objectives

In accordance with section 304(h) of the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) promulgates guidelines establishing test procedures (analytical methods) for the analysis of pollutants. EPA regulations require the use of these methods where measurements of waste constituents are required in applications for National Pollutant Discharge Elimination System (NPDES) permits or for reports required under NPDES permits. 40 CFR 136.1. EPA has codified these approved test procedures in the Code of Federal Regulations (CFR) at 40 CFR Part 136. For the purposes of this protocol, these test procedures are referred to as "EPA-approved" methods, regardless of whether they were developed by EPA, a voluntary consensus standards body (VCSB) such as ASTM International or Standard Methods, or by another government entity such as the U.S. Geological Survey (USGS).

EPA's regulations at 40 CFR 136.4 and 136.5 also establish procedures for EPA to review and approve the use of an alternate test procedure (ATP) in place of an EPA-approved method. These regulations govern the Agency's Alternate Test Procedure (ATP) program for CWA methods[1]. Section 136.4 describes the process for obtaining approval for nationwide use of an ATP. Section 136.4(a) first requires a written application for review of an ATP for nationwide use. Required elements of that application include, among other things, a detailed description of the proposed ATP and studies confirming the general applicability of the ATP for analysis of the pollutant or parameter for which approval is requested. The applicant must also provide comparability data for the performance of the ATP as compared to the existing approved method. Section 136.4(a)(4). The National Coordinator of the ATP program reviews the application and notifies the applicant of its suitability for use in CWA programs (Section 136.4(c)). If approval is recommended, EPA will propose to amend Part 136 to include the ATP and following public comment make a final decision on approving the ATP. In the event that the National Coordinator recommends against approval, the Coordinator will specify what additional information might lead to a recommendation for approval. These requirements are the basis for EPA's CWA ATP program administered by the Office of Water, Office of Science and Technology, Engineering and Analysis Division (EAD). Section 136.5 describes the process for obtaining approval for limited use of an ATP. Section 136.5 first requires a written application for review of an ATP for limited use to be submitted to the director of the State agency having responsibility for issuance of NPDES permits in cases where the request for use of an ATP concerns use in a State with an NPDES permit program approved pursuant to Section 403 for the Clean Water Act. In cases where the request is made in a State that has not been grated authority to administer the NPDES permit program or in cases where the State is the applicant, the request is submitted directly to the Regional ATP Coordinator who has the final authority to approve or reject applications for use of an ATP. Limited use approval may be restricted to use by a single facility on one or more discharges. In cases where the National ATP Coordinator has approved an applicant's request for nationwide use of an ATP, an applicant may request limited use approval of the method under §136.5. In these instances, limited use approval maybe extended all dischargers or facilities (and their associated laboratories) specified in the approval for the Region at the discretion of the Regional ATP Coordinator. The Regional ATP Coordinator will forward a copy of every approval and rejection notification to the National Alternate Test Procedure Coordinator.

In addition, as specified at 40 CFR 136.6, EPA allows users to make certain modifications to an approved method to address matrix interferences without the extensive review and approval process specified for an alternate test procedure at 40 CFR 136.4 and 136.5. Acceptable reasons for an analyst to modify a

[1] EPA also promulgates analytical methods under the Safe Drinking Water Act (SDWA) and has a similar ATP program. This protocol only addresses the CWA ATP program and does not apply to the SDWA ATP program.

method include analytical practices that lower detection limits, improve precision, reduce interferences, lower laboratory costs, and promote environmental stewardship by reducing generation of laboratory wastes. Acceptable modifications may use existing or emerging analytical technologies that achieve these ends provided that they do not depart substantially from the underlying chemical principles in methods currently approved in 40 CFR Part 136. The flexibility to modify methods without the need for approval as an ATP and the associated requirements that must be met before such modified methods may be used for CWA compliance monitoring are described in more detail at 40 CFR 136.6.

An ATP is a modification of an approved method or a procedure that uses the same determinative technique and measures the same analyte(s) of interest as the approved method. An ATP also may involve adding new analyte(s) of interest required in a specific permit to the target analyte list of an approved reference method. The ATP program provides laboratory professionals with the opportunity to enhance compliance monitoring and encourages use of innovative technologies. Approval for an ATP may be sought when the alternate procedure reduces analytical costs, overcomes matrix interference problems, improves laboratory productivity, or reduces the amount of hazardous materials used and/or produced. The applicant is responsible for validating its proposed alternate test procedure.

This protocol sets out EPA's views about what information and data will support approval of an ATP for organic and inorganic analytes under the ATP program for use in NPDES Compliance monitoring. As such, it provides a detailed explanation of the kinds of information and studies that generally will support a finding of a method's comparability to an existing approved method and thus its appropriateness for approval as an ATP for such analytes. This version of the ATP protocol describes validation processes for modifying methods that measure MDPs. Details regarding these MDP validation procedures are found in Appendix H of this document.

The use of a *different* determinative technique to measure the same analyte(s) of interest or a method that measures a *different* form or species of analyte or parameter than the approved method is considered a new method. EPA has established a different set of requirements for validation, submission and approval of new methods that are detailed in a separate protocol (USEPA 2015).

Note: Methods developed by voluntary consensus standard bodies (VCSBs) and other federal agencies are *not* processed for approval under the ATP Program. Instead EPA has developed a separate path to approval for these keeping with the National Technology Transfer and Advancement Act (NTTAA). EPA considers VCSB methods and those from other agencies in regulatory actions when periodically updating the list of approved methods at 40 CFR Part 136. EPA's "*Checklist for Methods to be Considered by EPA for Use in Compliance Monitoring Programs under the Clean Water Act"* (Appendix I) provides a list of items and information EPA considers in evaluating all new, updated, and ATP methods for use in wastewater compliance monitoring for approval.

1.2 Tiered System for Validation of Alternate Test Procedures

EPA recognizes that a formal interlaboratory method validation may not be necessary to demonstrate suitability for approval for all situations and may be prohibitively costly to implement, especially for small laboratories and regulated entities. Therefore, the protocol describes a three-tiered, cost-effective approach to method validation that would tailor the validation study to reflect the intended use of the method. EPA has specified approved methods that contain (or are supplemented with) QC acceptance criteria (Appendix G) for most combinations of analyte and determinative technique. When considering how to demonstrate that its ATP for organic and inorganic analytes is able to meet or exceed the QC acceptance criteria of the EPA-approved reference method (see Section 1.3.1) for the applicable combination of analyte and determinative technique, an applicant should review the tiers below and

decide what the most appropriate tier for the applicant's ATP is based on its intended use. An applicant is required to demonstrate that its ATP is able to meet or exceed the QC acceptance criteria of the EPA-approved reference method (see Section 1.3.1) for the applicable combination of analyte and determinative technique. The three method validation tiers are listed below.

Tier 1: These types of ATP should be validated for use in one or more matrix type(s). EPA approval of a Tier 1 ATP would generally require successful single-laboratory testing in the matrix type(s) of interest. Tier 1 ATPs are reviewed by the State issuing the NPDES permit where the State is not the requesting party, and forwarded to EPA Regional staff, along with a recommendation for or against approval. Where the State is the requesting party, applications for Tier 1 ATPs are sent directly to the EPA Regional staff

Tier 2: ATPs for use by all laboratories for nationwide use for only one matrix type. The application for approval should generally demonstrate successful testing of the ATP in a three-laboratory validation study. Tier 2 ATPs will be reviewed by the National ATP staff at EPA Headquarters and if positively reviewed, will be recommended for approval. These methods are then proposed for promulgation in the CFR

Tier 3: ATPs for use by all laboratories (nationwide use) for all matrix types. The application for approval should generally demonstrate successful testing of the ATP in a nine-laboratory validation study. Tier 3 ATPs are reviewed by the National ATP staff at EPA Headquarters and if positively reviewed are recommended for approval. These methods are then proposed for promulgation in the CFR

Note: Matrix type, in the context of these tiers, is defined as a sample medium (e.g., air, soil, water, sludge) with common characteristics across a given industrial subcategory. For example, C-stage effluents from chlorine bleach mills, effluent from the continuous casting subcategory of the iron and steel industrial category, publicly owned treatment works (POTW) sludge, and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory are each a matrix type. (A list of industrial categories with existing effluent guidelines can be found at: https://www.epa.gov/eg/industrial-effluent-guidelines).

1.3 Scope of Alternate Test Procedures

This protocol for validation, submission, and approval of an ATP offers flexibility to modify approved methods, provided that a laboratory demonstrates and documents that the modified method produces results equal or superior to those produced by the EPA-approved reference method for the applicable combination of analyte and determinative technique.

1.3.1 EPA-approved Reference Methods

EPA has approved one or more reference methods that contain (or are supplemented with) standardized QC procedures and QC acceptance criteria for each combination of regulated analyte and determinative technique. Appendix G of this document contains the QC acceptance criteria for the approved inorganic methods. The approved organic methods include the QC acceptance criteria within the text of the method itself.

The QC acceptance criteria associated with the EPA-approved reference methods are the performance criteria against which ATPs are evaluated. Method performance is deemed to be acceptable when results produced by an ATP meet or exceed the QC acceptance criteria associated with the corresponding EPA-

approved reference method. Using these established QC acceptance criteria as the method performance measure allows EPA to implement the ATP program more efficiently.

1.3.2 Modifications to Front-end Techniques

A front-end technique is any technique in the analytical process that precedes the determinative technique. Front-end techniques include all procedures, equipment, solvents, etc., that are used in the preparation and cleanup of a sample prior to analyte detection and measurement. Laboratories may modify any and all front-end techniques for non-MDPs provided that the modification:

- Is not explicitly prohibited in the corresponding approved method, and
- Can be demonstrated to produce results equal or superior to results produced by the approved method.

This flexibility includes the ability to modify the chemistry of the front-end of the method, for example, changing the extraction solvent and substituting liquid-liquid for solid-liquid extraction. ATP approval is *not* required if changes to the front-end techniques are within the allowed flexibility of 40 CFR 136.6.

Note: Changes to the front-end chemistry or extraction solvent may affect the stability of the analyte(s) of interest, potentially leading to analyte transformation or degradation. Depending on the nature of the front-end change, the developer of a modified method may need to demonstrate that analyte stability is *not* adversely affected in either the original sample or in the sample extract for at least the duration of the established holding time(s) in the reference methods.

The developer of a modified method always has the option of asking EPA or another regulatory authority for a technical opinion on the acceptability of the validation data that supports the method modification.

1.3.3 Adding New Target Analytes

EPA will permit method developers to modify the scope of an approved method by adding additional analytes if required in a specific permit. This allowance is in response to public comment on previous rules (59 FR 62456, December 5, 1994; 58 FR 65622, December 15, 1993). Method developers seek this approval when they want to adapt an existing method to obtain occurrence data for a new analyte. EPA believes these requests have merit when there is a potential for new regulatory requirements and when technological advances make the measurement of additional analytes feasible (e.g., adding lead to the scope of EPA Method 200.7). Under this ATP protocol, developers can obtain approval for adding analytes to an approved method if the following conditions are met:

(1) It has been demonstrated that the added analyte does not interfere with determination of the analytes of concern in the approved method.

(2) QC acceptance criteria are developed and used for determination of the added analyte; *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program.*

(3) The reason for adding the analyte is not to avoid the sample preservation or sample (or extract) holding time conditions that are already required for that analyte in another approved method. (This criterion precludes the addition of analytes to an approved method with less rigid sample collection or holding time criteria.)

1.3.4 Method-defined Analytes

As specified at 40 CFR 136.6, the term *"method-defined analyte"* means an analyte (or parameter) that is defined solely by the method used to determine the analyte (generically referred to in this document as a method-defined parameter or MDP). Such an analyte may be a physical parameter, a parameter that is not a specific chemical, or a parameter that may be comprised of a number of substances. Examples include, but are not limited to:

- Acidity
- Alkalinity
- Biological oxygen demand (BOD)
- Chemical oxygen demand (COD)
- Color
- Oil and grease
- pH (hydrogen ion)
- Conductivity (specific conductance)
- Temperature
- Total dissolved solids (TDS)
- Total organic carbon (TOC)
- Total suspended solids (TSS)
- Total phenolics, and
- Turbidity.

Modifications to methods that measure MDPs have the potential to change what is being measured. Therefore, *any* modifications to those methods beyond that specifically allowed in the approved methods require EPA review and approval as alternate test procedures by the appropriate approval authority (see Table 1).

In order to more clearly distinguish the ATP requirements for MDPs from those for the more traditional type of analytes, the discussion data and information that, in EPA's view, will generally demonstrate the suitability of the ATP for measurement of MDPs has been placed in Appendix H of this document.

2.0 OVERVIEW OF THE ATP APPROVAL PROCESS

The process for obtaining approval of an ATP for organic and inorganic analytes is summarized in Figure 1. Depending on the tier, ATPs may be reviewed by (1) the State authority that issues the NPDES permit, and/or by EPA Regional staff, or (2) EPA Headquarters staff. The relevant authority will review the application, including the justification for the ATP provided by the applicant and determine whether an ATP is necessary (e.g., the approved method may already allow the modification proposed or the modification falls within the flexibility allowed at 40 CFR 136.6, so ATP approval is not needed or warranted). Where the State is not the requesting party, the State will review Tier 1 ATP applications and forward these to EPA Regional staff with a recommendation for or against approval. Where the State is the requesting party, the EPA Regional staff will review the Tier 1 ATP applications. If, after initial review, EPA Headquarters accepts a Tier 2 or Tier 3 application, the applicant should move forward with preparing a method development and validation study plan in consultation with National ATP staff.

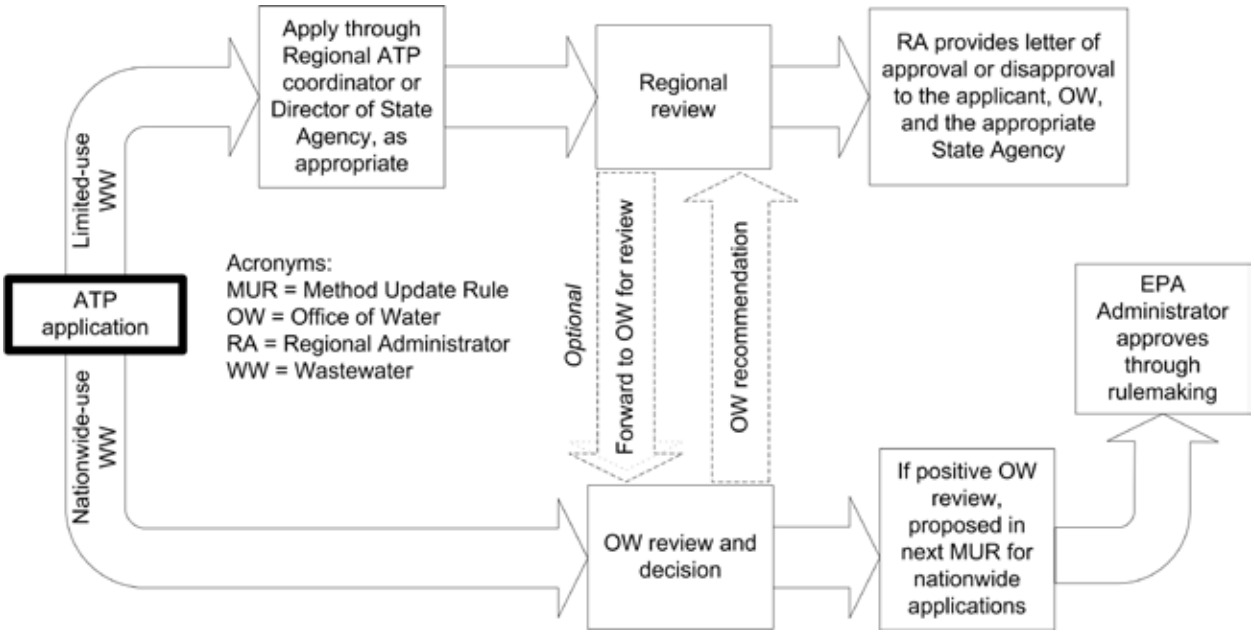

Figure 1. Flowchart summarizing the ATP application process for methods under the CWA Program

In order to expedite the approval process, the applicant should submit to EPA its plan for developing the necessary data to demonstrate the suitability of ATP for approval. For Tier 2 and Tier 3 ATPs, once the applicant has received EPA's view concerning its study plan, the applicant should move forward with the study and submit the study report to the ATP staff. If the validation study results confirm that the applicant's method is sufficiently rugged and provides data of comparable quality, EPA will generally notify the applicant that it intends to pursue approval via the rulemaking process. If this is not the case, ATP staff may identify additional information or data required. If the laboratory studies fail to satisfactorily verify the comparability of the applicant's method, the applicant should address the problems encountered and follow-up with further laboratory validation studies.

