



# **Protocol for EPA Approval of Alternate Test Procedures for Organic and Inorganic Analytes in Wastewater and Drinking Water**

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## Foreword

This document provides instructions for validation, submission, and EPA approval of applications for approval of alternate test procedures (ATPs) that determine inorganic and organic analytes. This document serves as a supplement to the ATP guidelines at 40 CFR 136.4, 136.5, and 141.27. This ATP protocol has been revised to significantly reduce the number of analyses necessary to demonstrate method equivalency by removing the requirement for side-by-side analyses using two different methods. Instead, applicants are required to demonstrate method equivalency by meeting quality control (QC) acceptance criteria associated with EPA-designated approved methods for different combinations of regulated analyte and determinative technique.

Under EPA's ATP program, a method developer may apply to gain approval for the use of an alternate procedure to test for a specific regulated constituent. EPA anticipates that the standardized procedures described herein will expedite the approval of ATPs, 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 and national primary drinking water regulations (NPDWRs).

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. Methods that use a different determinative technique to measure the same analyte(s) of interest as an approved method are considered new methods. The requirements for EPA approval of new methods are detailed in a separate protocol.

This document is not a legal instrument and does not establish or affect legal obligations under Federal regulations. EPA reserves the right to change this protocol without prior notice.

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## **1.0 INTRODUCTION**

### **1.1 Background and Objectives**

As required by the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA), the U.S. Environmental Protection Agency (EPA) promulgates guidelines establishing test procedures (analytical methods) for data gathering and compliance monitoring under National Pollution Discharge Elimination System (NPDES) permits and national primary drinking water regulations (NPDWRs). These test procedures are approved at 40 *Code of Federal Regulations* (CFR) part 136 for wastewater and 40 CFR part 141 for drinking water. In addition, the guidelines at 40 CFR 136.4 and 136.5 and 40 CFR 141.27, allow entities to apply for Agency permission to use an alternate test procedure (ATP) in place of an approved method. These guidelines are the basis for the Agency's alternate test procedure (ATP) program for water methods that is administered by the Office of Water, Office of Science and Technology, Analytical Methods Staff (AMS).

Under the ATP program, an organization or individual may submit an application for approval of a modified version of an approved method or a procedure that uses the same determinative technique and measures the same analyte(s) of interest as an approved method, to be used as an alternate to an approved method. The applicant is responsible for validating its proposed alternate test procedure. The Agency reviews the ATP validation package, approves or disapproves the application, and for nationwide applications, promulgates successful ATPs in the CFR.

With the goal of making the ATP program more accessible while maintaining data quality, EPA has revised its chemical ATP protocol to replace the side-by-side comparative validation study with a three-tiered validation protocol. This revised ATP protocol significantly reduces the number of analyses necessary to demonstrate method equivalency by removing the requirement for side-by-side analyses using two different methods. Instead, applicants demonstrate method equivalency by meeting quality control (QC) acceptance criteria associated with EPA-designated approved methods for different combinations of regulated analyte and determinative technique.

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. The use of a different determinative technique to measure the same analyte(s) of interest as an approved method is considered a new method. The requirements for EPA approval of new methods are detailed in a separate protocol.

The ATP program provides chemists with the opportunity to use best professional judgement 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 interferences problems, improves laboratory productivity, or reduces the amount of hazardous materials used and/or produced in the laboratory.

Any person or organization may apply to gain approval for the use of an ATP for determination of a specific constituent which is regulated under the NPDES permit program or the NPDWRs. Under the protocol, the ATP applicant may develop and validate its proposed ATP either using the procedures described in this document or the classical interlaboratory validation procedures provided by organizations such as ASTM<sup>1</sup> and AOAC-International.<sup>2,3</sup>

## 1.2 Tiered System for Validation of Alternate Test Procedures

EPA recognizes that a formal interlaboratory method validation may not be suitable for all situations and may be prohibitively costly to implement, especially for small laboratories and regulated entities. Therefore, EPA has developed a three-tiered, cost-effective approach to method validation that classifies the intended use of a method and requires a method validation study that reflects the level of use associated with each tier. For method equivalency demonstration in the tiered validation system, EPA has specified approved methods that contain (or are supplemented with) QC acceptance criteria (Appendix E) for most combinations of analyte and determinative technique. An applicant is required to demonstrate that its ATP is able to meet the QC acceptance criteria of the EPA-designated approved method (or other EPA-specified document) for the applicable combination of analyte and determinative technique. The three method validation tiers are listed below.

**Tier 1** ATPs may only be used by a single laboratory facility (limited-use) for one or more matrix type(s). A matrix type 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. Tier 1 validation requirements are for single-laboratory testing in the matrix type(s) of interest.

**Tier 2** ATPs may be used by all laboratories (nationwide use) for only one matrix type. Validation requirements are for a three-laboratory validation study.

**Tier 3** ATPs may be used by all laboratories (nationwide use) for all matrix types. Validation requirements are for a nine-laboratory validation study.

## 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-designated approved method for the applicable combination of analyte and determinative technique.

### 1.3.1 EPA-Designated Approved Methods

The ATP process is based on the use of designated QC acceptance criteria against which method modifications are tested for equivalency. Using QC acceptance criteria as the performance measure allows EPA to implement a more efficient ATP program.

An approved method, which contains (or is supplemented with) standardized QC procedures and QC acceptance criteria, has been designated for each combination of regulated analyte and determinative technique (Appendix E for inorganic methods, organic methods have QC acceptance criteria in the text of the method). The QC acceptance criteria associated with the EPA-designated approved method are the performance criteria against which ATPs of methods employing that combination of analyte and

determinative technique are tested. Method equivalency is demonstrated when results produced by an ATP meet or exceed the QC acceptance criteria associated with the EPA-designated approved method.

### **1.3.2 Modifications to Front-end Techniques**

A front-end technique is any technique in the analytical process conducted at the laboratory that precedes the determinative technique (see definition below). Front-end techniques include all procedures, equipment, solvents, etc., that are used in the preparation and cleanup of a sample for analysis. Laboratories may modify any and all front-end techniques provided the modification is not explicitly prohibited in the approved method that is being modified and provided the modification can be demonstrated to produce results equal or superior to results produced by an EPA-designated approved method for each combination of analyte and determinative technique. 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. However, if changing the chemistry of the method might affect the extract holding times specified in the approved method, a new extract holding time study must be performed. The developer of a modified method always has the option of asking EPA or other regulatory authority for a technical opinion on the acceptability of the developer's validation data that supports the method modification.

### **1.3.3 Adding New Target Analytes**

EPA will permit method developers to modify the analytical scope of an approved method by adding additional analytes. This action is in response to public comment on previous rules (59 FR 62456, December 5, 1994; 58 FR 65622, December 15, 1993) to extend the scope of an approved method to the determination of other analytes. 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 historical monitoring data might be useful in making process, treatment, or regulatory decisions. Examples of monitoring for a new analyte include industrial or POTW monitoring for ethers in a discharge, public water supply (PWS) monitoring for unregulated pesticides or pesticide metabolites, and PWS monitoring for analytes on the drinking water priority list. EPA also believes these requests have merit 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 conditions below are met:

- (1) It can be demonstrated that the analyte does not interfere with determination of the analytes of concern in that method
- (2) QC acceptance criteria are developed by the applicant and employed for determination of the target analyte; see *Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water*.
- (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 "method shopping," whereby a user might add analytes to an approved method with less rigid sample collection or holding time criteria.)



## 2.0 APPLICATION REQUIREMENTS

Every ATP application shall be made in triplicate and include a completed ATP application form (provided in Appendix A) with required attachments.

### 2.1 Submission Addresses

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

**Table 1: Submission of Alternate Test Procedure Applications**

TIER	LEVEL OF USE	APPLICANT	SUBMIT APPLICATION TO <sup>1</sup>	APPROVAL AUTHORITY
Tier 1	Limited Use for Wastewater	EPA Regional laboratories	EPA Regional Administrator (Regional ATP Coordinator) <sup>2</sup>	EPA Regional Administrator
		States, commercial laboratories, individual dischargers, or permittees in States that do not have authority	EPA Regional Administrator (Regional ATP Coordinator) <sup>2</sup>	
		States, commercial laboratories, individual dischargers, or permittees in States that have authority	Director of State Agency issuing the NPDES permit <sup>2</sup>	
Tier 2	Nationwide Use	All applicants	Director, Analytical Methods Staff, EPA Headquarters	EPA Administrator
Tier 3	Nationwide Use	All applicants	Director, Analytical Methods Staff, EPA Headquarters	EPA Administrator

<sup>1</sup> See Appendix B for EPA addresses.

<sup>2</sup> The Regional Administrator may choose to forward Tier 1 (LU) applications to the Director of the Analytical Methods Staff (AMS) for an approval recommendation.

Upon receipt of the application, the AMS ATP staff will assign an identification number to the application. The applicant should use the identification number in all future communications concerning the application.

## 2.2 Application Information

Information required on the ATP application form includes: the name and address of the applicant; the date of submission of the application; the method number and title of the proposed ATP; the EPA-approved method that was modified to develop the proposed ATP, the EPA-designated approved method that will be used for demonstration of equivalency; the analytes(s) for which the ATP is proposed; the type of application (i.e., wastewater, drinking water, or a combined wastewater/drinking water application); the level of use desired (i.e., limited use or nationwide use); the tier level at which the proposed ATP will be validated; and the applicant's NPDES permit number, the issuing agency, the type of permit and the discharge serial number if applicable.

The following items should be submitted with the application: the justification for proposing the ATP; the proposed ATP prepared in standard EPA format; a method comparison 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; and, 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.

All of the above-listed attachments do not need to be submitted with the initial application. If an applicant is unsure whether or not a modification is allowed within the method-specified flexibility, the applicant may request EPA to determine the necessity for a full ATP validation. *The minimum information required for EPA to 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 inherent flexibility of the approved method.

Additionally, before proceeding with ATP validation, an applicant may choose to submit its validation study plan for EPA review and comment. For modifications to methods that measure method-defined parameters, such as oil and grease, a detailed validation study plan must be submitted and agreed upon prior to conducting the study.

The elements required for a complete application at each tier are presented in Table 2. EPA must receive all required application information and attachments before the application is considered complete.

**Table 2. Application Requirements**

<b>Tier</b>	<b>Level of Use</b>	<b>Application Requirements</b>
Tier 1	Limited Use	<ul style="list-style-type: none"> <li>• Completed application form</li> <li>• Justification for ATP</li> <li>• Method in EPA format</li> <li>• Method comparison table</li> <li>• Validation study report</li> </ul>
Tier 2	Nationwide Use	<ul style="list-style-type: none"> <li>• Completed application form</li> <li>• Justification for ATP</li> <li>• Method in EPA format</li> <li>• Method comparison table</li> <li>• Validation study report</li> <li>• Method development information and documentation</li> </ul>
Tier 3		

### **2.2.1 Justification for ATP**

The entity that proposes an ATP should provide a brief justification for why the ATP is being proposed. Examples include but are not limited to: the method successfully overcomes some or all of the interferences associated with the approved method; the ATP significantly reduces the amount of hazardous wastes generated by the laboratory; or the cost of analyses are significantly reduced when using the ATP.

### **2.2.2 Standard EPA Method Format**

In accordance with the standard EPA format advocated by EPA's Environmental Monitoring Management Council (EMMC), methods must contain 17 specific topical sections in a designated order. The 17 sections listed in Appendix C to this document are mandatory for all methods. Additional numbered sections may be inserted starting with Section 11.0, *Procedure*, as appropriate for a particular method. For detailed information on the EPA format for proposed methods, see the Guidelines and Format document.<sup>4</sup>

### **2.2.3 Method Comparison Table**

As part of the application, the applicant must perform an in-depth comparison of the proposed ATP with the EPA approved method that has been modified, and document the comparison in a two-column method comparison table. The two-column method comparison table shall 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 in the method comparison table. The applicant should highlight any differences between the proposed ATP and the approved method that has been modified. If the proposed method 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.

#### **2.2.4 Validation Study Report**

The applicant must conduct a validation study and provide a comprehensive validation study report with the ATP application. The validation study report must include the following elements:

- 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 (optional for Tier 1)
- Appendix C - Supporting Data (Raw Data and Example Calculations)

These elements are described in Section 3.6.

#### **2.2.5 Method Information and Documentation to Facilitate EPA Preparation of Preamble and Docket**

For Tier 2 and 3 applications, the ATP will be approved by the EPA Administrator through rulemaking. In these cases, the applicant shall provide to EPA information and documentation that will aid EPA in preparing the preamble and docket for the proposed rule that will be published in the *Federal Register*. Information to be provided includes: a detailed background and summary of the method, a discussion of QC acceptance criteria development, and a description and discussion of the interlaboratory method validation study and any other method studies conducted during method development and validation. Specifically, the applicant shall 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 indicates whether the method is associated with a sampling method.
- Identifies the matrix(ces) for which the method has been found satisfactory.
- Describes method limitations and indicate any means of recognizing cases where the method may not be applicable to the specific matrix types.
- Outlines the basic steps involved in performing the test and data analysis.
- Lists options to the method, if applicable.
- Describes and discusses the validation study report, including study design and objectives, study limitations, study management, technical approach, data reporting and validation, results, data analysis discussion, and conclusions.

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. In addition to method information, the applicant must provide copies of all relevant supporting documents used in developing the ATP, for EPA's inclusion in the rule docket.

## **2.3 Proprietary Information in Applications**

All information provided to the Federal government is subject to the requirements of the Freedom of Information Act. Therefore, any proprietary information submitted with the proposed ATP application should be marked as 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*. Allegedly confidential 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 so state. Please be advised, however, that any methods to be proposed in the *Federal Register* cannot be claimed as 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.

### 3.0 METHOD VALIDATION

#### 3.1 Introduction

Method validation is the process by which a laboratory or vendor substantiates the performance of a method modification by demonstrating that the modified method can meet the QC acceptance criteria in the EPA-designated method or other EPA-specified document. Appendix E to this protocol contains the QC acceptance criteria for inorganic methods. The QC acceptance criteria for organic methods are contained in the text of the methods (for organic methods that do not contain QC acceptance criteria consult with EPA). ATPs must be validated to prove that they accurately measure the concentration of an analyte in an environmental sample. If, during a compliance inspection or audit, it is determined that a regulated party is using an unvalidated modified method, the data generated by the unvalidated method will be considered unacceptable for compliance monitoring or reporting. The validation requirements listed 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 Level	Laboratory Use	Applicable to . . .
Tier 1	Single Laboratory (Limited use)	One or more matrix types from any industry
Tier 2	All Laboratories (Nationwide use)	One matrix type within one industrial subcategory; or all PWSs
Tier 3	All Laboratories (Nationwide use)	All matrix types from all industrial subcategories

Under Tier 1, single laboratories will be allowed to validate and use modified test methods without the burden of conducting an interlaboratory validation study, whereas methods intended for multi-laboratory use in a given industrial subcategory (Tier 2) or for multi-laboratory use for all industrial subcategories (Tier 3) require interlaboratory testing.