3.0 APPLICATION

This section describes the information that EPA would expect in an application for approval of an ATP for organic and inorganic analytes to demonstrate its appropriateness for approval and provides information on the approval authorities for the three tiered approach described in Section 1.2 of this protocol. This section also describes how to treat any proprietary information submitted with an application.

Note: Where the State is not the requesting party, Tier 1, Limited Use ATPs are subject to State authority review prior to EPA Regional approval. State authorities may have additional requirements and/or authority-specific application forms that are beyond the scope of this protocol. Therefore, applicants for Tier 1 ATPs should consult such authorities regarding Tier 1 ATP requirements.

Applications may be submitted by email, in hardcopy, or on electronic media by U.S. mail or other carrier. Hard copy applications and supporting documentation should be submitted in triplicate. Applicants are advised to consult the recipient before submitting large files via email.

3.1 Submission Addresses

A summary of where to submit ATP applications and the approval authorities for each tier is provided in Table 1.

Table 1: Submission of Alternate Test Procedure Applications

Tier	Level of Use	Typical Applicant	Submit Application to[1]	Approval Authority
Tier 1	Limited Use for Wastewater[2]	EPA Regional laboratories, States, commercial laboratories, individual dischargers, or permittees in States that do not have authority to implement the NPDES permit program	EPA Regional ATP Coordinator[3]	EPA Regional ATP Coordinator (as designated by the EPA Regional Administrator)
		Commercial laboratories, individual dischargers, or permittees in States that have authority to implement the NPDES permit program	Director of State Agency issuing the NPDES permit[4]	
Tier 2	Nationwide Use in a Single Wastewater Matrix Type	All applicants	National ATP Coordinator, EPA Headquarters	EPA Administrator
Tier 3	Nationwide Use in All Wastewater Matrix Types	All applicants	National ATP Coordinator, EPA Headquarters	EPA Administrator

[1] See Appendix C for EPA addresses.

[2] Per 40 CFR 136.4(c)(5): "Whenever the National Coordinator has approved an applicant's request for nationwide use of an alternate test procedure, any person may request an approval of the method for limited use under §136.5 from the EPA Region." In these instances, limited use approval maybe extended all dischargers or facilities (and their associated laboratories) specified in the approval for the Region (limited use approval under §136.5) at the discretion of the Regional ATP Coordinator.

[3] The Regional ATP Coordinator may choose to request assistance with the Tier 1 (limited use) applications from the National ATP Coordinator for an approval recommendation.

[4] Per 40 CFR 136.5, in States with authority to issue NPDES permits, the State agency has primary responsibility for reviewing Tier 1 ATP applications. The State agency will forward the application to the Regional ATP Coordinator with a recommendation for or against approval. Where the State is the applicant for the ATP, the application goes directly to the Regional ATP Coordinator.

On receipt of the application, the ATP Coordinator will assign an identification number to the application. The applicant should use the identification number in all future communications about the application.

3.2 Application Information

A copy of a model ATP application form is included in Appendix A. The information requested on the ATP application form includes the following:

- Name and address of the applicant,
- Application submission date,
- Method number and title of the proposed ATP,
- Citation (i.e., number) of the EPA-approved method that was modified to develop the proposed ATP,
- Approved reference method (see Section 1.3.1) that contains the QC acceptance criteria that will be used for comparison,
- Analytes(s) for which the ATP is proposed,
- Level of use desired (i.e., limited use or nationwide use),
- Tier at which the proposed ATP will be validated, and
- Applicant's NPDES permit number, issuing agency, type of permit, and the discharge serial number (if applicable).

In addition, the applicant should provide the following items:

- The proposed ATP prepared in standard EPA method format,
- A table that gives a side-by-side comparison of the proposed ATP and the EPA-approved method that was modified,
- The method validation study report, including supporting data,
- For nationwide applications that will undergo rulemaking, method development information and documentation that EPA can use in preparing the preamble and docket for the proposed rule, and
- For limited use applications, applicants should identify the NPDES permit numbers for all discharges for which the applicant is seeking approval to apply the alternate test procedure (if applicable).

Note 1: Not all of these documents would need to be submitted with the initial application. The applicant should submit a validation study plan for EPA review and comment before proceeding with ATP validation. Recommended study plan elements are described in Appendix E of this protocol.

Note 2: As stated in Section 1.3, the information that should demonstrate the suitability for approval of ATPs that measure MDPs may be found in Appendix H of this document.

If an applicant is unsure whether or not a modification is allowed within the method-specified flexibility, the applicant may request that EPA determine the necessity for a full ATP validation. *The minimum information required for EPA to make this determination or begin reviewing an application is the completed application form, the proposed method in standard EPA format, and the method comparison table*. From this information, EPA can determine whether a full ATP validation is required or whether the proposed modification is within the allowed flexibility of 40 CFR 136.6.
The elements that should be provided for an application at each tier are presented in Table 2. For Tier 2 and 3 applications, the National ATP Coordinator at EPA Headquarters will not process an application until the Coordinator determines that the applicant has submitted adequate information to evaluate the application. As noted at the beginning of Section 3.0, Tier 1 applicants should consult the relevant State authority issuing the NPDES permit to determine if there are also State requirements for those applications.

Table 2. Recommended Application Elements

Tier	Level of Use	Application Elements
Tier 1	Limited Use	• Completed application form submitted to the EPA Regional ATP Coordinator or the Director of State Agency issuing the NPDES permit • Justification for the ATP • Method in EPA format • Validation Study Plan[1] • Method comparison table • Validation study report
Tier 2[1]	Nationwide Use	• Completed application form submitted to National ATP Coordinator, EPA Headquarters • Justification for the ATP • Method in EPA format • Validation Study Plan[1] • Method comparison table • Validation study report • Method information and documentation
Tier 3[1]		

[1] The applicant should submit a validation study plan with the initial application for a Tier 2 or 3 ATP for EPA review and comment before proceeding with the study.

3.2.1 Justification for the ATP

Because EPA review and evaluation of proposed ATPs can entail considerable effort, EPA strives to minimize the submission of unnecessary method modifications or modifications that are already allowed in approved methods. Therefore, the entity that proposes an ATP should provide a brief justification for why the ATP is being proposed. Examples of useful justifications include, but are not limited to:

- The ATP successfully overcomes some or all of the interferences associated with the approved method
- The ATP reduces the amount of hazardous wastes generated by the laboratory
- The cost of or time required for analyses is reduced, or
- The quality of the data is improved.

The Agency acknowledges that there may be some trade-offs between meeting QC acceptance criteria and encouraging use of potentially beneficial alternate methods. For example, a proposed ATP may be far more rapid and less expensive to perform, but have slightly lower precision than the currently approved methods for a given analyte. Depending on the chemical being measured, ATP staff may consider the ATP application because the alternate method could allow more frequent monitoring with no added cost. More frequent monitoring may result in enhanced information quality for that chemical. The Agency may consider relaxing certain QC acceptance criteria for a given ATP, depending on the analyte and the benefits likely to be realized.

It is highly recommended that the method developer consult with ATP staff concerning their proposed candidate method and its justification prior to extensive method development. Candidate methods that are insufficiently justified will not be considered further.

3.2.2 EPA Method Format

In accordance with the standard EPA format originally developed by EPA's Environmental Monitoring Management Council in 1996 (Reference 4), methods should contain 17 specific topical sections in a designated order. These 17 sections are listed in Appendix D. Any additional numbered sections should

be inserted starting with Section 11.0, *Procedure*, as appropriate for a particular method. For detailed information on the EPA format for proposed methods, refer to *Guidelines and Format for Methods to Be Proposed at 40 CFR Part 136 or Part 141* (Guidelines and Format document), EPA-821-B-96-003.

3.2.3 Method Comparison Table

Applicants should perform an in-depth comparison between their proposed ATP and the corresponding EPA-approved method and document the comparison in a two-column table. The table should include the number and title of each method, the latest revision date of the proposed ATP, and a detailed discussion of each of the 17 topics required by the standard EPA method format. Each topic should be discussed on a separate row. The applicant should highlight any differences between the proposed ATP and the approved method. If the proposed ATP is an automation of a previously approved manual method, any differences in kinetics and interferences should be presented and a comparison of the final ratios of the concentrations of the reactants in the proposed and approved methods included.

3.2.4 Validation Study Report

The applicant should conduct a validation study of the ATP that meets the validation study design described in Section 4.2 of this protocol. Once the validation study is complete, the applicant should prepare a comprehensive report on the validation study and submit a copy of that report with the ATP application. The validation study report should include the following elements, which are described further in Appendix E:

- Background
- Study Design and Objectives
- Study Implementation
- Data Reporting and Validation
- Results
- Data Analysis/Discussion
- Conclusions
- Appendix A - The Method
- Appendix B - Validation Study Plan
- Appendix C - Supporting Data (Raw Data and Example Calculations)

3.2.5 Method Information and Documentation

For Tier 2 and 3 applications, a successful ATP will be approved by the EPA Administrator through rulemaking. In these cases, in order to expedite the approval process, the applicant should provide information and documentation that will aid EPA in preparing the preamble and docket for publication of a proposed rule in the *Federal Register*. Specifically, it will be useful for the applicant to submit information that:

- Defines the purpose and intended use of the method.
- States what the method is based upon, noting any relationship of the method to other existing analytical methods and indicating whether the method is associated with a sampling method.
- Identifies the matrix type(s) for which the method has been found satisfactory.
- Describes method limitations and indicates any means of recognizing cases where the method may not be applicable to the specific matrix types.
- Outlines the basic steps involved in sample and data analysis.
- Lists options within the method, if applicable.

- Describes and discusses the validation study in a study report that includes study design and objectives, study limitations, study management, technical approach, data reporting and validation, results, data analysis discussion (including, for MDPs, development of QC acceptance criteria), and conclusions.
- Copies of all relevant supporting documents used in developing the ATP (including any other studies conducted during method development and validation), for EPA's possible inclusion in the rule docket.

Previous method rules that may serve as examples of the type of information and the appropriate level of detail necessary include: 49 FR 43234, October 26, 1984; 56 FR 5090, February 7, 1991; 60 FR 53988, October 18, 1995; and 61 FR 1730, January 23, 1996.

3.3 Proprietary Information in Applications

All information provided to the Federal government is subject to Freedom of Information Act requirements. Therefore, any information submitted with the proposed ATP application that the applicant considers proprietary **must** be marked as "business confidential." EPA staff will handle such information according to the regulations in subparts A and B of 40 CFR Part 2.

In accordance with 40 CFR 2.203, a business that submits information to EPA 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*.

Note: Confidential Business Information (CBI) must be submitted as hard copy and must not be emailed.

Confidential claims to portions of otherwise non-confidential documents should be clearly identified by the business, and may be submitted separately to facilitate identification and handling by EPA. If the business desires confidential treatment only until a certain date, or until the occurrence of a certain event, the notice should state this. However, applicants are advised that any methods to be proposed in the *Federal Register* cannot involve claims of confidential business information.
If a claim of business confidentiality is not made at the time of submission, EPA will make such efforts as are administratively practicable to associate a late claim with copies of 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.

4.0 METHOD VALIDATION

4.1 Introduction

ATP validation is the process by which an applicant demonstrates that the modified method accurately measures the concentration of an analyte in an environmental sample and can meet or exceed the QC acceptance criteria in the EPA-approved reference method or other EPA-specified document. The validation recommendations described below were developed to reflect the level of intended use of the ATP. This is accomplished through a three-tiered approach, as shown in Table 3.

Table 3. Tiered Validation Strategy

Tier	Laboratory Use	Applicable to . . .
Tier 1	Limited use[1]	One or more matrix types from one or more industries. Approved in Regions for use within the Region.[2]
Tier 2	All Laboratories (Nationwide use)	One matrix type[3] within one industrial subcategory
Tier 3	All Laboratories (Nationwide use)	All matrix types[3] from all industrial subcategories

[1] Whenever the National Coordinator has approved an applicant's request for nationwide use of an alternate test procedure, any person may request an approval of the method for limited use under §136.5 from the EPA Region (40 CFR 136.4(c)(5)). In these instances, limited use approval may be extended to all dischargers or facilities (and their associated laboratories) specified in the approval for the Region at the discretion of the Regional ATP Coordinator (40 CFR 136.5(d)).

[2] See 40 CFR 136.5

[3] Section 4.2 provides more information on the matrix types applicable to each tier.

Please contact the appropriate Regional ATP Coordinator for specific method validation recommendations applicable to Tier 1 ATPs. Methods intended for multi-laboratory use in a given industrial subcategory (Tier 2), or for multi-laboratory use for all industrial subcategories (Tier 3), should be validated through interlaboratory testing as described in the Section 4.2.

4.2 Summary of Validation Study Designs

Approval of ATPs will require the applicant to show that the ATP performs comparably to an existing part 136 method. That is the applicant should validate that the ATP is capable of yielding reliable data for compliance monitoring purposes. For most ATPs, applicants are should demonstrate acceptable method performance by meeting or exceeding the QC acceptance criteria associated with the EPA-approved reference methods for different combinations of regulated analyte and determinative technique. Appendix G to this protocol contains the QC acceptance criteria for inorganic methods. The QC acceptance criteria for organic methods generally are contained in the text of the methods. For organic methods that do not contain QC acceptance criteria, applicants should consult with EPA to determine how best to proceed.

Note: The exception to the summary requirements above is for ATPs that measure MDPs. Validation requirements for ATPs that measure MDPs are provided in Appendix H of this document.

All validation study results should be documented in accordance with the validation study designs outlined below. Table 4 and Sections 4.2.1 – 4.2.3 below summarize the validation study designs for non-MDP wastewater ATPs at each of the three tier levels.

All ATPs must be approved by the proper approval authority before they can be used or reported for compliance monitoring.

Note: The validation requirements specified in this document for Tier 1 (limited use) ATPs are intended to serve as guidance for the Regions regarding the minimum validation that would be required if a recommendation for or against approval is requested from the National ATP Coordinator. The Regions or States may impose more stringent validation requirements at their discretion.

Table 4. Summary of Recommended Validation Approaches for Non-MDP Wastewater Alternate Test Procedures(1)

	Number of		Number of Analyses					
Method Application	**Labs**	**Matrix types**	**Back-ground Analysis**	**IPR-Reagent Water(2)**	**PT Sample(3)**	**MS/ MSD(4)**	**MDL(5)**	**Total**
Tier 1 - Single-lab First matrix type	1	1	1	4	1	2	14	22
Each additional matrix type (8 max.)	1	1-8	1-8	0(6)	0	2(7) (16 max)	0(6)	3 (24 max)
Tier 2 - Multi-lab, single matrix type	3	1	3	12	3	6(7)	42	66
Tier 3 - Multi-lab, all matrix types	9	9	9	36	9	18(7)	126	198

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc. Nine is the maximum number of matrix types (or facilities) to validate a modified wastewater method at Tier 1 or Tier 3.

(2) Initial precision and recovery (IPR) reagent water analyses are used to validate a method modification. The number of IPR analyses is four times the number of laboratories used to validate a method modification because each laboratory performs a four-replicate IPR test.

(3) The proficiency testing (PT) sample should be obtained from a third party vendor and should be analyzed by each laboratory participating in the study. If sewage sludge or ocean water are matrices of interest, PT samples for those matrices are required as well.

(4) The matrix spike/matrix spike duplicate (MS/MSD) test would demonstrate that the EPA-approved method MS/MSD QC acceptance criteria have been met.

(5) A method detection limit (MDL) test would be performed in each laboratory, using the alternate test procedure. As of August 2017, 40 CFR Part 136 Appendix B requires analysis of a minimum of seven spiked samples and seven blanks per laboratory to determine an MDL. Validation studies will comply with most recent MDL study requirements published in Appendix B of 40 CFR Part 136.

(6) The MDL and reagent water IPR tests do not have to be repeated after the first matrix type is validated.

(7) The MS/MSD analyses would demonstrate that MS/MSD recovery and precision criteria associated with the EPA-approved reference method have been met. The number of MS/MSD analyses is two times the number of matrix types tested (i.e., one MS/MSD pair per laboratory).

4.2.1 Tier 1 Validation Studies for Wastewater

Any person may request the Regional Alternate Test Procedure (ATP) Coordinator to approve the use of an alternate test procedure in the Region. The primary intent of Tier 1 is to allow use of a modified method by a single laboratory. Tier 1 is expected to be used by commercial laboratories, dischargers, and state and municipal laboratories repetitively testing samples from the same site(s) on a routine basis. Tier 1 can be applied to one or more matrix types. Additional Information regarding the application and validation requirements for and approval of limited use ATPs may be found at 40 CFR 136.5. Please contact the appropriate Regional ATP Coordinator for additional information regarding specific method validation study designs for these types of ATPs. See Appendix C for a list of Regional ATP Coordinators.

Tier 1 - Single Matrix Type

Tier 1 - Single Matrix Type validation studies are performed in a single laboratory on a single matrix type plus analysis of a proficiency testing (PT) sample (see Section 4.3.12). Results of the validation study and the method modification are applicable in the laboratory that validated the ATP for this matrix type, and the results may not be used by another laboratory or for another matrix type.

Tier 1 - Multiple Matrix Types

If a laboratory intends to apply the method to fewer than nine matrix types, the laboratory should validate the method on each matrix type. Results of the validation study and the method modification are applicable in the laboratory that validated the ATP for these matrix types; the results may not be used by another laboratory or for another matrix type. The maximum number of matrix types to which the ATP should be applied to demonstrate that it will likely be successful for all other matrix types is nine. The specific tests to be conducted on the first matrix type and for each additional matrix type are shown in Table 4.

Matrices that must be tested for a multiple matrix type validation of a wastewater ATP for use in all matrix types are given in Table 5.

4.2.2 Tier 2 Validation Studies for Wastewater

The primary intent of Tier 2 is to allow all regulated entities and laboratories to apply an ATP to a single sample matrix type from a single industry. EPA has determined that Tier 2 will encourage the development and application of techniques that overcome matrix interference problems specific to effluents of certain industrial subcategories, lower detection limits, improve the reliability of results, lower the costs of measurements, and/or improve overall laboratory productivity when analyzing samples from a given industry.

Tier 2 validation studies are performed in a minimum of three laboratories. Samples of the same matrix type (e.g., final effluent, extraction-stage effluent) are collected from one or more facilities in the same industrial subcategory. In contrast to Tier 1, once an ATP has been validated under Tier 2, the results can be used by other laboratories as long as it is applied to samples from the validated matrix type within the industrial subcategory, and as long as the other laboratories meet or exceed all of the method's QC acceptance criteria. If the ATP is to be applied to another matrix type, the modification should be validated separately on that matrix type.

4.2.3 Tier 3 Validation Studies for Wastewater

The primary intent of Tier 3 is to allow nationwide use of an ATP by all regulated entities and laboratories for all matrix types. Tier 3 validation studies are performed in a minimum of nine laboratories, each with a different matrix type, for a total of nine samples. Suggested sample matrix types that should be used in the validation study are given in Table 5.

Table 5. Matrix Types Recommended for Multiple Matrix Type Validation Studies

1.	Effluent from a POTW
2.	ASTM D 5905 - 98 (Reapproved 2013), *Standard Specification for Substitute Wastewater*
3.	Sewage sludge, if sludge will be in the permit
4.	ASTM D 1141 - 98 (Reapproved 2013), *Standard Specification for Substitute Ocean Water*, if ocean water will be in the permit
5.	Untreated and treated wastewaters up to a total of nine matrix types (see https://www.epa.gov/eg/industrial-effluent-guidelines for a list of industrial categories with existing effluent guidelines)
	At least one of the above wastewater matrix types should have at least one of the following characteristics: • Total suspended solids (TSS) greater than 40 mg/L • Total dissolved solids (TDS) greater than 100 mg/L • Oil and grease greater than 20 mg/L • NaCl greater than 120 mg/L • $CaCO_3$ greater than 140 mg/L

4.3 Detailed Procedures for Conducting Validation Studies

When validating ATPs, laboratories must adhere to the standardized QC operations and criteria detailed in the EPA-approved reference method (or other EPA-specified document) and incorporate these operations and criteria into the ATP. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix G of this document. QC acceptance criteria for other classes of analytes (e.g., pesticides) are often published in the reference method or in other EPA documents.

Laboratories should use both a reference matrix (usually reagent water) and field samples for the validation study. For multi-lab validation studies (e.g., Tiers 2 and 3), the applicant is responsible for ensuring that each laboratory in the study fulfills the validation study design specifications detailed in Sections 4.3.2 to 4.3.11 and provides all of the data that support the ATP application. However, it is important that the validation study accurately reflect the ruggedness of the ATP and any limitations regarding clarity of the ATP procedures. Therefore, a vendor or other applicant to should not directly assist laboratories participating in the validation study with implementation of the ATP methodology or equipment during the course of the study (e.g., the vendor or applicant may provide training and advice to participant laboratories regarding the equipment or methodology *prior to* the start of the study, but the study samples are to be analyzed by the study participants under "routine" conditions). Direct participation by the vendor or applicant will compromise the results of the study. The applicant also is responsible for the **technical and statistical evaluation** of the validation study results in order to produce the validation study report.

4.3.1 Method Compilation

Prior to conducting a validation study, the applicant responsible for modifying the method should detail the full method in accordance with EPA's *Guidelines and Format for Methods to Be Proposed at 40 CFR Part 136 or Part 141* (Guidelines and Format document), EPA-821-B-96-003. The documented method

should be distributed to each laboratory participating in the validation study to ensure each laboratory is validating the same set of procedures.

4.3.2 Method Detection Limit Study

Each laboratory participating in the Tier 1, 2, or 3 validation study must perform a method detection limit (MDL) study in accordance with the procedure given at 40 CFR Part 136, Appendix B while using the procedures specified in the modified method. The final results for each MDL study aliquot must be provided by each laboratory in the validation study, along with the details of the spiking levels and MDL calculations, and each laboratory should keep the raw data that supports those MDL study results on file and available for review.

In order to successfully validate the ATP, each laboratory participating in the validation study must demonstrate that it can achieve an MDL that is less than or equal to the minimum level (ML) of the EPA-approved reference method, or less than 1/10 the regulatory compliance limit, whichever is greater. For approved methods that do not explicitly include ML values or other quantitation levels, consult Appendix G of this document for default ML targets.

The allowance for an MDL higher than that of the approved reference method, but that supports a regulatory compliance limit, recognizes that a method modification that overcomes interferences may not achieve an MDL that is as low as the MDL achieved by the reference method (or other EPA-specified document), but is potentially more valuable in allowing determination of the analyte(s) of interest at the regulatory compliance limit in a complex sample matrix.

4.3.3 Calibration

Each laboratory participating in the validation study must perform a calibration in accordance with the procedures specified in the ATP. Each participating laboratory must demonstrate that it can meet or exceed the calibration criterion and achieve an ML or other quantitation level that is specified in the EPA-approved reference method (or other EPA-specified document), or in the applicable regulations.

4.3.4 Initial Precision and Recovery

Each laboratory participating in the study must obviously perform initial precision and recovery (IPR) analyses using only the procedures specified in the method. The IPR test is performed by analyzing four replicates of reagent water spiked with the analytes of interest. This IPR test should be performed for both the ATP and the corresponding approved method.

In order to successfully validate the ATP, each participating laboratory must demonstrate that it can meet or exceed the IPR precision and recovery criteria given for the EPA-approved reference method (or other EPA-specified document) using both the ATP and the corresponding approved method.

4.3.5 Field Sample Collection and Analyses

After laboratories participating in the Tier 1, 2, or 3 validation study have successfully completed the IPR analyses, the method modification should be validated on the matrix type(s) chosen for the validation study. The numbers of analyses required are described below.

Samples of each matrix type should be properly collected in sufficient quantity to support the validation study. The volume required will vary by tier, and by the volume required in the analytical method or ATP. Because the composition of many treated effluents may vary over time, composite sampling

equipment may be used to minimize that temporal variability. When a regulation or a reference method specifies collecting grab samples for compliance monitoring, it still may be feasible to use composite sampling equipment to collect a bulk effluent sample for use in a validation study. Alternatively, multiple grab samples may be collected and combined to create a bulk sample of sufficient quantity to support the validation study.

Note: The validation study plan should describe the sample collection procedures that will be employed and the homogenization procedures that will be used to produce replicate aliquots of the bulk sample for distribution and/or testing by the study participants.

All field samples should be analyzed by the laboratory as received from the study coordinator to determine the background concentration of the target analyte prior to preparation of the MS and MSD aliquots. This will ensure that the MS and MSD aliquots are fortified at an appropriate concentration. That is, the MS/MSD pair shall be fortified with the target analyte a concentration equal to the regulatory limit, if the ATP is for use to demonstrate compliance with a specific permit, or at one to five times the background concentration of the sample, *whichever is higher*.

Note: Analyzing the field samples *before* preparing the MS/MSD aliquots may contradict the specific requirements in some reference methods that stipulate that the MS/MSD aliquots be prepared and analyzed in the same batch as the field samples. However, for the purposes of validating an ATP, it is essential that the MS/MSD aliquots generate meaningful data about the performance of the ATP in the matrix of interest.

4.3.5.1 Tier 1 - Single Matrix Type Validation Studies

In a Tier 1 - Single Matrix Type study performed to validate an ATP, the laboratory should determine the background concentration of an unspiked sample prior to analyzing an MS/MSD pair for the matrix type being tested, for a total of 3 field sample analyses (i.e., 1 background, 1 MS, and 1 MSD). The laboratory performing the validation study must demonstrate that it can meet or exceed the MS/MSD precision and recovery QC acceptance criteria given for the EPA-approved reference method (or other EPA-specified document). In all, Tier 1- single matrix type validation studies for ATPs will require, at minimum, analysis of 14 MDL samples (7 spiked samples and 7 method blanks), 4 IPR reagent water samples, 1 PT sample and 3 field samples (1 background, 1 MS and 1 MSD), for a total of 22 analyses.

4.3.5.2 Tier 1 - Multiple Matrix Type Validation Studies

In Tier 1 - Multiple Matrix Type studies performed to validate ATPs, the laboratory should determine the background concentration and analyze an MS/MSD pair for each matrix type being tested, up to a total of 9 matrix types. Since 3 field sample analyses are required for each matrix type (1 background, 1 MS, and 1 MSD), and between 1 and 9 matrix types may be tested, a Tier 1- Multiple Matrix Type validation study will require analysis of 6 - 21 field samples. The laboratory performing the study should demonstrate that it can meet or exceed the MS/MSD precision and recovery QC acceptance criteria given for the EPA-approved reference method (or other EPA-specified document) for *each* matrix type being tested. all, Tier 1- multiple matrix type validation studies for ATPs will require, at minimum, analysis of 14 MDL samples (7 spiked samples and 7 method blanks), 4 IPR reagent water samples, 1 PT sample and between 6 and 24 field sample analyses (1 background, 1 MS, and 1 MSD for each additional matrix type to a maximum of 8 additional matrix types). A Tier 1- multiple matrix type validation study will require a minimum of between 27 and 46 total analyses since between 2 and 8 additional matrix types may be tested.

4.3.5.3 Tier 2 Single Matrix Type Validation Studies

In a Tier 2 validation study, each of the 3 laboratories will determine the background concentration and analyze an MS/MSD pair for the field sample received. Because there are 3 laboratories, each of which performs 3 field sample analyses (1 background, 1 MS, and 1 MSD), Tier 2 validation studies will require analysis of 9 field samples in total. Each laboratory participating in the study should demonstrate that it can meet or exceed the MS/MSD precision and recovery QC acceptance criteria given for the EPA-approved reference method (or other EPA-specified document). Since there are 3 laboratories, each of which performs analysis of 14 MDL samples (7 spiked samples and 7 method blanks), 4 IPR reagent water samples, 1 PT sample and 3 field samples (1 background, 1 MS, and 1 MSD), Tier 2 validation studies will require a minimum of 66 total analyses.

4.3.5.4 Tier 3 Validation Studies

In a Tier 3 validation study, each of the 9 laboratories participating in the study will determine the background concentration and analyze an MS/MSD pair for the field sample received. Because there are a total of 9 laboratories, each performing 3 field sample analyses (1 background, 1 MS, and 1 MSD), a Tier 3 validation study will require analysis of 27 field samples in total. Each laboratory participating in the study should demonstrate that it can meet or exceed the MS/MSD precision and recovery QC acceptance criteria given for the EPA-approved reference method (or other EPA-specified document). Since there are nine laboratories, each of which performs analysis of 14 MDL samples (7 spiked samples and 7 method blanks), 4 IPR reagent water samples, 1 PT sample and 3 field samples (1 background, 1 MS, and 1 MSD), a Tier 3 validation study will require a minimum of 198 total analyses.

4.3.6 Ongoing Precision and Recovery

Each batch of samples that includes field samples, but not the IPR samples, must include an OPR sample. (As noted above, field samples are analyzed *after* each laboratory participating in the study has successfully completed the IPR analyses.) In order to successfully validate the ATP, each participating laboratory must demonstrate it can meet or exceed the OPR recovery criteria given in the EPA-approved reference method or other EPA-specified document.

4.3.7 Calibration Verification

The field samples discussed in Section 4.3.5 should be analyzed in a separate batch from the initial calibration sequence, so that calibration verification is performed. In order to successfully validate the ATP, each laboratory participating in a Tier 1, 2, or 3 validation study should verify calibration as described in the method. In order to successfully validate the ATP, each participating laboratory also should demonstrate it can meet or exceed the acceptance criteria given for the EPA-approved reference method (or other EPA-specified document) for calibration verification.

4.3.8 Method Blanks

Each laboratory that participates in a Tier 1, 2, or 3 validation study should prepare and analyze at least one method blank with the sample batch containing the matrix samples. The actual number of blank samples analyzed by each laboratory must meet or exceed the frequency specified in the method. In order to successfully validate the ATP, each participating laboratory should demonstrate it can meet or exceed the QC acceptance criteria for blanks that are specified in the reference method or other EPA-specified document.

4.3.9 Surrogate or Labeled Compound Recovery

For methods that use surrogates or labeled compounds, each laboratory participating in the Tier 1, 2, or 3 validation study should spike all field and QC samples with the surrogates/labeled compounds at the concentrations specified in the method. In order to successfully validate the ATP, each participating laboratory must demonstrate it can meet or exceed the surrogate or labeled compound recovery criteria specified in the EPA-approved reference method (or other EPA-specified document).

4.3.10 Absolute and Relative Retention Time

Each laboratory participating in a Tier 1, 2, or 3 validation study of a chromatographic method should determine the absolute and/or relative retention times of the analytes of interest where required by the method. To successfully validate the ATP, each participating laboratory should demonstrate that it can meet or exceed the absolute and relative retention time criteria that are specified in the EPA-approved reference method (or other EPA-specified document) if applicable.

4.3.11 New Analytes

As described in Section 1.3.3, EPA will allow the addition of new analytes to approved methods as method modifications under this protocol when required by a specific permit. Laboratories will be required to demonstrate acceptable method performance in accordance with the requirements summarized above for other Tier 1, 2, and 3 ATPs. In addition, laboratories are required either to develop QC acceptance criteria for the added analyte or demonstrate that the existing QC acceptance criteria can be met for the added analyte; see *Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater*.

4.3.12 Proficiency Testing Results

Each laboratory participating in a Tier 1, 2, or 3 validation study should include analysis of a proficiency testing (PT) sample obtained from an approved vendor. An example list of approved vendors can be found at: http://www.nelac-institute.org/ptproviders.php (other lists may exist as well). This PT sample will be analyzed in addition to each of the matrix types required to be analyzed as part of the validation study and will be analyzed as it is received from the vendor. The same PT sample or samples obtained from the same vendor with the same lot number or preparation batch number will be analyzed by all laboratories participating in the validation study.