#### 3.2 Summary of Validation Requirements

EPA has developed a tiered validation approach that coordinates validation requirements with the level of intended use of the ATP. Tier 1 (LU) represents validation in a single laboratory, Tier 2 (NW) represents interlaboratory validation in one industrial subcategory, and Tier 3 (NW) represents interlaboratory validation in multiple matrix types. ATPs may be used after validation at the appropriate level is performed and formal approval is granted by the appropriate authority. Tier 1 (LU) contains two levels of validation, depending on whether the individual laboratory will be applying the ATP to a single matrix type or to multiple matrix types. The Tier 1- Single Matrix Type category allows the laboratory to apply the ATP to a single matrix type. The Tier 1- Multiple Matrix Type category allows a single

laboratory to apply the ATP to an unlimited number of matrix types after the method has been validated on a minimum of nine matrix types.

Table 4 summarizes the validation requirements for wastewater ATPs. Table 5 summarizes the validation requirements for drinking water ATPs. Please note that only Tier 2 or Tier 3 (NW) validations are applicable to drinking water; the Office of Ground Water and Drinking Water (OGWDW) no longer accepts Tier 1 (LU) ATP applications for drinking (potable) water programs.

**Table 4. Summary of Validation Requirements for Wastewater Alternate Test Procedures<sup>(1)</sup>**

Method Application	Number of		Number of Analyses Required		
	Labs	Matrix types	IPR-reagent water <sup>(2)</sup>	MS/MSD	MDL <sup>(3)</sup>
<b>Tier 1-Single-lab</b>					
First matrix type	1	1	4	2 <sup>(4)</sup>	7
Each additional matrix type (8 max.)	1	1	0 <sup>(5)</sup>	2 <sup>(4)</sup>	0 <sup>(5)</sup>
<b>Tier 2-Multi-lab, single matrix type</b>	3	1	12	6 <sup>(6)</sup>	21
<b>Tier 3-Multi-lab, multiple matrix types</b>					
All matrix types	9 <sup>(7)</sup>	9	36	18 <sup>(6)</sup>	63

**Notes:**

- (1) Numbers of analyses in this table do not include background analyses or additional QC tests such as calibration, blanks, etc. Validation requirements are based on the intended application of the method. Nine would be the maximum number of matrix types (or facilities) that would be required to validate a modified wastewater method at Tier 1 or 3.
- (2) IPR reagent water analyses would be used to validate a method modification. The required number of IPR analyses would be four times the number of laboratories required to validate a method modification because each laboratory would perform a 4-replicate IPR test.
- (3) A method detection limit (MDL) test would be performed in each laboratory using the alternate test procedure. 40 CFR part 136 Appendix B requires a minimum of seven analyses per laboratory to determine an MDL. Each lab involved in validation of a wastewater modification would demonstrate that the modified method would achieve the detection limits specified in the EPA-designated approved method.
- (4) The MS/MSD test would demonstrate that the EPA-designated approved method MS/MSD QC acceptance criteria have been met.
- (5) The MDL, reagent water IPR, and sample matrix IPR tests would not have to be repeated after the first matrix type or facility was validated.
- (6) The MS/MSD analyses would demonstrate that MS/MSD recovery and precision criteria associated with the EPA-designated approved method have been met. The required number of MS/MSD analyses would be two times the number of facilities or matrix types tested.
- (7) The number of laboratories and samples would vary if a conventional interlaboratory study is used.

**Table 5. Summary of Validation Requirements for Drinking Water Alternate Test Procedures<sup>(1)</sup>**

Method Application	Number of		Number of Analyses Required		
	Labs	PWSs	IPR- reagent water <sup>(2)</sup>	MS/MSD	MDL <sup>(3)</sup>
Tier 2-Multilab	3	3	12	6 <sup>(4)</sup>	21

**Notes:**

- (1) Numbers of analyses in this table do not include background analyses or additional QC tests such as calibration, blanks, etc.
- (2) IPR reagent water analyses would be used to validate a method modification and to establish QC acceptance criteria for initial precision and recovery (IPR) and ongoing precision and recovery (OPR) for a new method. The required number of IPR analyses would be four times the number of laboratories required to validate a method modification because each laboratory would perform a 4-replicate IPR test.
- (3) A method detection limit (MDL) test would be performed in each laboratory using the alternate test procedure. 40 CFR part 136 Appendix B requires a minimum of seven analyses per laboratory to determine an MDL.
- (4) For validation of a method modification, the MS/MSD analyses would demonstrate that the EPA-designated approved method MS/MSD recovery and precision have been met.

All ATPs must be validated to demonstrate that the method is capable of yielding reliable data for compliance monitoring purposes. Test results from validation of an ATP are used to demonstrate that the ATP produces results equivalent to results produced by the EPA-designated approved method. Equivalency is established by demonstrating that the ATP generates results that meet or exceed the QC acceptance criteria of the EPA-designated approved method. Appendix E to this protocol contains the QC acceptance criteria for inorganic methods. The QC acceptance criteria for organic methods are contained in the text of the methods (for organic methods that do not contain QC acceptance criteria consult with EPA). EPA must approve all ATPs. All validation study results must be documented in accordance with the requirements outlined below.

### 3.3 Tier 1, 2, and 3 Validation Studies

The tiered approach to validation encourages laboratories to take advantage of new technologies, overcome matrix interference problems, lower detection limits, improve the reliability of results, lower the costs of measurements, or improve overall laboratory productivity without undertaking costly and time-consuming interlaboratory studies. 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 2 studies are expected to be used by vendors, commercial laboratories, water supply laboratories, dischargers, and state and municipal laboratories repetitively testing samples from multiple sites within the same industrial subcategory on a routine basis. Tier 3 studies are expected to be used by vendors,



commercial laboratories, dischargers, and state and municipal laboratories testing a wide variety of sample matrices from diverse sites.

### **3.3.1 Tier 1 Validation Studies (for Wastewater Only)**

The primary intent of Tier 1 is to allow use of a modified method by a single laboratory. Tier 1 can be applied to one or more matrix types, excluding drinking water matrices; the Office of Ground Water and Drinking Water (OGWDW) no longer accepts Tier 1, limited-use drinking (potable) water applications.

#### *Tier 1 - Single Matrix Type*

Tier 1-Single Matrix Type validation studies are performed in a single laboratory on a single matrix type. Results of the validation study and the method modification are applicable in this laboratory to this matrix type and cannot be used by another laboratory or for another matrix type.

#### *Tier 1 - Multiple Matrix Types*

If a laboratory intends to apply the method to more than one matrix type, the laboratory must validate the method on each matrix type. The maximum number of matrix types to which the ATP must be applied to demonstrate that it will likely be successful for all other matrix types is nine matrix types for wastewater ATPs. EPA chose this upper limit of matrix tests for Tier 1- multiple matrix types validation, because the maximum number of matrices tested should not be greater than the number required for Tier 3 validation of a wastewater method (nine). Therefore, after testing nine different wastewater matrix types, no subsequent matrix type tests are required, and the method can be used for any matrix type. The specific tests to be conducted on the first wastewater matrix type or and those for each additional matrix type are enumerated in Tables 4 and 5. In all cases, the laboratory must try to determine if the measurement result for the target analyte using a new matrix type differs from the result obtained in a reagent water matrix or in a previously validated matrix type sample.