The concentrations of the target analytes in the PT sample should be relevant to any regulatory limits associated with the matrix type(s) of interest. PT vendors that prepare samples for periodic Discharge Monitoring Report Quality Assurance (DMRQA) studies may be able to provide assistance with selection of concentrations for the PT samples.

The study coordinator will be responsible for obtaining the PT sample from the vendor, along with the certificate of analysis that specifies the certified value and acceptance limits for reporting results. The study coordinator will also be responsible for distributing the sample to the laboratories that will be performing the analyses for the validation study (or in the case of a Tier 1 study to the analyst responsible for performing the analyses) without providing them with the certificate of analysis (e.g., "blind" as to the expected results). The study coordinator is also responsible for informing each laboratory participating in the validation study (or in the case of a Tier 1 study, the analyst responsible for performing the analyses) that the sample is to be analyzed only once just as it is received and is not to be diluted or fortified for analysis as an MS/MSD pair. In addition, the study coordinator should include a copy the certificate of analysis as an addendum to the validation study report.

5.0 EPA REVIEW AND APPROVAL

5.1 EPA's Office of Water Review of ATP Applications

All requests for approval of ATPs must undergo review and approval by the approval organization listed in Table 1 of Section 3.1. Limited-use ATPs (Tier 1) will be approved by the EPA Regional ATP Coordinator. ATP applications for nationwide use (Tiers 2 and 3) will be approved through rulemaking. ATPs prepared under this protocol should demonstrate an improvement when compared to the EPA-approved reference method that offers one or more of the following advantages: better method sensitivity or selectivity, lower analytical costs, fewer matrix interference problems, improvement in laboratory productivity, or reduction in the amount of hazardous materials used and/or produced in the laboratory.

EPA's Office of Water (OW) will review all Tier 2 and Tier 3 nationwide use ATPs and will review limited-use (Tier 1) applications if requested by the EPA Regional Office or state agency. OW may be assisted in its technical review by contractor personnel. When a formal ATP application is received, it will be checked for completeness. If the documentation is incomplete, OW will contact the applicant and request missing documentation before proceeding with its review.

At a minimum, an application should include a completed ATP application form, the test procedure in EPA standard format, and the method comparison table, before OW will review the package. If these elements are present, OW will assess the application to determine if the modification falls within the flexibility provided at 40 CFR 136.6. If the modification falls within the flexibility provided at 40 CFR 136.6 the application will be returned to the applicant with no further action. If the modification does not fall within the flexibility provided, then a full ATP validation is required.

Once all elements of the ATP application are present, including the validation study report and supporting data, OW will begin its internal review of the ATP for scientific merit, consistency, and appropriateness. The internal review may involve multiple programs and workgroups. Should any problems or questions arise during the review, OW or its technical support contractor will communicate with the applicant to resolve outstanding issues. Depending on the circumstances, OW may return the application to the applicant for revision. OW review of ATP applications will involve the three steps briefly described below.

The first step of OW's technical review will evaluate the description of the alternate method and method comparison table, and assess the ATP's applicability for approval at 40 CFR 136. If the alternate method is not applicable to 40 CFR 136 and/or the method description or method comparison table are not acceptable, OW will notify the applicant and describe the basis for rejection of the application. If this information is acceptable, the evaluation will proceed.

In the second step of OW's review, the performance of the ATP is compared to the performance of the corresponding EPA-approved method. At a minimum, results produced using the ATP must meet the QC acceptance criteria of the corresponding reference method (for methods addressing non-method-defined parameters) or demonstrate that there are no systematic differences in performance between the ATP and the corresponding EPA-approved method (for methods addressing method-defined parameters). If method performance is acceptable, the review will continue.

As the third and final step, OW will perform a detailed audit of the alternate method test data. The evaluation of test data in applications can be accomplished more quickly if machine-readable files of test data (and analysis software where different from EPA software) are provided with the application. Data files should be in a PC-compatible format, suitable for input directly into statistical analysis software.

Note: Although EPA will review the data from the validation study and conduct its own statistical test on the study results, the applicant is responsible for the technical and statistical evaluation of the validation study results *prior to* submitting the study report.

5.2 Approval Recommendation

EPA will complete its review and notify the applicant of its approval recommendation as expeditiously as practicable after receipt of an application containing the information necessary for EPA's evaluation. For limited-use applications (Tier 1), the Regional ATP Coordinator will notify the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. The EPA Region will issue the formal approval for use of the Tier 1 ATP. The approval may be restricted to use only with respect to a specific discharge or facility (and its laboratory) or, at the discretion of the Regional ATP Coordinator, to all dischargers or facilities (and their associated laboratories) specified in the approval for the Region.

For all nationwide use ATP applications for use in Clean Water Act programs (Tiers 2 or 3), OW will notify the applicant of EPA's recommendation, and if the ATP is recommended for approval, will initiate the rulemaking process through which the ATP is formally approved by the EPA Administrator.

5.3 Rulemaking Process

EPA periodically updates the lists of analytical methods approved for Clean Water Act compliance monitoring at 40 CFR 136 to provide increased flexibility to the regulated community and laboratories in their selection of analytical methods for use in Clean Water Act programs. EPA also uses these periodic "method update rules" (MURs) to formalize the approval status of nationwide ATPs which have been positively reviewed. Using the method information provided with the ATP application to develop the justification and record support, EPA will prepare the proposed rule for approval of wastewater methods, compile the rule docket, pass the proposed rule through internal and/or external review at EPA, and submit it to the Office of the Federal Register (OFR) for publication. *Preparation, approval, and publication of a proposed rule generally requires a minimum of nine months, but may take longer, depending on the number of methods involved in the rulemaking effort.* When published, the proposed rule requests public comment and allows a specified comment period. At the end of the comment period, EPA may forward any significant comments to the ATP applicant with a request that they provide technical assistance to EPA in drafting responses to comments. All comments that have scientific or legal merit, or raise substantive issues with the proposed rule, must be answered to complete the rulemaking process.

EPA will review any technical responses provided by the applicant and complete the response-to-comments document for the final rule. EPA will then prepare the final rule, compile the rule docket, and submit the final rule to the OFR for publication. The final rule will state the date that the rule becomes effective, typically 30 days after rule publication. As of this effective date, the method is approved by EPA and will be included in the appropriate table(s) at 40 CFR 136 in the next CFR update. *It generally requires a minimum of fifteen months, but may take longer, after the proposed rule is published to receive and respond to comments, prepare and process the final rule through internal EPA review, and publish the final rule in the Federal Register.*

6.0 REFERENCES

1. ASTM, 1994. *Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water.* Designation D-2777-13. *Annual Book of ASTM Standards,* Vol. 11.04.

2. Youden, W.J. and E.H. Steiner, 1975. *Statistical Manual of the AOAC.* AOAC- International. 1111 N. 19th Street; Suite 210, Arlington, VA 22209.

3. Wernimont, G.T., 1985. *Use of Statistics to Develop and Evaluate Analytical Methods.* AOAC-International.

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

5. USEPA, 1999. *Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water*. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-98-003.

6. USEPA, 1999. *Protocol for EPA Approval of Alternate Test Procedures for Organic and Inorganic Analytes in Wastewater and Drinking Water.* U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-98-002.

7. USEPA, 2018. *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program*. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-001.

APPENDIX A SAMPLE ATP APPLICATION FORM

EPA Office of Water Alternate Test Procedure Application Form for Chemical Analytes			
Applicant Name and Address:			***EPA Use Only* ATP Case No.**
Date Application Submitted:			
Alternate Test Procedure: *(Method number & title*)			
Alternate to Approved Method:			
EPA-Approved Reference Method used for Comparison:			
Analyte(s):		**Is this a Method-Defined Parameter (Yes/No)?**	
Type (WW, DW, or WW/DW):			
Level of Use: (Limited Use or Nationwide Use)		**Validation Tier: (1, 2 or 3)**	
FOR LIMITED-USE APPLICATIONS ONLY:			
ID number of existing or pending permit:			
Issuing agency:			
Type of permit:			
Discharge serial number:			
ATTACHMENTS: Each item below includes a reference to the section of the ATP protocol that describes the material in detail			
____ **Justification for ATP *(Sec. 3.2.1)***			
____ **Alternate Test Procedure (Method in standard EPA format) *(Sec. 3.2.2)***			
____ **Method Comparison Table *(Sec. 3.2.3)***			
____ **Validation Study Plan *(Appendix E)***			
____ **Validation Study Report *(Sec. 3.2.4)***			
____ **Method Information and Documentation for Preamble and Docket *(Sec. 3.2.5)***			
____ **Other** _____			
Submit Application and Attachments in Triplicate			

APPENDIX B DATA COLLECTION CERTIFICATION

It is the expectation of the ATP program that all data will be collected as outlined in the validation study plan. If a data set needs to be recollected (e.g., QC failure, instrument failure, matrix effects etc.) this should be clearly be documented in the final report and the initial data along with the recollected data should be submitted. It is not permissible to collect multiple data sets and submit the "best one". Occasionally, blind samples (performance evaluation samples) will be distributed by the ATP program to assess method performance. Successful analysis of these samples will be required as part of the candidate method approval process. Laboratory fraud is a serious issue and 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 as outlined in the validation study plan.

_____

Applicant (print name)

_____ _____

Applicant (signature) **(Date)**

Questions, comments or applications should be directed to:

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Note: The names and addresses in this list are current as of the date of this document, and are subject to change. Please consult with the individual EPA Regional Office for the current ATP contact.

APPENDIX D STANDARD EPA METHOD FORMAT

The following is a listing of the 17 elements of the standard EPA method format. Applicants should consult the Guidelines and Format document (USEPA, 1996, Reference 4 in Section 6 of the main body of this document) for a detailed description of the required content for each section and other formatting guidelines and conventions.

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 at the end of the method. Refer to the specific section number of the glossary.

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 are described in this section. For each QC analysis, the complete analytical procedure, the frequency of required analyses, and interpretation of results are specified.

10.0 Calibration and Standardization

This section describes the method/instrument calibration and standardization process, and 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, and equations and definitions of constants used to calculate final sample analysis results.

13.0 Method Performance

This section provides method performance criteria for the method, including precision/bias statements regarding detection limits and source/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. Note: Each method should be a free-standing document, providing all information necessary for the method user to perform the method may be found. 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 total within the method.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

This section contains all method tables and figures (diagrams and flowcharts), and may contain validation data referenced in the body of the method.

APPENDIX E Validation Study Plan and Study Report

1.1 Development of a Validation Study Plan

Prior to conducting Tier 1, 2, or 3 validation studies, the ATP applicant (e.g., the organization responsible for conducting the study) should prepare and submit a detailed study plan. As noted earlier, for ATPs that measure method-defined parameters, a detailed validation study plan should be submitted and agreed upon prior to conducting the study (see Appendix H). For Tier 1 ATP validation studies involving analytes which are not method-defined, development of a validation study plan is not required, though it is recommended.

The validation study plan should contain the elements described in Sections 1.1.1 through 1.1.6.

1.1.1 Background

The Background section of the validation study plan should:

- Identify the ATP method as a modification of an approved method
- Identify intended use of the ATP method (Tier 1, Tier 2 or Tier 3)
- Include a summary of the ATP method
- Cite the organization and method number (given in 40 CFR Parts 136 or 405 - 503) for the approved method (e.g., EPA Method 353.1)
- Describe the reasons for and extent of the modification, the logic behind the technical approach to the modification, and the result of the modification
- Identify the matrices, matrix types, and/or media to which the ATP method is believed to be applicable
- List the analytes measured by the ATP method including corresponding CAS Registry numbers (if applicable)
- Indicate whether any, some, or all known metabolites, decomposition products, or known commercial formulations containing the analyte are included in the measurement. For example, a method designed to measure acid herbicides should include the ability to measure the acids and salts of these analytes; a total metals method should measure total metals.

1.1.2 Objectives

The Objectives section of the validation study plan should describe overall objectives and data quality objectives of the study.

1.1.3 Study Management

The Study Management section of the validation study plan should:

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

1.1.4 Technical Approach

The Technical Approach section of the validation study plan should:

- Indicate at which tier the study will be performed
- Describe the approach that will be followed by each organization involved in the study
- Describe how sample matrices and participating laboratories will be selected

- Explain how samples will be collected and distributed
- Specify the numbers and types of analyses to be performed by the participating laboratories
- Describe how analyses are to be performed

1.1.5 Data Reporting and Evaluation

This 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.

1.1.6 Limitations

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

1.2 Validation Study Report

Applicants responsible for developing ATPs at Tiers 1, 2, or 3 should document the results of the validation study in a formal validation study report that contains the elements described in this section and presents these elements in the same order 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 ATP.

The information and supporting data required in the validation study report should be sufficient to enable EPA to support a claim of acceptable performance of a method modification. If data are collected by a contract laboratory, the organization responsible for using the method (e.g., permittee, POTW, or other regulated entity) is responsible for ensuring that all method-specified requirements are met by the contract laboratory and that the validation study report contains all required 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. If a validation study plan was prepared, it 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 in implementing the study.

The validation study report should contain a signed Data Collection Certification form (see Appendix B of this document) and the elements described in Sections 1.2.1 through 1.2.10 below.

1.2.1 Background

The Background section of the validation study report should describe the method modification that was validated and identify the organization responsible for developing the ATP. The background section of the validation study report should:

- Include a method summary
- Cite the organization and method number and title for the ATP
- Cite the method number (given in 40 CFR Part 136) of the approved method that is being modified
- Cite the method number (given in 40 CFR Part 136) of the EPA-approved reference method that is being used to demonstrate acceptable ATP performance
- Describe the reasons for and extent of the modification, the logic behind the technical approach to the modification, and the result of the modification
- Identify the matrices, matrix types, and/or media to which the modified method is intended to apply

- List the analytes measured by the modified method including corresponding CAS Registry numbers (Alternatively, this information may be provided on the data reporting forms in the Supporting Data appendix to the validation study report.)
- Indicate whether any, some, or all known metabolites, decomposition products, or known commercial formulations containing the analyte are included in the measurement. (For example, a method designed to measure acid herbicides should include the ability to measure the acids and salts of these analytes.)
- State the purpose of the study.

1.2.2 Study Design and Objectives

The Study Design and Objectives section of the validation study report should describe the study design, and identify overall objectives and data quality objectives of the study. Any study limitations should be identified. The validation study plan may be appended to the validation study report to provide the description of the study design. If no validation study plan was prepared, the study design should be described in this section (see *Section 4.3, Detailed Procedures for Conducting Validation Studies,* in the main body of this document for required elements of the study design).

1.2.3 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 organization that was responsible for managing the study
- Identify the laboratories, facilities, and other organizations that participated in the study; describe how those participants were selected; and explain the role of each organization involved in the study
- Indicate at which Tier level the study was performed
- Delineate the study schedule that was followed
- Describe how sample matrices were chosen, including a statement of compliance with Tier specific validation study specifications for matrix type selection
- Explain how samples were collected and distributed
- Specify the numbers and types of analyses performed by the participating laboratories
- Describe how analyses were performed
- Identify any problems encountered or deviations from the study plan and their resolution/impact on study performance and/or results

1.2.4 Data Reporting and Validation

This section of the validation study report should describe the procedures that were used to report and validate study data. While EPA does not require the use of a standard format for analytical data submission, a validation study data reporting form may be found in Appendix F of this document.

1.2.5 Results

This section of the validation study report presents the study results. Raw data and example calculations are required as part of the results and shall be included in an appendix to the validation study report (see Section 1.2.10 below).

1.2.6 Data Analysis/Discussion

This section of the validation study report should provide a statistical analysis and discussion of the study results. The discussion should address any discrepancies between the results and the QC acceptance criteria of the EPA-approved reference method.

1.2.7 Conclusions

The Conclusions 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).

1.2.8 Appendix A - The Method Compilation

A written version of the modified method prepared in accordance with EPA's Guidelines and Format document, should be appended to the validation study report (see Reference 4 in Section 6 of the main body of this document).

1.2.9 Appendix B - Validation Study Plan

If a validation study plan was prepared, it should be appended to the validation study report.

1.2.10 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.

1.2.10.1 Raw Data

The Results section of the validation study report should be supported by an appendix containing all raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory. This verification consists of tracing the instrument output (peak height, area, or other signal intensity) to the final result reported. Raw data are method-specific and may include any of the following:

- Sample numbers or other identifiers used by the both the ATP applicant and the laboratory(ies) that participated in the study
- Sample preparation (extraction/digestion) dates
- Analysis dates and times
- Sequence of analyses or run logs
- Sample volume
- Extract volume prior to each cleanup step
- Extract volume after each cleanup step
- Final extract volume prior to injection
- Digestion volume
- Titration volume
- Percent solids or percent moisture
- Dilution data, differentiating between dilution of a sample and dilution of an extract or digestate
- Instrument(s) and operating conditions
- GC and/or GC/MS operating conditions, including detailed information on
  - Columns used for determination and confirmation (column length and diameter, stationary phase, solid support, film thickness, etc.)
  - Analysis conditions (temperature programs, flow rates, etc.)
  - Detectors (type, operating conditions, etc.)
- Chromatograms, ion current profiles, bar graph spectra, library search results
- Quantitation reports, data system outputs, and other data to link the raw data to the results reported. (Where these data are edited manually, explanations of why manual intervention was necessary should be included)

- Direct instrument readouts; i.e., strip charts, printer tapes, etc., and other data to support the final results
- Laboratory bench sheets and copies of all pertinent logbook pages for all sample preparation and cleanup steps, and for all other parts of the determination

Raw data are required for all samples, calibrations, verifications, blanks, matrix spikes and duplicates, and other QC analyses required by the EPA-approved reference method. Data should be organized so that an analytical chemist can clearly understand how the analyses were performed. The names, titles, addresses, and telephone numbers of the analysts who performed the analyses and of the quality assurance officer who will verify the analyses should be provided. For instruments involving data systems (e.g., GC/MS), raw data should be made available in appropriate electronic formats upon request.

1.2.10.2 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. Useful examples include both detected compounds and undetected compounds. If the laboratory or the method employs a standardized reporting level for undetected compounds, this should be made clear in the example, as should adjustments for sample volume, dry weight (solids only), etc.

APPENDIX F SAMPLE DATA REPORTING FORM

This appendix provides an example data reporting form. The form illustrates those aspects of data reporting which are expected, regardless of the specific format used; specifically, data should be presented in a clear and logical format, and should be labeled clearly.

In addition to using an appropriate data reporting format, submitting the data in an appropriate electronic format can be very helpful in expediting the review of an ATP. Data files should be in PC-compatible format, suitable for input directly into statistical analysis software.

Sample ATP Data Reporting Form[1]

ATP Method Title*		Revision Date	__/__/__

*Include Method Number and Revision Number

Please record all data and quality control (QC) performance results (for comparison against QC acceptance criteria) from your validation study using this data form. If you have additional data, please attach it to this form in a tabular format, being sure to label all columns and rows clearly.

For Tier 1 Studies (Single-Laboratory Use): Complete **1** form for each matrix type
For Tier 2 (Nationwide Use; Single Matrix) or Tier 3 (Nationwide Use; Multiple Matrices): Complete **1** form for each participant laboratory.

Linear Calibration Data

Units of Concentration:_____ Units of Response: _____ Number of Points:_____

Analyte Conc.							
Response							
RF/CF/RR*							

*Response Factor/Calibration Factor/Relative Response

Method Detection Limit (MDL) Data

Spiking Concentration used for MDL Study (include units): _____

MDL Data							

Initial Precision Recovery (IPR) Data

Spiking Concentration used for IPR Study (include units): _____

IPR Data				

Matrix Spike / Matrix Spike Duplicate (MS/MSD) Data

Spiking Concentration used for MS/MSD Study (include units): _____

MS Concentration	
MSD Concentration	
Background Concentration	

ATP QC Performance Results

Calibration		Spike	IPR Recovery and Precision			OPR Data Precision		MS/MSD Recovery and RPD			MDL/ML	
Points	Lin	Conc	Low	High	Precision	Low	High	Low	High	RPD	MDL	ML

[1] For multi-analyte methods, present additional Data and QC acceptance criteria for each analyte in a tabular format, making sure to include proper labels, and attach to this form.

APPENDIX G QUALITY CONTROL ACCEPTANCE CRITERIA

Table G1 Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1B

No	Analyte- Detector	Reference Method	Spike conc.	Calibration points	Linearity	Specification								
						IPR			OPR		MS/MSD			
						% Recovery and Precision			% Recovery		% Recovery		RPD	ML
						Low	High	SD	Low	High	Low	High		
1.	Aluminum - Flame	202.1	500 µg/L	3	10 %	81	117	18	79	119	79	119	20	15 µg/L
	" - Furnace	202.2	500 µg/L	5	25 %	71	127	28	68	130	68	130	31	20 µg/L
	" - ICP	200.7	500µg/L	3	10 %	81	121	20	79	123	79	123	22	50 µg/L
2.	Ammonia - distill													
	" - Nessler	350.2	1 mg/L	3	10 %	81	121	20	79	123	79	123	22	50 µg/L
	" - Titr	350.2	1 mg/L	3	10 %	73	129	28	70	132	70	132	31	1.0 mg/L
	" - ISE	350.3	1 mg/L	3	10 %	79	127	24	77	129	77	129	26	30 µg/L
	" - Phenate	350.1	1 mg/L	1	---	87	115	14	86	116	86	116	15	10 µg/L
3.	Antimony - Flame	204.1	1 mg/L	1	---	77	117	20	75	119	75	119	22	1.0 mg/L
	Antimony - Furnace	204.2	200 µg/L	5	25 %	70	118	24	68	120	68	120	26	20 µg/L
	Antimony - ICP	200.7	200 µg/L	3	10 %	71	121	25	68	124	68	124	28	20 µg/L
4.	Arsenic													
	" - Hydride	206.3	100 µg/L	3	10 %	71	127	28	68	130	68	130	31	2.0 µg/L
	" - Furnace	206.2	100 µg/L	3	10 %	82	118	18	80	120	80	120	20	5.0 µg/L
	" - ICP	200.7	100 µg/L	3	10 %	73	129	28	70	132	70	132	31	20 µg/L
	" - Color (SDDC)	206.4	40 µg/L	3	10 %	72	128	28	69	131	69	131	31	10 µg/L
5.	Barium - Flame	208.1	1 mg/L	3	10 %	97	101	2.0	97	101	97	101	2.2	1.0 mg/L
	" - Furnace	208.2	1 mg/L	5	25 %	82	122	20	80	124	80	124	22	10 µg/L
	" - ICP	200.7	1 mg/L	3	10 %	90	110	10	89	111	89	111	11	2 µg/L
6.	Beryllium - Flame	210.1	100 µg/L	3	10 %	85	109	12	84	110	84	110	13	50 µg/L
	" - Furnace	210.2	50 µg/L	5	25 %	79	119	20	77	121	77	121	22	1.0 µg/L
	" - ICP	200.7	100 µg/L	3	10 %	79	119	20	77	121	77	121	22	1.0 µg/L
7.	Boron - Color	212.3	240 µg/L	5	25 %	54	146	46	49	151	49	151	51	100 µg/L
	" - ICP	200.7	1 mg/L	3	10 %	76	126	25	74	128	74	128	27	10 µg/L
8.	Bromide	320.1	2.8 mg/L	3	10 %	70	122	26	67	125	67	125	29	2 mg/L
9.	Cadmium - Flame	213.1	100 µg/L	3	10 %	88	110	11	87	111	87	111	12	50 µg/L
	Cadmium - Furnace	213.2	100 µg/L	3	10 %	84	114	15	83	115	83	115	16	0.5 µg/L
	Cadmium - ICP	200.7	100 µg/L	3	10 %	84	118	17	83	119	83	119	18	2 µg/L
10.	Calcium - Flame	215.1	200 µg/L	3	10 %	82	120	19	80	122	80	122	21	200 µg/L
	Calcium - ICP	200.7	10 mg/L	3	10 %	86	120	17	84	122	84	122	19	20 µg/L
	Calcium - Titr	215.2	10 mg/L	3	10 %	84	124	20	82	126	82	126	22	2 mg/L
11.	Chloride - Titr/Hg	325.3	100 mg/L	3	10 %	92	108	7.6	92	108	92	108	8.4	---
	Chloride - Auto	325.1	100 mg/L	3	10 %	93	109	8.2	82	110	82	110	9.0	1 mg/L
12.	Chlorine - Ampere	330.1	1 mg/L	3	10 %	79	115	18	77	117	77	117	20	---
	Chlorine - Iodo	330.3	1 mg/L	5	25 %	78	116	19	76	118	76	118	21	0.1 mg/L
	Chlorine - Back titr	330.2	1 mg/L	3	10 %	68	124	28	65	127	65	127	31	---
	Chlorine - DPD-FAS	330.4	1 mg/L	3	10 %	79	119	20	77	121	77	121	22	0.1 mg/L
	Chlorine - Spectro	330.5	1 mg/L	3	10 %	82	120	19	80	122	80	122	21	0.2 mg/L
13.	Chromium VI - AA	218.4	100 µg/L	3	10 %	84	112	14	83	113	83	113	15	10 µg/L
14.	Chromium - Flame	218.1	100 µg/L	3	10 %	67	123	28	64	126	64	126	31	15 µg/L
	Chromium - Furnace	218.2	100 µg/L	3	10 %	83	117	17	82	118	82	118	18	5 µg/L
	Chromium - ICP	200.7	100 µg/L	3	10 %	84	118	17	82	119	82	119	18	10 µg/L
15.	Cobalt - Flame	219.1	500 µg/L	3	10 %	85	113	14	84	114	84	114	15	500 µg/L
	Cobalt - Furnace	219.2	100 µg/L	3	10 %	85	113	14	83	115	83	115	16	5 µg/L
	Cobalt - ICP	200.7	100 µg/L	3	10 %	86	116	15	84	118	84	118	17	5 µg/L
16.	Copper - Flame	220.1	100 µg/L	3	10 %	90	110	10	89	111	89	111	11	100 µg/L
	Copper - Furnace	220.2	100 µg/L	5	25 %	86	112	13	84	114	84	114	15	5 µg/L
	Copper - ICP	200.7	100 µg/L	3	10 %	86	116	15	84	118	84	118	17	10 µg/L
17.	Cyanide - Spectro	335.2	250 µg/L	3	10 %	65	129	32	62	132	62	132	35	60 µg/L

Table G1 Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1B

No	Analyte- Detector	Reference Method	Spike conc.	Calibration points	Linearity	Specification								ML
						IPR			OPR		MS/MSD			
						% Recovery and Precision			% Recovery		% Recovery		RPD	
						Low	High	SD	Low	High	Low	High		
18.	Fluoride - Elec/man	340.2	1 mg/L	3	10 %	85	115	15	84	116	84	116	16	100 µg/L
	Fluoride - SPADNS	340.1	1 mg/L	3	10 %	79	127	24	77	129	77	129	26	100 µg/L
	Fluoride - Auto	340.3	1 mg/L	3	10 %	87	117	15	85	119	85	119	17	50 µg/L
19.	Hardness - Color/auto	130.1	100 mg/L	3	10 %	93	109	8. 4	92	110	92	110	9.2	10 mg/L
	Hardness - Titr/EDTA	130.2	100 mg/L	3	10 %	93	107	7.2	92	108	92	108	7.9	30 mg/L
20.	pH - Electrode	150.1	N/A	2	---			2.2					2.4	N/A
21.	Iron - Flame	236.1	500 µg/L	3	10 %	87	113	13	86	114	86	114	14	300 µg/L
	Iron - Furnace	236.2	100 µg/L	5	25 %	80	124	22	78	126	78	126	24	5 µg/L
	Iron - ICP	200.7	500 µg/L	3	10 %	88	116	14	86	118	86	118	16	100 µg/L
22.	TKN - Digest	351.3	2 mg/L	5	25 %	49	153	52	44	158	44	158	57	50 µg/L
	TKN - Titr	351.3	5 mg/L	3	10 %	82	118	18	80	120	80	120	20	50 µg/L
	TKN - Nessler	351.3	5 mg/L	5	25 %	78	122	22	76	124	76	124	24	50 µg/L
	TKN - Electrode	351.3	5 mg/L	5	25 %	69	129	30	66	132	66	132	33	50 µg/L
	TKN - Phenate	351.1	5 mg/L	5	25 %	78	122	22	76	124	76	124	24	50 µg/L
	TKN - Block/color	351.2	5 mg/L	3	10 %	79	119	20	77	121	77	121	22	100 µg/L
23.	Lead - Flame	239.1	300 µg/L	3	10 %	87	113	13	86	114	86	114	14	40 µg/L
	Lead - Furnace	239.2	100 µg/L	3	10 %	84	116	16	82	118	82	118	18	5 µg/L
	Lead - ICP	200.7	300 µg/L	3	10 %	84	118	17	82	120	82	120	19	20 µg/L
24.	Magnesium - Flame	242.1	2 mg/L	3	10 %	83	115	16	81	117	81	117	18	20 µg/L
	Magnesium - ICP	200.7	2 mg/L	3	10 %	84	120	18	82	122	82	122	20	50 µg/L
25.	Manganese - Flame	243.1	100 µg/L	3	25 %	86	112	13	85	113	85	113	14	100 µg/L
	Manganese - Furnace	243.2	100 µg/L	3	10 %	83	113	15	81	115	81	115	17	1 µg/L
	Manganese - ICP	200.7	100 µg/L	3	10 %	86	114	14	84	116	84	116	16	2 µg/L
26.	Mercury - CV/Man	245.1	4 µg/L	5	25 %	84	126	26	71	129	71	129	29	0.2 µg/L
	Mercury - CV/Auto	245.2	4 µg/L	3	10 %	77	121	22	75	123	75	123	24	0.2 µg/L
27.	Molybdenum - Flame	246.1	300 µg/L	3	10 %	67	131	32	64	134	64	134	35	300 µg/L
	Molybdenum - ICP	200.7	100 µg/L	3	10 %	80	118	19	78	120	78	120	21	10 µg/L
28.	Nickel - Flame	249.1	100 µg/L	3	10 %	83	117	17	81	119	81	119	19	0.2 µg/L
	Nickel - Furnace	249.2	100 µg/L	3	10 %	84	116	16	83	117	83	117	17	5 µg/L
	Nickel - ICP	200.7	100 µg/L	3	10 %	82	120	19	80	122	80	122	21	20 µg/L
29.	Nitrate	352.1	1 mg/L	5	25 %	77	125	24	75	127	75	127	26	0.1 mg/L
30.	NO_2-NO_3 - Cd/Man	353.3	1 mg/L	3	10 %	79	119	20	77	121	77	121	22	10 µg/L
	NO_2-NO_3 - Cd/Auto	353.2	1 mg/L	3	10 %	88	110	11	87	111	87	111	12	50 µg/L
	NO_2-NO_3 - Cd/Hydra	353.1	1 mg/L	3	10 %	88	110	11	87	111	87	111	12	10 µg/L
31.	*o*-Phosphate - Auto	365.1	300 µg/L	3	10 %	86	112	13	84	114	84	114	15	10 µg/L
	o-Phosphate - Man	365.2	300 µg/L	3	10 %	89	113	12	87	115	87	115	14	10 µg/L
32.	DO - Winkler	360.2	1 mg/L	3	10 %	98	102	2.0	98	102	98	102	2.2	50 µg/L
	DO - Electrode	360.1	1 mg/L	3	10 %	98	102	2.0	98	102	98	102	2.2	50 µg/L
33.	Phenol - Color/Man	420.1	500 µg/L	3	10 %	59	123	32	56	126	56	126	35	5 µg/L
	Phenol - Color/Auto	420.2	500 µg/L	3	10 %	41	121	40	37	125	37	125	44	2 µg/L
34.	Phosphorus - Asc/Man	365.2	1 mg/L	3	10 %	82	112	15	81	113	81	113	16	10 µg/L
	Phosphorus - Asc/Man	365.3	1 mg/L	3	10 %	79	115	18	77	117	77	117	20	10 µg/L
	Phosphorus - Asc/Auto	365.1	1 mg/L	3	10 %	81	111	15	80	112	80	112	16	10 µg/L
	Phosphorus - Block	365.4	1 mg/L	3	10 %	80	112	16	79	113	79	113	17	10 µg/L
35.	Potassium - Flame	258.1	10 mg/L	3	10 %	84	116	16	82	118	82	118	18	100 µg/L
	Potassium - ICP	200.7	10 mg/L	3	10 %	82	120	19	80	122	80	122	21	1 mg/L
36.	Selenium - Furnace	270.2	100 µg/L	3	10 %	77	117	20	75	119	75	119	22	5 µg/L
	Selenium - ICP	200.7	300 µg/L	5	25 %	80	120	20	78	122	78	122	22	50 µg/L
37.	Silica - Color/Man	370.1	5 mg/L	3	10 %	64	120	28	61	123	61	123	31	2 mg/L
	Silica - ICP	200.7	1 mg/L	5	25 %	-82	190	136	-96	204	-96	204	150	50 µg/L