Matrices that must be tested for Tier 1- multiple matrix type validation of a wastewater ATP are given in Table 6. As with a Tier 1- single matrix type validation study, Tier 1- multiple matrix type validation studies are performed in a single laboratory and, therefore, cannot be transferred to another laboratory. If a wastewater method is validated by a single laboratory in two to eight discrete matrix types, the validation is applicable to those matrix types only. However, once a laboratory has validated the method on nine matrix types, and those matrix types possess the characteristics required in Table 5, the validation is applicable to all other matrix types.

If results of Tier 1- multiple matrix type validation studies are to be applied to a different medium (e.g., air, water, soil, sludge), each medium must be represented in the samples tested in the validation study.

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**Table 6. Matrix Types Required for Multiple Matrix Type Validation Studies**

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1. Effluent from a POTW
  2. ASTM D 5905 - 96, *Standard Specification for Substitute Wastewater*
  3. Sewage sludge, if sludge will be in the permit
  4. ASTM D 1141 - 90 (Reapproved 1992), *Standard Specification for Substitute Ocean Water*, if ocean water will be in the permit
  5. Drinking water, if the method will be applied to drinking water samples (nationwide-use only)
  6. Untreated and treated wastewaters to a total of nine matrix types
- 

At least one of the above wastewater matrix types must 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<sub>3</sub> greater than 140 mg/L
- 

### **3.3.2 Tier 2 Validation Studies for Wastewater and Drinking Water**

The primary intent of Tier 2 is to allow all regulated entities and laboratories to apply an ATP to a single sample matrix type in a single industry. Since drinking water is considered a single matrix type and PWSs represent a single industry, Tier 2 facilitates nationwide use of a modified drinking water method.

EPA believes that implementation of 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, or improve overall laboratory productivity when analyzing samples from a given industry.

Significant industries within Tier 2 are: PWSs, publicly-owned treatment works (POTWs), and individual industrial subcategories that are defined in the regulations at 40 CFR parts 405 - 503. At present, there are approximately 650 industrial subcategories defined in the Part 405 - 503 regulations, each of which constitutes an individual industry under this protocol.

Tier 2 validation studies are performed in a minimum of three laboratories. Samples of the same matrix type (e.g., drinking water, final effluent, extraction-stage effluent,) are collected from one or more facilities in the same industrial subcategory. In all cases, the laboratory must try to determine if the measurement result for the target analyte using an ATP differ from the result obtained in a reagent water matrix or in a previously validated matrix type or PWS sample.

Drinking water sources tested for Tier 2 validation of a drinking water ATP must include samples collected from PWSs with water quality characteristics that are sufficiently different so that sample matrix effects, if any, can be observed. Selection of suitable PWSs requires a knowledge of the chemistry of the method. Analysts may review an applicable approved or published method for indications of matrix effects that are unique to the analyte separation and measurement technologies used in the ATP. Water quality characteristics that can affect analysis of drinking water samples include, but are not limited to, pH, total organic carbon content, turbidity, total organic halogen content, ionic strength, sulfate contamination, metal contamination, and trihalomethane contamination of the drinking water sample.

For POTWs, if an ATP is validated on final effluent only, that method would be applicable to final effluent only, and the title of the method must reflect that the method is applicable to final effluent only. If influent to treatment, primary effluent, and sludges are to be monitored, the method must be validated separately on these sample matrix types.

In contrast to Tier 1, once an ATP has been validated, the validation study results can be transferred to other laboratories, and the other laboratories may freely use the method, as long as the method is applied to analysis of samples of the validated matrix type from within the industrial subcategory, and as long as the other laboratories meet all of the method's QC acceptance criteria. If the ATP is to be applied to another matrix type, the modification must be validated separately on that matrix type.

### **3.3.3 Tier 3 Validation Studies**

The primary intent of Tier 3 is to allow nationwide use of an ATP by all regulated entities and laboratories for all matrix types. The increased flexibility at Tier 3 should allow vendors to establish that new devices and reagents produce results that are acceptable for compliance monitoring purposes, and should allow commercial laboratory chains to apply new technologies or modified techniques throughout their chain of laboratories to 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. The minimum requirements for sample matrix types that must be used in the validation study are given in Table 6. If the method is to be applied to drinking water, at least one matrix employed in the study should be of the drinking water type. If the method is to be applied to more than one sample medium (e.g., air, water, soil, sludge), a separate validation must be performed on each medium.

When validating a method modification directed at overcoming a matrix interference problem in a specific matrix type, a minimum of three samples representative of those matrix types must be included in the matrix types required by Item 6 in Table 6. For example, if an ATP is intended to overcome matrix interferences associated with effluents containing high concentrations of polymeric materials from indirect industrial discharges in the Thermoplastic Resins subcategory of the Organic Chemicals, Plastics, and Synthetic Fibers industrial category, the modification must be tested on a minimum of three such discharges. Where possible, EPA will assist the developer of the ATP in identifying sources for samples of such discharges.

### **3.4 Development of a Validation Study Plan**

Prior to conducting Tier 1, 2, or 3 validation studies, 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, such as oil and grease, a detailed validation study plan must be submitted and agreed upon prior to conducting the study. For Tier 1 ATP validations 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 3.4.1 through 3.4.6.

#### **3.4.1 Background**

The Background section of the validation study plan should:

- Identify the ATP method as a modification of an approved method
- Identify the program use of the ATP method (drinking water or waste water or both)
- Include a summary of the ATP method
- Cite the organization and method number (given in 40 CFR parts 136, 141, and 405 - 503) for the approved method
- 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 or EMMI numbers
- 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 must measure total metals.

#### **3.4.2 Objectives**

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

#### **3.4.3 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

#### **3.4.4 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

#### **3.4.5 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.

#### **3.4.6 Limitations**

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

### **3.5 Detailed Procedures for Conducting Validation Studies**

When validating ATPs, laboratories must adhere to the standardized QC detailed in the EPA-designated approved method (or other EPA-specified document) and incorporate these criteria into the ATP. Laboratories must use a reference matrix (usually, reagent water) and field samples for the validation study.

#### **3.5.1 Method Compilation**

Prior to conducting a validation study, the organization responsible for modifying the method should detail the full method in accordance with EPA's Guidelines and Format document.<sup>4</sup> If the organization that develops an ATP is a consensus standards organization or government organization with a standardized format, that organization's standard format may be used. The documented method should be distributed to each laboratory participating in the validation study to ensure that each laboratory is validating the same set of procedures.

#### **3.5.2 Method Detection Limit Study**

Each laboratory participating in the Tier 1, 2, or 3 validation study shall use the procedures specified in the modified method and perform a method detection limit (MDL) study in accordance with the procedure given at 40 CFR part 136, Appendix B.

For validation studies of an ATP, each laboratory participating in the study must demonstrate an MDL that meets the criteria specified for the EPA-designated approved method. For wastewater methods, the MDL must be equal to or less than the ML of the EPA-designated approved method or less than 1/10

the regulatory compliance limit, whichever is greater. The allowance of a higher MDL for a modified wastewater method to support a regulatory compliance limit recognizes that a method modification that overcomes interferences may not achieve as low an MDL as the EPA-designated approved 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. For drinking water ATPs, the required detection limits are specified for regulated chemical contaminants at 40 CFR part 141. For unregulated drinking water contaminants, the detection limits in the EPA-designated approved method or other EPA-specified document should be used.

Each laboratory must perform its MDL study on an instrument that is calibrated at a range that will encompass the minimum level (ML) for wastewater ATPs or one-half the maximum contaminant level (MCL) for drinking water ATPs.

### **3.5.3 Calibration**

Following completion of the MDL study, each laboratory participating in the study must perform a calibration in accordance with the procedures specified in the ATP.