Table G1 Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1B

No	Analyte- Detector	Reference Method	Spike conc.	Calibration points	Linearity	Specification								
						IPR			OPR		MS/MSD			
						% Recovery and Precision			% Recovery		% Recovery		RPD	ML
						Low	High	SD	Low	High	Low	High		
38.	Silver - Flame	272.1	100 µg/L	3	10 %	88	112	12	86	114	86	114	14	100 µg/L
	Silver - Furnace	272.2	100 µg/L	3	10 %	83	115	16	82	116	82	116	17	1 µg/L
	Silver - ICP	200.7	100 µg/L	3	10 %	83	117	17	82	118	82	118	18	5 µg/L
39.	Sodium - Flame	273.1	30 µg/L	3	10 %	90	116	13	88	118	88	118	15	30 µg/L
	Sodium - ICP	200.7	10 mg/L	3	10 %	86	122	18	85	123	85	123	19	100 µg/L
40.	Sulfate - Color/Auto	375.1	50 mg/L	3	10 %	83	115	16	82	116	82	116	17	10 mg/L
	Sulfate - Grav	375.3	50 mg/L	3	10 %	85	113	14	83	115	83	115	16	10 µg/L
	Sulfate - Turbid	375.4	50 mg/L	3	10 %	83	115	16	81	117	81	117	18	1 mg/L
41.	Surfactants	425.1	3 mg/L	3	10 %	83	119	18	81	121	81	121	20	25 µg/L
42.	Thallium - Flame	279.1	100 µg/L	3	10 %	85	115	15	83	117	83	117	17	600 µg/L
	Thallium - Furnace	279.2	100 µg/L	3	10 %	81	115	17	80	116	80	116	18	5 µg/L
	Thallium - ICP	200.7	100 µg/L	3	10 %	73	127	27	70	130	70	130	30	50 µg/L
43.	Tin - Flame	282.1	10 mg/L	3	10 %	83	109	13	32	110	32	110	14	10 mg/L
44.	Titanium - Flame	283.1	2 mg/L	3	10 %	85	115	15	84	116	84	116	16	2 mg/L
45.	Vanadium - Flame	286.1	2 mg/L	3	10 %	81	121	20	79	123	79	123	22	2 mg/L
	Vanadium - Furnace	286.2	200 µg/L	3	10 %	82	118	18	80	120	80	120	20	10 µg/L
	Vanadium - ICP	200.7	200 µg/L	3	10 %	87	113	13	86	114	86	114	14	10 µg/L
46.	Zinc - Flame	289.1	100 µg/L	3	10 %	87	113	13	85	115	85	115	15	50 µg/L
	Zinc - Furnace	289.2	100 µg/L	3	10 %	81	119	19	79	121	79	121	21	0.2 µg/L
	Zinc - ICP	200.7	100 µg/L	3	10 %	83	121	19	81	123	81	123	21	5 µg/L

Legend for acronyms and abbreviations in Table G1:

Reference Method:	QC acceptance criteria are for modifications to the reference method specified in Table IB.
Spike conc.	The concentration at which the QC acceptance criteria were determined.
Calibration points:	The number of points required for calibration
Linearity:	The relative standard deviation (RSD) of the calibration factor or response factor below which an averaged calibration factor or response factor may be used in place of a calibration curve. For an averaged response or calibration factor above this number, a calibration curve must be used. For reference methods that allow the use of a correlation coefficient (r) to judge linearity (e.g., more recent versions of Method 200.7), the same r value may be used in place of the RSD value listed in this table.
% Recovery:	The amount of analyte recovered expressed as a percent (applies to recovery entries for the IPR, OPR, and MS/MSD)
IPR and OPR recovery (low/high)	The lower and upper QC acceptance criteria for % recovery in the initial precision and recovery (IPR) test or the ongoing precision and recovery (OPR) test. For the IPR, these limits apply individually to the recovery in each aliquot, *not* to the mean recovery of all four aliquots.
SD:	The standard deviation (SD) of the four % recoveries in the IPR test.
MS/MSD recovery (low/high):	The lower and upper QC acceptance criteria for % recovery of the matrix spike and matrix spike duplicate
RPD:	The upper limit on the QC acceptance criterion for precision expressed as the relative percent difference (RPD) for the MS/MSD test. RPD = 100% x [*MS - MSD* / $^1/_2$(MS + MSD)]
ML value:	The minimum level (ML) is the concentration in a sample that is equivalent to the concentration of the lowest calibration point, taking into account all method-specified sample processing weights and volumes.

Table G2 Standardized QC, QC Acceptance Criteria, and Performance Data for Methods for Method-defined Analytes in 40 CFR Part 136, Table IB [1]

Analyte - Detector	Reference Method	Spike conc	Calibration		Calibration Verification		Precision and Recovery					Matrix Spike/Matrix Spike Duplicate (MS/MSD)			Detection or Quantitation Limit	Method Performance	
							Initial (IPR)			Ongoing (OPR)							
							Recovery (%)		Preci-sion	Recovery (%)		Recovery (%)		Preci-sion			
			# Pt	Linearity	Low	High	Low	High	RSD	Low	High	Low	High	RPD	ML	Rec (%)	RSD
Acidity - endpoint	SM 2310B	20 mg/L														100	9
Alkalinity - endpoint	SM 2320B	120 mg/L														93	4.2
BOD_5 - Iodometric	SM 5210B	300mg/L								56	76				LDL 2 mg/L	66	15.4
COD - Spectrophotometric	EPA 410.4	50 mg/L	3				90	110				90	110		Range 3 mg/L	93	14
Color - Spectrophotometric	NCASI 253	100 CU	6	R^2 >0.991	90	110	80	120	10	75	125				MDC 10 CU		
Hydrogen ion - Electrometric	SM 4500-H^+ B	7.3 pH													0.1 pH		SD 0.26 pH
Oil and grease-HEM - Gravimetry	EPA 1664A	40 mg/L	2		Note 2		83	101	11	78	114	78	114	18	5 mg/L	93	8.7
TOC - Persulfate-UV Oxidation	SM 5310C	10 mg/L														93	7
Total solids - Gravimetry	SM 2540B																SD 6.0
Total dissolved solids - Gravimetry	SM 2540C	293 mg/L															7.2
Total suspended solids - Gravimetry	SM 2540D	24 mg/L															10
Temperature - Thermometer	SM 2550B														0.1 °C		

Note 1. Some QC acceptance criteria may not be appropriate for some analytes in this table.

Note 2 Within ±10% of Class S weight at 2 mg and with ±0.5% at 1000 mg

APPENDIX H METHOD-DEFINED PARAMETERS (MDPs)

This appendix provides the recommended validation requirements associated with ATPs for a method-defined parameter (MDP). As noted throughout the main document, these details are provided in this appendix to distinguish the validation requirements for ATPs for MDPs more clearly from the validation requirements of ATPs for the more traditional analytes.

1.1 Definition of a Method-defined Analyte or Parameter

As defined at 40 CFR 136.6 and noted in Section 1.3.4 in the main body of this document, the term *"method-defined analyte"* means an analyte (or parameter) that is defined solely by the method used to determine the analyte (generically referred to in this document as an MDP). Such an analyte may be a physical parameter, a parameter that is not a specific chemical, or a parameter that may be comprised of a number of substances. Examples include, but are not limited to:

- Acidity,
- Alkalinity,
- Biological oxygen demand (BOD),
- Chemical oxygen demand (COD),
- Color,
- Oil and grease,
- pH (hydrogen ion),
- Conductivity (specific conductance),
- Temperature,
- Total dissolved solids (TDS),
- Total organic carbon (TOC),
- Total suspended solids (TSS),
- Total phenolics, and
- Turbidity.

ATPs that measure MDPs have the potential to change what is being measured. Therefore, *all* ATPs that measure MDPs require EPA approval prior to use in NPDES compliance monitoring. Furthermore, the three-tiered validation approach to ATPs described in the main body of this document for non-MDPs should not be used in the case of ATPs for MDPs. Rather, all ATPs for MDPs should be validated and reviewed using the process described in this appendix.

1.2 Approaches to Validation of ATPs for MDPs

EPA would not expect to be able to approve any applications for ATPs that failed to establish the suitability of the method to measure the MDP through side-by-side comparison studies using the ATP and the EPA-approved reference method. These are necessary to ensure there are no systematic differences in method performance, and that the comparison data may be evaluated to ensure that any differences in what is being measured are not masked by between-sample variability.

1.2.1 Tier 1: Side-by-side Comparison for Use in a Single Laboratory

For ATPs that measure MDPs that are intended for limited use in a single laboratory (Tier 1), the laboratory must perform and document side-by-side comparison of the ATP and the EPA-approved reference method. This study should include analysis of a minimum of 3 replicate samples collected on any 7 days over a minimum 30-day period using each method. This will require analysis of a total of 42 field samples (21 by the ATP and 21 by the EPA-approved reference method for a single matrix study). If the laboratory wishes to use the ATP for analysis of more than one matrix type a similar model should

be used for each additional matrix type up to a maximum of nine matrix types. If the laboratory wishes to use the ATP for analysis of any matrix type, the study design should be similar to the Phase I single-laboratory study comparison study described in Section 1.2.3.1 for Tier 3 ATPs.

If all six results for a given day associated with any sample are less than the minimum level (< ML) of the reference method, these results should not be used in the comparison because it is necessary to have actual measured values to test equivalency. In the event that a test result less than the ML is obtained, samples should be collected on an additional day (i.e., the number of tests should be increased to provide a minimum of seven paired triplicate results for the comparison).

1.2.2 Tier II: Side-by-side Comparison for Nationwide Use in a Single Matrix Type

Similarly, in the case of ATPs that measure MDPs that are intended for nationwide use in a single matrix type (Tier 2), in order to establish its suitability for use, the applicant should provide data from validation studies that are conducted in two phases: a single-laboratory phase that includes side-by-side comparison of the new method and the EPA-approved reference method, and a multi-laboratory phase. In the single-laboratory phase, comparability would be established by performing a statistical comparison of the results obtained from the analysis of minimum of three replicate samples of the appropriate matrix type collected on any seven days over a minimum 30-day period by both the ATP and the approved reference method. The single-laboratory comparison study should also include analysis of a proficiency testing sample obtained from an approved vendor and analyzed in triplicate using both the ATP and the approved reference method. If the ATP single-laboratory data are determined to be generally comparable to those from the approved reference method, then a second phase will be conducted to generate method performance data across multiple laboratories and to establish applicable quality control (QC) acceptance criteria.

Given the nature of the side-by-side testing, a carefully prepared validation study plan is an essential component of the validation and approval process for ATPs that measure MDPs. The applicant may prepare separate study plans for the two phases of the process, or where practical, a single plan may be developed that supports both phases.

1.2.2.1 Phase I: Side-by-side Comparison in a Single Laboratory

In Phase I of the comparison study, a minimum of three replicate samples of the appropriate matrix type collected on any seven days over a minimum 30-day period will be analyzed in a single laboratory by both the ATP and the approved reference method, and should be used to assess whether there is a statistically significant difference between the results produced by the ATP and the results produced by the approved corresponding reference method.

The design of the side-by-side comparison is left up to the ATP applicant. However, a detailed validation study plan **must be** prepared by the applicant and submitted to EPA for review and comment, and the plan **must be** agreed upon by all parties prior to conducting the comparison study. This will ensure that the plan provides the demonstration necessary for EPA to evaluate the ATP MDP's suitability. Although EPA may be consulted for additional guidance during the development of the study plan, it is the applicant's responsibility to write the study plan and submit it to EPA for review. The minimum elements to provide the showing necessary for EPA's evaluation for the design of the Phase I study are provided below and summarized in Section 1.2.2.3, Table H-1 of this appendix.

- *Number/Types of Real-World Sample Types*: A minimum of three replicate samples of the appropriate matrix type types should be collected on any seven days over a minimum 30-day period and analyzed by each method. If preparation of multiple spike levels is feasible for the method-defined parameter, then use of multiple spike levels is recommended, but a minimum of **seven** samples per spike level is

expected unless the applicant explains why they are unnecessary. However, in most cases, seven samples are the minimum number needed to capture the expected variability. If spiking is not feasible, a range of samples should be targeted that would be expected to yield background concentrations that vary by at least one order of magnitude.

- *Laboratories*: The Phase I Comparison Study should be performed in a single laboratory to minimize the sources of variability. This laboratory should have familiarity with both the approved method and the ATP to ensure that any differences in performance are not the result of inexperience with one or both methods. However, it is important that the validation study accurately reflect the ruggedness of the ATP and any limitations regarding clarity of the ATP procedures. Therefore, the laboratory should not be affiliated with the ATP applicant.

- *Replication*: The recommended number of replicates to be analyzed per method and sample within the side-by-side study is **three**.

To ensure the laboratory can perform both methods acceptably, the laboratory must meet all QC analysis criteria specified in the approved reference method using both the approved reference method and ATP, prior to the statistical comparisons of the method data. Moreover, the specific statistical tests that will be used to compare the results of the ATP with those from the reference method **must be** described in the study plan. See Section 1.3 of this appendix for a discussion of the relevant statistical considerations.

If a statistical assessment indicates that Phase I study results produced by the ATP are comparable to those produced by the approved reference method based on the statistical test described in the validation study plan, then the ATP will be deemed to be sufficiently comparable to proceed to Phase II of the study.

1.2.2.2 Phase II: Interlaboratory Study

In Phase II of the validation study, results of the analyses of synthetic and real-world samples in **three** laboratories will be used to characterize interlaboratory method performance and establish interlaboratory QC acceptance criteria for the alternate test procedure. The study design and specific QC tests for the Phase II study will generally follow the guidelines presented for Tier 2 validation as described in Section 4.3 of this document, and acceptance criteria will be developed as described in Appendix G of the "Protocol for Validation and Review of New Methods for Regulated Organic and Inorganic Analytes in Wastewater". However, not all QC tests will be applicable to all method-defined parameters. For example, matrix spike samples are not applicable to methods that measure method-defined analytes such as pH or temperature.

Despite careful planning, situations may arise in which the results from one of the three laboratories in the study may not represent the performance of the ATP or the other laboratories. Applicants may wish to plan for such a contingency in the Phase II study plan by utilizing more than three laboratories, or by documenting relevant corrective action procedures that all laboratories in the study will use *prior to* repeating study analyses.

Outlier testing is not recommended for either the single-lab or multi-laboratory phases of the study. However, if the applicant has reason to believe that some of the results from the validation study truly do not represent the performance of the method, then they should contact EPA to discuss whether and how an outlier test could be applied.

It is important that Phase II accurately reflect the ruggedness of the ATP and any limitations regarding clarity of the ATP procedures. Therefore, a vendor or other applicant should not directly assist laboratories participating in Phase II of the study with implementation of the ATP methodology or equipment during the course of the study (e.g., the vendor or applicant may provide training and advice to

participant laboratories regarding the equipment or methodology *prior to* the start of the study, but the study samples are to be analyzed by the study participants under "routine" conditions). Direct participation by the vendor or applicant will compromise the results of the study.

1.2.2.3 Analyses Recommended for Both Phases of a Tier 2 Validation Study of an ATP for a MDP

The following tables summarize the recommended minimum numbers of analyses involved in both phases of the validation study for an ATP involving an MDP

Table H-1a Summary of Validation Recommendations for Tier 2 MDP ATPs – Phase I[1]

Study Phase	Procedure	Number of		Number of Analyses Required					
		Labs	Matrix Samples[2]	Replicates per Matrix Sample[3]	IPR in Reagent Water[4]	PT Sample	MS/MSD[5]	MDL[(6)]	Total
Phase I	ATP	1	7	3	4	1	14	14	54
	Reference Method	1	7	3	4	1	14	14	54

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc.
(2) In Phase I, the matrix samples are collected on any seven days over a minimum 30-day period and analyzed using each method.
(3) Each laboratory analyzes each matrix sample in triplicate.
(4) The IPR analyses only apply to MDPs where the approved reference method also includes the IPR test.
(5) Each laboratory analyzes one MS/MSD pair for each matrix sample.
(6) A method detection limit (MDL) test would be performed in each laboratory, using the ATP and the approved reference method. As of August 2017, 40 CFR Part 136 Appendix B requires analysis of a minimum of seven spiked samples and seven blanks per laboratory to determine an MDL. Validation studies will comply with most recent MDL study requirements published in Appendix B of 40 CFR Part 136.

Table H-1b. Summary of Recommended Validation Approaches for Tier 2 MDP ATPs – Phase II[(1)]

	Number of		Number of Analyses					
Study Phase	Labs	Matrix types	Back-ground Analysis	IPR-reagent water[(2)]	PT Sample[(3)]	MS/MSD	MDL[(4)]	Total
Phase II	3	1	3	12	3	6[(5)]	42	66

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc.
(2) Initial precision and recovery (IPR) reagent water analyses are used to validate a new method in a clean matrix. The number of IPR analyses is four times the number of laboratories used to validate a method modification because each laboratory performs a four-replicate IPR test.
(3) The proficiency testing (PT) sample should be obtained from a third-party vendor and should be analyzed by each laboratory participating in the study. If sewage sludge or ocean water are matrices of interest, PT samples for those matrices are required as well.
(4) A method detection limit (MDL) test would be performed in each laboratory, using the new method. As of August 2017, 40 CFR Part 136 Appendix B requires analysis of a minimum of seven spiked samples and seven blanks per laboratory to determine an MDL. Validation studies will comply with most recent MDL study requirements published in Appendix B of 40 CFR Part 136.
(5) The MS/MSD analyses would be used to establish MS/MSD recovery and precision for the new method. The number of MS/MSD analyses is two times the number of matrix types tested (i.e., one MS/MSD pair per laboratory).

1.2.3 Tier 3: Side-by-side Comparison for Nationwide Use in Any Matrix Type

ATPs that measure MDPs that are intended for nationwide use in all matrix types (Tier 3), shall require validation studies that will be conducted in two phases: a single-laboratory phase, and a multi-laboratory phase that includes side-by-side comparison of the new method and the EPA-approved reference method, and a multi-laboratory phase. In the single-laboratory phase, comparability will be established by performing a statistical comparison of the results obtained from the analysis of various sample types by both the ATP and the approved reference method, including the analysis of a proficiency testing sample obtained from an approved vendor. If the ATP single-laboratory data are determined to be generally comparable to those from the approved reference method, then a second phase will be conducted to generate method performance data across multiple laboratories and establish applicable quality control (QC) acceptance criteria.

Given the nature of the side-by-side testing, a carefully prepared validation study plan is an essential component of the validation and approval process for ATPs that measure MDPs. The applicant may prepare separate study plans for the two phases of the process, or where practical, a single plan may be developed that supports both phases.

1.2.3.1 Phase I: Side-by-side Comparison in a Single Laboratory

In Phase I of the comparison study, a wide variety of synthetic and real-world samples agreed upon (by EPA and the applicant) prior to analysis will be analyzed in a single laboratory, and will be used to assess whether there is a statistically significant difference between the results produced by the ATP and the results produced by the approved corresponding reference method.

The design of the side-by-side comparison is left up to the ATP applicant. However, a detailed validation study plan **must be** prepared by the applicant and submitted to EPA for review and comment, and the plan **must be** agreed upon by all parties prior to conducting the comparison study. Although EPA may be consulted for additional guidance during the development of the study plan, it is the applicant's responsibility to write the study plan and submit it to EPA for review. The minimum requirements regarding the design of the Phase I study are provided below and summarized in Section 1.2.3.3, Table H-2 of this appendix.

- *Number/Types of Real-World Sample Types*: A minimum of **nine** real-world sample types must be collected from a variety of sources and analyzed by each method. To better identify any sample-specific differences between the ATP and the approved reference method, analyses should be performed across a wide range of sample types (a list of industrial categories with existing effluent guidelines can be found at: https://www.epa.gov/eg/industrial-effluent-guidelines). If preparation of multiple spike levels is feasible for the method-defined parameter, then use of multiple spike levels is recommended, but a minimum of nine sample types per spike level are required. If spiking is not feasible, a range of sample types should be targeted that would be expected to yield background concentrations that vary by at least one order of magnitude.

- *Laboratories*: The Phase I Comparison Study should be performed in a single laboratory to minimize the sources of variability. This laboratory should have familiarity with both the approved reference method and the ATP to ensure that any differences in performance are not the result of inexperience with one or both methods. However, it is important that the validation study accurately reflect the ruggedness of the ATP and any limitations regarding clarity of the ATP procedures. Therefore, the laboratory should not be affiliated with the ATP applicant.

- *Replication*: The recommended number of replicates to be analyzed per method and sample within the side-by-side study is **three**.

To ensure the laboratory can perform both methods acceptably, the laboratory must meet all QC analysis criteria specified in the approved method using both, the approved method and ATP, prior to the statistical comparisons of the method data. Moreover, the specific statistical tests that will be used to compare the results of the ATP with those from the reference method **must be** described in the study plan. See Section 1.3 of this appendix for a discussion of the relevant statistical considerations.

If a statistical assessment indicates that Phase I study results produced by the ATP are comparable to those produced by the approved reference method based on the statistical test described in the validation study plan, then the ATP will be deemed to be sufficiently comparable to proceed to Phase II of the study.

1.2.3.2 Phase II: Interlaboratory Study

In Phase II of the validation study, results of the analyses of synthetic and real-world samples in **nine** laboratories will be used to characterize interlaboratory method performance and establish interlaboratory QC acceptance criteria for the alternate test procedure. The study design and specific QC tests for the Phase II study will generally follow the guidelines presented for Tier 3 validation as described in Section 4.3 of this document, and acceptance criteria will be developed as described in Appendix G of the "Protocol for Validation and Review of New Methods for Regulated Organic and Inorganic Analytes in Wastewater". However, not all QC tests will be applicable to all method-defined parameters. For example, matrix spike samples are not applicable to methods that measure method-defined analytes such as pH or temperature.

Despite careful planning, situations may arise in which the results from one of the nine laboratories in the study may not represent the performance of the ATP or the other laboratories. Applicants may wish to plan for such a contingency in the Phase II study plan by utilizing more than nine laboratories, or by documenting relevant corrective action procedures that all laboratories in the study will use *prior to* repeating study analyses.

Outlier testing is not recommended for either the single-lab or multi-laboratory phases of the study. However, if the applicant has reason to believe that some of the results from the validation study truly do not represent the performance of the method, then they should contact EPA to discuss whether and how an outlier test could be applied.

It is important that Phase II accurately reflect the ruggedness of the ATP and any limitations regarding clarity of the ATP procedures. Therefore, it is not permissible for a vendor or other applicant to directly assist laboratories participating in Phase II of the study with implementation of the ATP methodology or equipment during the course of the study (e.g., the vendor or applicant may provide training and advice to participant laboratories regarding the equipment or methodology *prior to* the start of the study, but the study samples are to be analyzed by the study participants under "routine" conditions).

1.2.3.3 Analyses Required for Both Phases of a Tier 3 Validation Study of an ATP for a MDP

The following tables summarize the recommended minimum numbers of analyses for both phases of the validation study for an ATP involving an MDP.

Table H-2a Summary of Validation Recommendations for Tier 3 MDP ATPs[1]

Study Phase	Procedure	Number of		Number of Analyses Required					
		Labs	Matrix types	Replicates per Matrix Type[2]	IPR in Reagent Water[3]	PT Sample	MS/MSD[4]	MDL[(5)]	Total
Phase I	ATP	1	9	3	4	1	18	14	64
	Reference Method	1	9	3	4	1	18	14	64

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc. Nine is the maximum number of matrix types that should be used to validate a modified wastewater method at Tier 1 or Tier 3.
(2) In Phase I the laboratory analyzes each of the nine matrix types in triplicate by each method.
(3) The IPR analyses only apply to MDPs where the reference method also includes the IPR test.
(4) In Phase I, the laboratory should analyze one MS/MSD pair for each of the nine matrix types by each method.
(5) A method detection limit (MDL) test would be performed in each laboratory, using the new method and the approved reference method. As of August 2017, 40 CFR Part 136 Appendix B requires analysis of a minimum of seven spiked samples and seven blanks per laboratory to determine an MDL., validation studies will comply with most updated MDL study requirements published in Appendix B of 40 CFR Part 136.

Table H-2b. Summary of Recommended Validation Approaches for Tier 3 MDP ATPs – Phase II[(1)]

	Number of		Number of Analyses					
Study Phase	Labs	Matrix types	Back-ground Analysis	IPR-reagent water[(2)]	PT Sample[(3)]	MS/ MSD	MDL[(4)]	Total
Phase II	9	9	9	36	9	18[(5)]	126	198

Notes:

(1) Numbers of analyses in this table do not include additional QC tests such as calibration, blanks, etc.
(2) Initial precision and recovery (IPR) reagent water analyses are used to validate a new method in a clean matrix. The number of IPR analyses is four times the number of laboratories used to validate a method modification because each laboratory performs a four-replicate IPR test.
(3) The proficiency testing (PT) sample should be obtained from a third-party vendor and should be analyzed by each laboratory participating in the study. If sewage sludge or ocean water are matrices of interest, PT samples for those matrices are required as well.
(4) A method detection limit (MDL) test would be performed in each laboratory, using the ATP. As of August 2017, 40 CFR Part 136 Appendix B requires analysis of a minimum of seven spiked samples and seven blanks per laboratory to determine an MDL. Validation studies will comply with most updated MDL study requirements published in Appendix B of 40 CFR Part 136.
(5) The MS/MSD analyses would be used to establish MS/MSD recovery and precision for the new method. The number of MS/MSD analyses is two times the number of matrix types tested (i.e., one MS/MSD pair per laboratory).

1.3 Statistical Considerations in Evaluating for MDPs

Demonstrating comparability of the results for a new method for a MDP presents a number of challenges for both the applicant and EPA. By their very nature, the results for method-defined parameters are a direct function of the sum of all of the steps in the method used to generate them. Thus, an ATP that achieves "better" results for an MDP is *not* an appropriate goal, and common statistical tests such as the Student's *t*-test of mean results, the *F*-test of variances, or an analysis of variance (ANOVA) are *not* useful for MDPs.

For the purposes of evaluating ATPs for MDPs, EPA employs the Root Mean Square Deviation (RMSD). The RMSD measures variations in the new method results *both above and below* the results from the reference method. For example, the average results for the ATP across all samples may be close to those obtained with the reference method, yet the variability of the ATP data may be quite high (results are accurate on average but are imprecise), or the differences between the methods vary widely from sample to sample. The RMSD computes the squared deviation of the results from the ATP from the results of the reference method on the same sample, and sums those squared deviations across all the samples in the validation study to provide an overall measure of agreement between the two sets of results (ATP and reference method). A generalized formula for the RMSD applicable to an ATP evaluation is shown below:

$$RMSD = \sqrt{\frac{\sum_{j=1}^{J}(\bar{X}_{RMj} - \bar{X}_{ATPj})^2}{J}}$$

where: $\bar{X}_{RMj}$ = The "jth" sample mean from the reference method
$\bar{X}_{ATPj}$ = The "jth" sample mean from the ATP, and
J = The total number of samples being analyzed by the methods

The calculated RMSD is then compared to the upper limit $RMSD_{max}$, determined using the formula below:

$$RMSD_{\max} = \sqrt{\frac{MSE}{J} * (\sum_{j=1}^{J}\sum_{k=1}^{2}(\frac{1}{n_{jk}})) * F_{(0.95;J,n_T-(2*J))}}$$

where: J = the total number of samples, and
n_{jk} = the number of replicates for sample j and method k,
n_T = the total number of replicates across all samples and methods,
J = the total number of samples, and

MSE = the mean-squared error, as calculated below:

$$MSE = \frac{1}{n_T - (2*J)}\sum_{j=1}^{J}\sum_{k=1}^{2}(n_{jk} - 1) * s_{jk}^2$$

where: s_{jk} = the standard deviation of the replicates for sample j and method k (i.e., where the approved method is method 1 and the ATP is method 2),
n_{jk} = the number of replicates for sample j and method k,
n_T = the total number of replicates across all samples and methods, and
J = the total number of samples

Due to the natural variation in the MDP across samples, it is recommended that all results from both methods be log-transformed prior to calculating the RMSD and $RMSD_{max.}$

Using the RMSD, the goal is to demonstrate whether or not there is a statistically significant difference between the performance characteristics of the new method and the reference method[1]. By its derivation, the RMSD sums the deviations in *both* directions (i.e., ATP results above the reference method results and those below), rather than looking at the simple "inequality" of the two sets of results. If no

[1] The significance test used in the RMSD is equivalent to an *F*-test of significant difference that tests the compound null hypothesis that the mean log concentration is equal between the two methods, for each sample in the study.

statistically significant difference is observed with the RMSD, then the results for the ATP may be judged acceptable.

Another advantage of the RMSD, relative to other common statistical tests, is that using the other tests will generate a large number of statistical outcomes that would not produce a clear picture of the overall performance of a new method relative to the reference method. For example, for the Phase I study of a new method ATP application for nationwide use, 27 analyses are required (e.g., 9 separate sample matrices, analyzed in triplicate, in a single laboratory). Using t-tests and F-tests to compare the results across even nine samples could well result in a mix of outcomes across all the samples (i.e., 5 samples with statistically significant differences and 4 without such differences). Such a mix of outcomes for the new method would be difficult, if not impossible, to interpret in the context of comparability with the reference method.

1.4 Other Recommendations for ATPs for MDPs

Despite the more rigorous side-by-side testing warranted for ATPs for MDPs, all other aspects of the ATP development and approval process still apply. For example:

- The applicant should comply with the application in Section 3.2 of this document, use of the application form in Appendix A of this document, and inclusion of the Data Collection Certification form in Appendix B of this document with their validation study report

- The applicant should follow the procedures for proprietary information in Section 3.3 of this document.

- Requirements in Section 4.3 for documenting the ATP in EPA format, providing MDL data and the routine QC operation data described in Sections 4.3.3 to 4.3.10 of this document continue to apply.

- EPA review, approval, and rulemaking framework described in Section 5 of this document continue to apply

Note: As noted in Section 1.3 of this appendix, demonstrating comparability of the results for an ATP for a MDP presents a number of challenges. However, even if the use of the RMSD demonstrates there are not any statistically significant differences between the performance characteristics of the ATP and the reference method, EPA may choose not to consider ATPs for MDPs that alter the fundamental chemistry of the overall analytical process, including the determinative technique used for measurement of the MDP.

Given the nature of MDPs, all ATP applications for MDPs must be submitted to the National ATP Coordinator at EPA Headquarters. EPA Regional and State authorities **may not** approve ATPs for MDPs.

Note: As for all other ATP applications, the applicant is responsible for the technical and statistical evaluation of the validation study results and preparation of the study report.

APPENDIX I Checklist for Methods To Be Considered by EPA for Use in Compliance Monitoring Programs under the Clean Water Act

EPA uses the following checklist to evaluate requests for consideration of Alternate Test Procedures (ATPs), new methods, or modified[1] methods for use in Clean Water Act (CWA) compliance monitoring programs. The checklist addresses minimum submission requirements (documented in 40 CFR 136.6 and 136.7 and in the ATP Protocols), as well as other laws, regulations, and policies that EPA staff must consider when evaluating method submissions. Although the checklist is for internal use by EPA, applicants are encouraged to review the checklist to better understand the Agency's process for reviewing and considering applicant submissions. Two attachments are provided at the end of the checklist to assist EPA users and applicants in understanding the requirements. In addition, the checklist contains references to applicable laws, regulations, and policies that are not explicitly covered at 40 CFR 136.6 and 136.7 and in the ATP Protocols.