For validation of an ATP, each laboratory participating in the study must demonstrate that it can meet the linearity criterion and an ML or other quantitation level that is specified in the EPA-designated approved method (or other EPA-specified document), as may often be the case for drinking water methods, in the applicable regulations.

### **3.5.4 Initial Precision and Recovery**

After successfully calibrating the instrument, each laboratory participating in the study shall perform initial precision and recovery (IPR) analyses using the procedures specified in the method. The IPR consists of analyses of four replicates of reagent water spiked with the analytes of interest.

For validation of an ATP, each laboratory participating in the study must demonstrate that it can meet the IPR precision and recovery criteria given for the EPA-designated approved method.

### **3.5.5 Field Sample Analyses**

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

#### **3.5.5.1 Tier 1 - Single Matrix Type Validation Studies**

In a Tier 1- single matrix type study performed to validate an ATP, the laboratory must 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 three field sample analyses (background, MS, and MSD). The laboratory performing the validation study must demonstrate that it can meet the MS/MSD precision and recovery QC acceptance criteria given for the EPA-designated approved method. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix E of this document. QC acceptance

criteria for other classes of analytes (e.g. pesticides) are often published in the EPA-designated approved method compilation or in other EPA documents.

#### ***3.5.5.2 Tier 1 - Multiple Matrix Type Validation Studies***

In Tier 1- multiple matrix type studies performed to validate ATPs, the laboratory must determine the background concentration and analyze an MS/MSD pair for each matrix type being tested, up to a total of nine matrix types for wastewater. Since three field sample analyses are required for each matrix type (one background, one MS, and one MSD), and between two and nine matrix types may be tested for wastewater and between two and three for drinking water, a Tier 1- Multiple matrix type validation study will require analysis of 6 - 27 samples. The laboratory performing the validation study must demonstrate that it can meet the MS/MSD precision and recovery QC acceptance criteria given for the EPA-designated approved method. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix E of this document. QC acceptance criteria for other classes of analytes (e.g. pesticides) are often published in the EPA-designated approved method compilation or in other EPA documents.

#### ***3.5.5.3 Tier 2 Validation Studies***

In a Tier 2 validation study, each of the three laboratories will determine the background concentration and analyze an MS/MSD pair on the sample it receives. Because there are three laboratories, each of which performs three analyses (one background, one MS, and one MSD), Tier 2 validation studies will require analysis of 9 samples. Each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery QC acceptance criteria given for the EPA-designated approved method. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix E of this document. QC acceptance criteria for other classes of analytes (e.g. pesticides) are often published in the EPA-designated approved method compilation or in other EPA documents.

#### ***3.5.5.4 Tier 3 Validation Studies***

In a Tier 3 validation study, each of the nine laboratories participating in the study will determine the background concentration and analyze an MS/MSD pair on the sample it receives. Since there are a total of nine laboratories, each performing three field sample analyses (one background, one MS, and one MSD), a Tier 3 validation study will require analysis of 27 samples. Each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery QC acceptance criteria given for the EPA-designated approved method. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix E of this document. QC acceptance criteria for other classes of analytes (e.g. pesticides) are often published in the EPA-designated approved method compilation or in other EPA documents.

### ***3.5.6 Ongoing Precision and Recovery***

Each batch of samples which includes field samples, but not the IPR samples, must include an OPR sample. Each laboratory participating in the study that analyzes an OPR sample must demonstrate that it can meet the OPR recovery criteria given in the EPA-designated approved method (or other EPA-specified document).

### **3.5.7 Calibration Verification**

The field samples discussed in Section 3.5.5 must be analyzed in a separate batch of instrumental determinations from the initial calibration sequence, so that calibration verification is performed. Each laboratory participating in the Tier 1, 2, or 3 validation study must verify calibration as described in the method.

Each laboratory participating in the study and verifying calibration must demonstrate that it can meet the acceptance criteria given for the EPA-designated approved method (or other EPA-specified document) for calibration verification. QC acceptance criteria for most inorganic analyte-method combinations can be found at Appendix E of this document. QC acceptance criteria for other types of analytes (e.g. pesticides) are often published in the EPA-designated approved method compilation or in other EPA documents.

### **3.5.8 Contamination Level in Blanks**

Each laboratory that participates in a Tier 1, 2, or 3 validation study must prepare and analyze at least one method blank with the sample batch during which the matrix samples are prepared and analyzed. The actual number of blank samples analyzed by each laboratory must meet or exceed the frequency specified in the method.

For validation of an ATP, each laboratory participating in the study must demonstrate that it can meet the QC acceptance criteria for blanks that are specified in the method (or other EPA-specified document).

### **3.5.9 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 must spike all field and QC samples with the surrogates/labeled compounds at the concentrations specified in the method.

For validation of an ATP, each laboratory participating in the study must demonstrate that it can meet the surrogate or labeled compound recovery criteria specified in the EPA-designated approved method (or other EPA-specified document).

### **3.5.10 Absolute and Relative Retention Time**

Each laboratory participating in a Tier 1, 2, or 3 validation study of a chromatographic method must determine the absolute and relative retention times of the analytes of interest.

Each laboratory participating in the study must demonstrate that it can meet the absolute and relative retention time criteria that are specified in the EPA-designated approved method (or other EPA-specified document).



### 3.5.11 New Analytes

As described in Section 1.3.3, EPA proposes to consider the addition of new analytes to approved methods as acceptable method modifications under this protocol. Laboratories will be required to demonstrate equivalency 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; see *Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water*.

## 3.6 Validation Study Report

Laboratories or other organizations responsible for developing ATPs at Tiers 1, 2, or 3 must document the results of the validation study in a formal validation study report that is organized and contains the elements described in this section. There is one exception to this rule. For Tier 1 ATPs which are not intended for use with method-defined analytes, the completed Checklists<sup>(5)</sup>, along with the raw data and example calculations, are considered adequate to document method equivalency; a full validation study report is not necessary. 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 must be sufficient to enable EPA to support a claim of equivalent performance of a method modification. If data are collected by a contract laboratory, the organization responsible for using the method (e.g., permittee, POTW, PWS, 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 must be appended to and referenced in the validation study report. The validation study report must identify and discuss any deviations from the study plan that were made in implementing the study.

The validation study report must contain the elements described in Sections 3.6.1 through 3.6.10.

### 3.6.1 Background

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

- Include a method summary
- Cite the organization and method number and title for the ATP
- Cite the method number (given in 40 CFR parts 136, 141, and 405 - 503) for the approved method that is being modified
- Cite the method number (given in 40 CFR parts 136, 141, and 405 - 503) for the EPA-designated approved method that is being used for demonstrating method equivalency

- 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 believed to be applicable
- List the analytes measured by the modified method including corresponding CAS Registry or EMMI 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

### **3.6.2 Study Design and Objectives**

The Study Design and Objectives section of the validation study report must describe the study design, and identify overall objectives and data quality objectives of the study. Any study limitations must 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 must be described in this section (see Section 3.4 for required elements of the study design).

### **3.6.3 Study Implementation**

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

- Identify the organization that was responsible for managing the study
- Identify the laboratories, facilities, and other organizations that participated in the study; describe how participating laboratories were selected; and explain the role of each organization involved in the study
- 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 requirements 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

### **3.6.4 Data Reporting and Validation**

This section of the validation study report must 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 Section 9.3 of this document.

### **3.6.5 Results**

This section of the validation study report presents the study results. Results must be presented on the Checklists<sup>5</sup>, or if space does not allow, results may be submitted in a tabular format attached to the Checklists. 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 3.6.10).