Reviewer #1, Name and Organization:_____ Reviewer # 1 Initials and Date: _____

Reviewer #2, Name and Organization:_____ Reviewer # 2 Initials and Date: _____

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.

YES	NO	N/A	ITEM OR QUESTION TO BE ADDRESSED	COMMENTS/NOTES
☐	☐	■	**1a. Is this a completed ATP or a new method that has been reviewed by EPA? If yes, indicate type below.** ☐ ATP ☐ New Method	
☐	☐	■	**1b. If no, is this a request for EPA to consider approval of a method from a Voluntary Consensus Standards Body (VCSB) or other Government Agency (or their designated representative)?** ☐ VCSB Method ☐ Other Government Agency Method	

1 For the purposes of this checklist, the terms modified method, revised method, and updated method are synonymous and are intended to mean any method changes, updates, or revisions that are being submitted to EPA for review and approval at 40 CFR Part 136 to support CWA programs. Due to the increased flexibility allowed for method modifications under 40 CFR 136.6, most method changes, updates, or revisions submitted to EPA will consist of ATP applications for procedures involving method-defined analytes, procedures that involve changes to the chemistry of the method, determinative techniques, or applications for consideration of updated versions of previously approved methods.

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.				
YES	**NO**	**N/A**	**ITEM OR QUESTION TO BE ADDRESSED**	**COMMENTS/NOTES**
☐	☐	■	**2. Is a justification provided for consideration of the ATP, new method, or VCSB or other Government Agency method for use in CWA compliance monitoring programs?** This may include advantages over approved method(s) or may state that the method is a revised or updated version of an already approved method.	
☐	☐	■	**3. Is a copy of the method written in standard EPA format included?** *(*See the *Guidelines and Format* **document at** https://www.epa.gov/cwa-methods/alternate-test-procedure-documents) **Alternatively, method(s) may be written in another organization's format but must address and reference the topics specified below in Attachment A and Attachment B.** ☐ EPA Format ☐ Other Format that Addresses topics below and Attachments A and B	
☐	☐	■	**4. Does the method include all appropriate quality control (QC) elements or are they included as part of a compendium and referenced in the method?** *(see 40 CFR 136.7, reprinted as Attachment B to this checklist, for a list of required QC elements*) ☐ Included in method ☐ Included in compendium and referenced in method	
☐	☐	■	**5. Does the method specify acceptance criteria for required QC tests equal to or better than the method currently approved at 40 CFR Part 136?**	
☐	☐	■	**6a. Does the method include a unique method number and date/revision date?**	
☐	☐	☐	**6b. For methods submitted by a VCSB or another Government Agency, does the method contain a revision date or date of approval?** *Enter N/A if the application is not for a VCSB or other Government Agency method.*	
☐	☐	☐	**7. Is a copy of the approved reference method (with red-line strikeouts and additions) enclosed if the application is for a modified method or a revised version of an approved method?** *This applies to method modifications/revisions. Enter N/A if the submission is for a new method application.*	
☐	☐	☐	**8. Would utilization of the method be practical and comply with existing law and be compatible with agency and departmental missions, authorities, priorities and budget resources? [**stipulated by the National Technology Transfer Advancement Act, 15 U.S.C. 3701 et seq. (1996)] *This applies to VCSB applications. Enter N/A if the application is not for a VCSB method.*	

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.				
YES	**NO**	**N/A**	**ITEM OR QUESTION TO BE ADDRESSED**	**COMMENTS/NOTES**
☐	☐	☐	**9. If the method is from a VCSB or other Government Agency is the method in its final form and has it been approved/published by that VCSB or Government Agency?** *This applies to VCSB and other Government Agency methods only. Enter N/A for all other types of applications.*	
			Questions 10a through 10c address method validation study plans. These requirements only apply to new method applications, applications for methods involving method-defined parameters, and other ATP applications that go beyond the modifications explicitly allowed at 40 CFR 136.6. *Enter N/A to questions 10a through 10 c if the application is for an update to a previously approved method and the revisions do not affect the chemistry of the method, determinative technique or QC acceptance criteria.*	
☐	☐	☐	**10a. Was EPA consulted or did EPA participate in the development of the original study plan for validation of the method?**	
☐	☐	☐	**10b. If EPA was consulted or participated in the development of the original study plan for validation of the method, does the application include written documentation of EPA's participation** (e.g., copies of correspondence and records of any verbal communications with EPA staff by phone or in meetings)**?**	
☐	☐	☐	**10c. If EPA was consulted or participated in the development of the original study plan for validation of the method, were all EPA recommendations incorporated into the study plan?** *If yes, this must be documented in writing. If no, the submission should include a written explanation regarding EPA recommendations that were not adopted.*	
☐	☐	☐	**11. Is a copy of the validation study plan with validation study report and reference to the organization's study data requirements provided?** *Enter N/A if the application is for an update to a previously approved method and the revisions do not affect the chemistry of the method, determinative technique or QC acceptance criteria (including the Method Detection Limit).* *A "yes" answer is required for consideration of new method applications, applications for methods involving method-defined parameters, and other ATP applications that go beyond the modifications explicitly allowed at 40 CFR 136.6.*	

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.				
YES	**NO**	**N/A**	**ITEM OR QUESTION TO BE ADDRESSED**	**COMMENTS/NOTES**
			Questions 12a through 12j address method validation study reports and supporting documentation. These requirements only apply to new method applications, applications for methods involving method-defined parameters, and other ATP applications that go beyond the modifications explicitly allowed at 40 CFR 136.6. A yes answer is required for such applications. *Enter N/A to questions 12a through 12j if the application is for an update to a previously approved method and the revisions do not affect the chemistry of the method, determinative technique or QC acceptance criteria.*	
☐	☐	☐	**12a. Are supporting data documenting the Method Detection Limit (MDL) was determined as a part of the method validation study provided?** *Note:* EPA requires that all methods approved at 40 CFR 136, including ATPs, be supported by an MDL determined as specified at 40 CFR 136, Appendix B. This includes VCSB and other Government Agency methods, even if those organizations normally use other approaches for defining and determining detection limits.	
☐	☐	☐	**12b. Does the method validation include real world samples?** (*see list of effluent guidelines promulgated by EPA, sorted by industry category, https://www.epa.gov/eg/industrial-effluent-guidelines*)	
☐	☐	☐	**12c. Was the method validated to demonstrate compliance with existing analyte concentration ranges, sample collection, preservation, preparation and holding time requirements of the approved method?** (Data demonstrating compliance should be included in the submission)	
☐	☐	☐	**12d. Are quantitation range and limits supporting data provided?** A quantitation range corresponds to the range of analyte concentration (or other quantity) characterized for measurement accuracy (trueness and precision) during method validation**.** *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	
☐	☐	☐	**12e. Are supporting data that address instrument calibration provided?** The performance characteristic is sometimes referred to as "instrument linearity." *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.				
YES	**NO**	**N/A**	**ITEM OR QUESTION TO BE ADDRESSED**	**COMMENTS/NOTES**
☐	☐	☐	**12f. Are supporting data that address bias/trueness provided?** Trueness is a performance characteristic that addresses sources of known systematic error and bias is a measure of trueness. *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	
☐	☐	☐	**12g. Are supporting data that address precision (repeatability and reproducibility) provided?** Precision is a performance characteristic that reflects sources of random error in a measurement process. Methods designed for demonstrating compliance with regulatory requirements should be evaluated for both repeatability (within lab) and reproducibility (among labs). *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	
☐	☐	☐	**12h. Are data demonstrating method selectivity provided?** Selectivity is a performance characteristic that demonstrates the ability of the method to yield useful data for the analytes, analytes levels and matrices defined within the scope of the method. Selectivity is demonstrated by providing information that substantiates the identity of the analyte in presence of expected matrix constituents. *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	
☐	☐	☐	**12i. Are data demonstrating method ruggedness provided?** Ruggedness refers to the capacity of analytical method to remain unaffected by small variations in operating conditions or environmental conditions. The changes should reflect expected, reasonable variations that are likely to be encountered in different labs. *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	
☐	☐	☐	**12j. Are interlaboratory study/studies as defined in the ATP and New Method Protocols documents provided?** Interlaboratory studies determine whether an analytical method can be transferred for use in other laboratories and used for regulatory testing. Data from the interlaboratory study should be reported in tabular form and the raw data should be maintained and available for review. If appropriate, there should be a discussion describing the details of, and rationale for, any changes made to the method resulting from the interlaboratory study. *(see* "Chemical Methods Validation and Peer Review Guidelines (PDF)" at https://www.epa.gov/measurements/method-validation-and-peer-review-policies-and-guidelines)	

Use the check boxes to identify if following items were submitted or indicated. The Not Applicable (N/A) box may not be used to answer a question if it is blacked out.				
YES	**NO**	**N/A**	**ITEM OR QUESTION TO BE ADDRESSED**	**COMMENTS/NOTES**
			Questions 13a through 13g address applications for methods involving method-defined parameters. A yes answer is required for such applications. *Enter N/A to questions 13a through 13g if the application does not involve method-defined parameters.*	
☐	☐	☐	**13a. Is the request for one or more well-defined analytes that are NOT a 40 CFR 136.6 Method-Defined Parameter? The following is a list of some Method-Defined Parameters - Acidity, Alkalinity, BOD5, COD, Color, Oil & Grease, Total Solids, Total Dissolved Solids, Total Organic Carbon, Total Suspended Solids, Total Phenols, Temperature, or pH? Other parameters may be added at EPA's discretion.**	
☐	☐	☐	**13b. If the request is for a 40 CFR 136.6 Method-Defined Parameter, does the application include 1) comparative raw data resulting from side-by-side split sample or grab sample analyses performed in triplicate using both the new method and the approved method in a minimum of 9 distinct real world matrix types and 2) data from all required QC analyses performed using each method?**	
☐	☐	☐	**13c. If the request is for a 40 CFR 136.6 Method-Defined Parameter, is the chemistry or determinative step the same as the approved method?**	
☐	☐	☐	**13d. If the request is for a 40 CFR 136.6 Method-Defined Parameter (MDP) AND the chemistry or determinative step is different than the approved method, are the chemistry and determinative step used to identify and measure the MDP well explained and clearly defined as well as any potential interferences or difficulties with the method?**	
☐	☐	☐	**13e. Are data provided from a routinely run, freshly prepared method calibration curve that was used to quantify the analyte(s) in the samples analyzed as part of the validation study, including verification of the calibration curve using independent second source, quality certified, traceable standards?**	
☐	☐	☐	**13f. If the request is for a 40 CFR 136.6 Method-Defined Parameter, do the data submitted demonstrate comparable performance of the new method to the approved method?** *Note:* Comparable performance is determined by comparing the achievement of statistical RMSD comparability between the new method and the approved method from analyses of samples from a minimum of 9 distinct real world matrix types (split or grab - collected and analyzed at the same time), performed in triplicate AND by comparison of the QC acceptance criteria of the two methods.	
☐	☐	☐	**13g. Will the new method and the approved method measure the same forms and species of analyte?**	

Attachment A
Topics to be Covered in Written Method Submission

Scope and Application - This section of the method should clearly state the analyte(s) determined and the types of matrices to which the method is applicable. This section also may list the detection limit of the method and the range of concentrations over which the method is applicable.

Summary - This section briefly states the sample preparation (if any) and the underlying chemistry and determinative technique used in measurement of the target analyte(s). It also may list the method detection limit and the range of concentrations over which the method is applicable.

Definitions - This section should define the terms and abbreviations that are used in the method. The section should include definitions for abbreviations, especially those that relate to quality control, for example: LRB – Laboratory Reagent Blank, LFB – Laboratory Fortified Blank, LFM – Laboratory Fortified Matrix, MS and MSD – Matrix Spike and Matrix Spike Duplicate, MDL – Method Detection Limit, and QCS – Quality Control Sample.

Interferences - This section should identify common interferences, and where applicable, list ways to eliminate, reduce, or overcome them. Of particular note are interferences that may lead to loss or under reporting of target analyte(s).

Safety - This section should adequately address any safety concerns associated with the performance of the method (e.g., toxicity, carcinogenic reagents, or explosion risks).

Equipment and Supplies - This section should list all equipment (apparatus) and supplies to perform the procedures of the method.

Reagents and Standards - This section of the method should clearly list all reagents and standards needed to perform the analysis. It also may detail both preparation and storage of stock standard solutions from neat materials and preparation and storage of working standard solutions.

Sample Collection, Preservation and Storage - This section should list the proper types of sample containers, preservation techniques and holding times per the requirements of 40 CFR 136.3, Table II.

Quality Control - This section should list the minimum QC requirements and acceptance criteria for each of the QC tests applicable to the method (see 40 CFR 136.7 for a listing of QC elements that are required where applicable).

Calibration and Standardization - This section of the method should list the procedures for calibration of the instrument and the type of calibration used (i.e., linear, 2^{nd} order). It should specify a sufficient number of standards used to establish linearity or to clearly define any non-linear portion of the curve. This section also may specify procedures for periodic verification of calibration standards and specify acceptance criteria listed for calibration verification.

Procedure - This section should contain all of the critical steps required to perform the analysis of samples. If sample preparation steps such as distillation, digestion, or pH adjustment are required prior to analysis these steps should also be specified or referenced.

Data Analysis and Reporting - This section should explain how to calculate and report sample results. A statement indicating that only results that fall between the lowest and highest calibration standards should be reported unless the result is flagged as an estimated value. In addition, a statement should be included that samples with results exceeding the highest calibration standard should be diluted and re-analyzed.

Method Performance – This section should present any data or other information that demonstrate or indicate the expected performance characteristics of the method.

Pollution Prevention - This section should contain information on minimizing or preventing pollution known to be potentially attributable to use of the method.

Waste Management - This section should contain information on the minimization and proper disposal of any hazardous wastes known to be generated by use of the method?

References – This section should cite proper references and sources used in the development of the method. References should be restricted to associated or source material.

Tables, Diagrams, and Validation Data - This section of the method should contain all method tables and figures (diagrams and flowcharts). If performance data are included here, they should support the MDL, method range and QC acceptance criteria listed in the method.

Attachment B
40 CFR 136.7 Quality Assurance and Quality Control

The permittee/laboratory shall use suitable QA/QC procedures when conducting compliance analyses with any Part 136 chemical method or an alternative method specified by the permitting authority. These QA/QC procedures are generally included in the analytical method or may be part of the methods compendium for approved Part 136 methods from a consensus organization. For example, Standard Methods contain QA/QC procedures in the Part 1000 section of the Standard Methods Compendium. The permittee/laboratory shall follow these QA/QC procedures, as described in the method or methods compendium. If the method lacks QA/QC procedures, the permittee/laboratory has the following options to comply with the QA/QC requirements:

(a) Refer to and follow the QA/QC published in the ‘‘comparable’’ EPA method for that parameter that has such QA/QC procedures;

(b) Refer to the appropriate QA/QC section(s) of an approved Part 136 method from a consensus organization compendium;

(c)(1) Incorporate the following twelve quality control elements, where applicable, into the laboratory’s documented standard operating procedure (SOP) for performing compliance analyses when using an approved Part 136 method when the method lacks such QA/QC procedures. One or more of the twelve QC elements may not apply to a given method and may be omitted if a written rationale is provided indicating why the element(s) is/are inappropriate for a specific method.

(i) Demonstration of Capability (DOC);
(ii) Method Detection Limit (MDL);
(iii) Laboratory reagent blank (LRB), also referred to as method blank (MB);
(iv) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);
(v) Matrix spike (MS) and matrix spike duplicate (MSD), or laboratory fortified matrix (LFM) and LFM duplicate, may be used for suspected matrix interference problems to assess precision;
(vi) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);
(vii) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);
(viii) Control charts (or other trend analyses of quality control results);
(ix) Corrective action (root cause analysis);
(x) QC acceptance criteria;
(xi) Definitions of preparation and analytical batches that may drive QC frequencies; and
(xii) Minimum frequency for conducting all QC elements.

(2) These twelve quality control elements must be clearly documented in the written standard operating procedures (SOP) for each analytical method not containing QA.