The Checklists, instructions for their completion, and an example set of completed Checklists are provided in Appendix D. For method modifications, the first two Checklists document the technical details required to establish equivalency; the Certification Statement commits the persons involved in the method modification and their management to the statements made in the Checklists and the supporting information provided. The Checklist performance categories, developed with input from EPA's various programs, were designed to apply to as many of these programs as possible. These Checklists apply equally well to screening and field techniques and state-of-the-art laboratory procedures.

The completed Checklists verify that the modified method met all QC acceptance criteria of the EPA-designated approved method (or other EPA-specified document), for purposes of assessing method equivalency.

### **3.6.6 Data Analysis/Discussion**

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

### **3.6.7 Conclusions**

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

### **3.6.8 Appendix A - The Method Compilation**

The modified method compilation (or modified portion of the approved method) prepared in accordance with EPA's Guidelines and Format document<sup>4</sup>, must be appended to the validation study report.

### **3.6.9 Appendix B - Validation Study Plan**

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

### **3.6.10 Appendix C - Supporting Data**

The validation study report must be accompanied by raw data and example calculations that support the results presented in the report.

### 3.6.10.1 Raw Data

The Results section of the validation study report must include 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. The raw data are method-specific and may include any of the following:

- Sample numbers or other identifiers used by both the regulated entity and the laboratory
- 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 must 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-designated approved method. Data must 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 must be provided. For instruments involving data systems (e.g., GC/MS), raw data on magnetic tape or disk must be made available on request.

### 3.6.10.2 Example Calculations

The validation study report must 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.

## **4.0 EPA REVIEW AND APPROVAL**

### **4.1 EPA Review of Applications**

All requests for approval of proposed ATPs will undergo review and approval by EPA. Limited use ATPs (Tier 1) will be approved through an EPA letter of approval. ATPs proposed for nationwide use (Tiers 2 and 3) will be approved through rulemaking. Proposed test procedures prepared under this protocol should demonstrate an improvement when compared to the existing EPA-approved 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 Analytical Methods Staff (AMS) at EPA Headquarters will review all nationwide-use ATPs and will review limited-use applications if requested by the EPA Regional Office or State Agency. AMS may be assisted in its technical review by contractor personnel. When a formal ATP application is received, AMS will first check the documentation for completeness. If the documentation is incomplete, AMS will contact the applicant and request missing documentation before proceeding with its review.

At a minimum, an application must include a completed ATP application form, the proposed test procedure in EPA standard format, and the method comparison table, before AMS will review the package. If these elements are present, AMS will assess the application to determine whether a full ATP validation is required or whether the requested modification falls within the inherent flexibility of the method. In this case, AMS will notify the applicant whether or not ATP validation is required.

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

The first step of EPA's technical review will evaluate the description of the proposed method and method comparison table, and assess the ATP's applicability for approval at 40 CFR 136 or 141. If the proposed method is not applicable to 40 CFR 136 or 141 and/or the method description or method comparison table are not acceptable, EPA will recommend rejection of the application. If this information is acceptable, the evaluation will proceed.

In the second step of EPA's review, the performance of the ATP will be evaluated. The performance (sensitivity, precision, and accuracy) of the ATP will be compared to the performance of the EPA-designated approved method used to demonstrate method equivalency. This evaluation is based on the data provided by the applicant in the Checklists. At a minimum, the results produced using the ATP must meet the QC acceptance criteria of the EPA-designated approved method. If method performance is acceptable, the review will continue.

As the third and final step, EPA will perform a detailed audit of the proposed 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 on floppy disks with the application. Data files should be in IBM-PC compatible format, suitable for input directly into statistical analysis software, such as the Trimmed Spearman-Karber, Probit, Dunnett, and ICP programs.

## 4.2 Approval Recommendation

EPA will complete its review and notify the applicant of its approval recommendation within 90 days of receiving a complete application (see Table 2). For limited-use wastewater applications (Tier 1), AMS will notify the applicant of EPA's recommendation, and forward the recommendation to the appropriate Regional Administrator (see Table 1) for action. The Regional Administrator will issue the formal approval for use of the ATP.

For limited-use drinking water applications and all nationwide-use applications (Tiers 2 or 3), AMS 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.

## 4.3 Rulemaking Process

Using the method information provided with the ATP application to develop the preamble, EPA will prepare the proposed rule for approval, compile the rule docket, pass the proposed rule through internal 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 four months, and may take longer depending on the nature of the method.* When published, the proposed rule requests public comment and allows a specified comment period, generally 30 to 60 days. At the end of the comment period, EPA will forward any significant comments to the method applicant for 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 the comment 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 and/or 141 in the next CFR update. *It generally requires a minimum of eight months 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.*

If circumstances merit, EPA may issue a letter of approval to authorize use of the ATP during the rulemaking period.

## **5.0 REFERENCES**

1. ASTM, 1994. *Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water*. Designation D-2777-86 (Reapproved 1994). *Annual Book of ASTM Standards*,. Vol. 11.04.
2. Youden, W.J. and E.H. Stienner, 1975. *Statistical Manual of the AOAC*. AOAC- International. 1111 N. 19<sup>th</sup> 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, D.C. EPA- 821-B-96-003.
5. *Checklist for Initial Demonstration of Method Performance, Checklist for Continuing Demonstration of Method Performance, and Certification Statement*

**6.0 APPENDIX A - ATP APPLICATION FORM**

<b>EPA Office of Water Alternate Test Procedure Application Form for Chemical Analytes</b>			
<b>Applicant Name and Address:</b>		<i>EPA Use Only</i> <b>ATP Case No.</b>	
<b>Date Application Submitted:</b>			
<b>Alternate Test Procedure: (Method number &amp; title)</b>			
<b>Alternate to Approved Method:</b>			
<b>EPA-designated Approved Method for Equivalency Demonstration:</b>			
<b>Analyte(s):</b>			
<b>Type (WW, DW, or WW/DW):</b>			
<b>Level of Use: (LU or NW)</b>		<b>Validation Tier: (1, 2 or 3)</b>	
<b>FOR LIMITED-USE APPLICATIONS ONLY:</b>			
<b>ID number of existing or pending permit:</b>			
<b>Issuing agency:</b>			
<b>Type of permit:</b>			
<b>Discharge serial number:</b>			
<b>ATTACHMENTS:</b>			
<input type="checkbox"/> <b>Justification for ATP</b> <input type="checkbox"/> <b>Alternate Test Procedure (Method in standard EPA format)</b> <input type="checkbox"/> <b>Method Comparison Table</b> <input type="checkbox"/> <b>Validation Study Plan (optional)</b> <input type="checkbox"/> <b>Validation Study Report</b> <input type="checkbox"/> <b>Method Information and Documentation for Preamble and Docket</b> <input type="checkbox"/> <b>Other _____</b>			
<b>Submit Application and Attachments in Triplicate</b>			



## 7.0 APPENDIX B - HEADQUARTERS AND REGIONAL ATP CONTACTS

### Headquarters

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Director, Analytical Methods Staff (AMS)  
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QAO  
USEPA Region 10  
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### Region 5

## 8.0 APPENDIX C - STANDARD EPA METHOD FORMAT

The following is a listing of the 17 required method sections. Applicants should consult the Method Guidelines and Format document<sup>4</sup> 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 must 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 must 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.

## 9.0 APPENDIX D - EQUIVALENCY CHECKLISTS

### 9.1 Checklists and Instructions for Use

The *Checklist for Initial Demonstration of Method Performance and Certification Statement* (collectively called “Checklists”) and instructions for their completion are provided in this appendix section. The Checklists, drafted by the Environmental Monitoring Management Council (EMMC), were developed for general application across all EPA programs. As a result, the Checklists contain several categories that are not relevant to Office of Water’s ATP approval program; these categories are indicated as “NA” (not applicable). The EMMC instructions are annotated to clarify each checklist item’s applicability to the ATP approval program. Annotated sections are highlighted within text boxes as shown below.

#### **ATP Approval Protocol**

Annotated instructions.

**Checklist for Initial Demonstration of Method Performance**

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***For the demonstration of equivalency, provide a checklist for each matrix in each medium.***

Date:

Page \_\_\_ of \_\_\_

Laboratory Name &amp; Address:

Facility Name:

Discharge Point ID:

EPA Program and Applicable Regulation:

Medium:

(e.g., wastewater, drinking water, soil, air, waste solid, leachate, sludge, other)

Analyte or Class of Analytes:

(e.g., barium, trace metals, benzene, volatile organics, etc.)

Initial Demonstration of Method Performance (1)				
Category	Performance Criteria (2) Based on		Results Obtained	Perf. Spec. Achieved (✓)
	Measurement Quality Method	Reference Objective		
1. Written method (addressing all elements in the EMMC format) attached				
2. Title, number and date/rev. of "reference method", if applicable (3)				
3. Copy of the reference method, if applicable, maintained at facility				
4. Differences between PBM and reference method (if applicable) attached				
5. Concentrations of calibration standards				
6. %RSD or correlation coefficient of calibration regression				
7. Performance range tested (with units)				
8. Sample(s) used in initial demonstration have recommended preservative, where applicable.				

Initial Demonstration of Method Performance (1)				
Category	Performance Criteria (2) Based on		Results Obtained	Perf. Spec. Achieved (✓)
	Measurement Quality Method	Reference Objective		
9. Sample(s) used in initial demonstration met recommended holding times, where applicable				
10. Interferences				
11. Qualitative identification criteria used				
12. Performance Evaluation studies performed for analytes of interest, where available: Latest study sponsor and title: Latest study number:				
13. Analysis of external reference material				
14. Source of reference material				
15. Surrogates used, if applicable				
16. Concentrations of surrogates, if applicable				
17. Recoveries of surrogates appropriate to the proposed use, if applicable				
18. Sample preparation				
19. Clean-up procedures				
20. Method Blank Result				
21. Matrix (reagent water, drinking water, sand, waste solid, ambient air, etc.)				
22. Spiking system, appropriate to method and application				
23. Spike concentrations (w/ units corresponding to final sample concentration)				
24. Source of spiking material				
25. Number of replicate spikes				
26. Precision (analyte by analyte)				
27. Bias (analyte by analyte)				
28. Detection Limit (w/ units; analyte by analyte)				



**Certification Statement**

7/13/96

**Date:****Page \_\_\_ of \_\_\_****Laboratory Name & Address:****Facility Name:****Discharge Point ID:****EPA Program and Applicable Regulation:****Medium:****(e.g., water, soil, air)****Analyte or Class of Analytes:****(e.g., barium, trace metals, benzene, volatile organics, etc.; Attach separate list, as needed.)**

We, the undersigned, CERTIFY that:

1. The method(s) in use at this facility for the analysis/analyses of samples for the programs of the U.S. Environmental Protection Agency have met the Initial and any required Continuing Demonstration of Method Performance Criteria specified by EPA.

2. A copy of the method used to perform these analyses, written in EMMC format, and copies of the reference method and laboratory-specific SOPs are available for all personnel on-site.

3. The data and checklists associated with the initial and continuing demonstration of method performance are true, accurate, complete and self-explanatory<sup>1</sup>.

4. All raw data (including a copy of this certification form) necessary to reconstruct and validate these performance related analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized inspectors.

\_\_\_\_\_  
**Facility Manager's Name and Title**\_\_\_\_\_  
**Signature**\_\_\_\_\_  
**Date**\_\_\_\_\_  
**Quality Assurance Officer's Name**\_\_\_\_\_  
**Signature**\_\_\_\_\_  
**Date**

This certification form must be completed when the method is originally certified, each time a continuing demonstration of method performance is documented, and whenever a change of personnel involves the Facility Manager or the Quality Assurance Officer.

<sup>1</sup> True: Consistent with supporting data.

Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.

Complete: Includes the results of all supporting performance testing.

Self-Explanatory: Data properly labeled and stored so that the results are clear and require no additional explanation.



## EMMC Checklists Instructions

### **Checklists Overview:**

The Checklists were arrived at through consensus among EPA's programs by developing performance "categories" that allow use of the same Checklists across the Agency's various programs/projects. The Checklists may be applied to screening and field techniques as well as laboratory procedures.

Implementation of the Checklists is program-specific and a category that does not apply within a given EPA program will be indicated by NA (not applicable). Criteria for a specific EPA program are to be filled in under the "Performance Criteria" column; e.g., an Office of Water Reference Method may specify 20% RSD or a correlation coefficient of 0.995 for the category that specifies calibration linearity, whereas an Office of Solid Waste Project may specify a Measurement Quality Objective of 12% RSD or a correlation coefficient of 0.998 for this category.

For each EPA program, the Checklists are to be completed for each matrix within each medium for all matrices and media to which an alternate method or method modification applies.

#### **ATP Approval Protocol:**

- (1) Under the ATP approval protocol, the term "EPA-designated approved method" is used in place of EMMC's term "reference method"
- (2) EMMC's definition of the term "media" is equivalent to the ATP protocol's definition of "matrix type."

Each completed Checklist must be retained on file at the laboratory that uses the performance-based method (PBM) or method modification and at the regulated facility from which samples are collected, and must be submitted to the appropriate Regulatory Authority upon request to support analysis of those samples to which the PBM or modified method was applied.

#### **ATP Approval Protocol :**

Under the ATP approval protocol, the term "ATP" is used in place of "PBM".

### **Header:**

Each page of the checklist contains six lines of header information, consisting of:

\* **Date** (enter the date that the checklist was completed--Program/Project implementation plans should indicate whether the checklist must be submitted to the Regulatory Authority, as well as, retained on file at the laboratory and regulated facility).

\* **Laboratory Name & Address** (If a commercial contract laboratory uses the method on behalf of one or more applicable clients, enter the name and address of the laboratory.)

\* **Facility Name** (enter the name of the water treatment facility, system, or regulated facility or other program or project specified entity where the facility maintains an on-site analytical laboratory. If the method is being employed by a commercial contract laboratory on behalf of one or more applicable clients, enter the name of the laboratory followed by a listing of the appropriate clients).

**ATP Approval Protocol:**

This field is optional. Identify the facility from which the matrix samples were taken.

\* **Discharge Point Identification Number** (enter the discharge point identification number, if applicable).

\* **EPA Program & Applicable Regulation**(enter the name of the Agency Program or Project to whom the results will be reported, or under the auspices of which the data are collected, e.g., "CAA" for Clean Air Act monitoring and "SDWA" for analyses associated with the Safe Drinking Water Act).

\* **Medium** (enter the type of environmental sample, e.g., drinking water--NOTE a separate checklist should be prepared for each medium, e.g., for checklists associated with performance-based methods for SDWA, enter "Drinking Water" as the matrix type. As the evaluations of a performance-based method will involve matrix-specific performance measures, a separate checklist would be prepared for each matrix. The "medium is the environmental sample type to which the performance-based method applies, whereas the performance category "matrix", appearing in the body of the checklists refers to the specific sample type within the "Medium" that was spiked ,e.g., for "Medium" hazardous waste, the checklist category "Matrix" may be solvent waste.

**ATP Approval Protocol:**

Enter the matrix type as defined in the ATP protocol, instead of the medium.

\* **Analyte or Class of Analytes** where available (As many methods apply to a large number of analytes, it is not practical to list every analyte in this field, as indicated on the form, the class of analytes may be specified here, i.e., volatile organics. However, if such a classification is used, a separate list of analytes and their respective Chemical Abstract Service Registry Numbers (CAS #) must be attached to the checklist).

## Initial Demonstration of Method Performance Checklist:

The Initial Demonstration of Method Performance involves multiple spikes into a defined sample matrix (e.g., wastewater medium, paper plant effluent matrix), to demonstrate that the Performance-based Method meets the Program or Project Performance Criteria based on the performance of established “Reference Method” or based on “Measurement Quality Objectives” (formerly called Data Quality Objectives). This exercise is patterned after the “Initial Demonstration of Capability” delineated in a number of the Agency’s published methods (Reference Methods).

**Footnote #1** indicates that a detailed narrative description of the initial demonstration procedure is to be provided.

**Footnote #2** indicates that for multi-analyte methods, the range of performance criteria for the analytes may be entered, but an analyte-specific performance criteria is to be attached. ***In general, when using the checklists, if the criteria or performance are lengthy, attach as a separate sheet, and enter “see attached” for this item.***

**Footnote #3** indicates that if a reference method is the source of the performance criteria, the reference method should be appropriate to the required application and the listed criteria should be fully consistent with that reference method. The reference method name and EPA number (where applicable) should be delineated in the program/project implementation plan, e.g., by the Program Office or the Project Officer/Manager.

There are 34 numbered entries in the body of the checklist--***NOTE: UNDER NORMAL CIRCUMSTANCES, IT WOULD NEVER BE ACCEPTABLE TO ANSWER “NO” TO ANY OF THESE PERFORMANCE CATEGORIES, OR FAIL TO ATTACH THE REQUESTED MATERIALS :***

### ATP Approval Protocol:

Categories that do not apply to ATP method validation are marked with “NA”.

#### #1. Written Method (addressing all elements in the EMMC format)

The details of the method used for analysis must be described in a version of the method written in EMMC format. The EMMC method format includes the following: 1.0 Scope & Application; 2.0 Summary of Method; 3.0 Definitions; 4.0 Interferences; 5.0 Safety; 6.0 Equipment & Supplies; 7.0 Reagents & Standards; 8.0 Sample Collection, Preservation & Storage; 9.0 Quality Control; 10.0 Calibration & Standardization; 11.0 Procedures; 12.0 Data Analysis & Calculations; 13.0 Method Performance; 14.0 Pollution Prevention; 15.0 Waste Management; 16.0 References; 17.0 Tables, Diagrams, Flowcharts & Validation Data. While this format may differ from that used in standard operation procedures (SOPs) in a given laboratory, the use of a consistent format is essential for the efficient and effective evaluation by inspectors, program and project managers/officers.

**ATP Approval Protocol:**

See the *Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141* (EPA-821-B-96-003) for detailed guidance on the standard EPA method format.

**#2. Title, Number and date/revision of “Reference Method” if applicable.**

For example, Polychlorinated Dioxins and Furans, EPA Method 1613, Revision B, October, 1994.

**#3. Copy of the reference method, if applicable, maintained at the facility.**

A copy of the reference method must be kept available for all laboratory personnel, however, it need not be attached to the checklist itself.

**#4. Differences between PBM and reference method attached.**

The laboratory must summarize the differences between the reference method and the performance-based method and attach this summary to the checklist. This summary should focus on significant difference in techniques (e.g., changes beyond the flexibility allowed in the reference method), not minor deviations such as the glassware used.

**#5. Concentrations of calibration standards.**

The range of the concentrations of materials used to establish the relationship between the response of the measurement system and analyte concentration. This range must bracket any action, decision or regulatory limit. In addition, this range must include the concentration range for which sample results are measured and reported (when samples are measured after sample dilution/concentration).

**#6. % RSD or Slope/Correlation Coefficient of Calibration Regression.**

This performance category refers to quantitative measures describing the relationship between the amount of material introduced into the measurement system and the response of the system, e.g., analytical instrument. A *linear response* is generally expected and is typically measured as either a linear regression or inorganic analytes, or as the relative standard deviation (or coefficient of variation) of the response factors or calibration factors for organic analytes. Traditional performance specifications considered any regression line with a correlation coefficient ( $r$ ) of 0.995 or greater as linear. Also, for organic analytes, a relative standard deviation (RSD) of 25% or less is considered linear. The calibration relationship, however, is not necessarily limited to a linear relationship. However, it should be remembered if the Program/Project Office or Officer/Managers specifies other calibration relationships, e.g., quadratic fit, more calibration standards are generally necessary to accurately established the calibration. If applicable a *calibration curve*, graphical representation of the instrument response versus the concentration of the calibration standards, should be attached.

**#7. Performance Range Tested (with units).**

This range must reflect the actual range of sample concentrations that were tested and must include the concentration units. Since the procedures may include routine sample dilution or concentration, the performance range may be broader than the range of the concentrations of the calibration standards.

**#8. Samples(s) used in initial demonstration have recommended preservative, where applicable.**

Unless preservation have been specifically evaluated, this entry should be taken directly from the reference method/standard. If preservation has been evaluated, include the study description and conclusions of that evaluation, with a reference to the specific study description. The data must be attached.

**#9. Samples(s) used in the initial demonstration must be within the recommended holding times, where applicable.**

Unless holding time (time from when a sample is collected until analysis) has been specifically evaluated, this entry should be taken directly from the reference method/standard. If holding time has been evaluated, include the study description and conclusions of that evaluation here, with a reference to the specific study description. The data must be attached.

**#10. Interferences.**

Enter information on any known or suspected interferences with the performance-based method. Such interferences are difficult to predict in many cases, but may be indicated by unacceptable spike recoveries in environmental matrices, especially when such recovery problems were not noted in testing a clean matrix such as reagent water. The inferences associated with the reference method are to be indicated, as well as, the affect of these interferences on the performance-base method.

**#11. Qualitative identification criteria used.**

Enter all relevant criteria used for identification, including such items as retention time, spectral wavelengths, ion abundance ratios. If the instrumental techniques for the Performance-based method are similar to the reference method, use the reference method as a guide when specifying identification criteria. If the list of criteria is lengthy, attach it on a separate sheet, and enter "see attached" for this item.

**#12. Performance Evaluation Studies performed for analytes of interest, where available (last study sponsor and title;; last study number:).**

Several EPA Programs conduct periodic performance evaluation (PE) studies. Organizations outside of the Agency also may conduct such studies. Enter the sponsor, title, and date of the most recent study in which the performance-based method was applied to the matrix of interest. *For the performance-based method to be acceptable, the performance on such studies must be "fully successful", i.e., within the study QC acceptance criteria.*

**#13. Analysis of external reference material.**

Enter the results of analyses on reference material from a source different from that used to prepare calibration standards (where applicable). This performance category is especially important if Performance Evaluation Studies are not available for the analytes of interest.

**#14. Source of reference material.**

Enter criteria, if applicable, for traceability of materials used to verify the accuracy of the results, e.g., obtained from the National Institute of Science and Technology (NIST).

**#15. Surrogates used if applicable.**

Surrogates may be added to samples prior to preparation, as a test of the entire analytical procedure. These compounds are typically brominated, fluorinated or isotopically labeled compounds, with structural similarities to the analytes of interest. Also, they are not expected to be present in environmental samples. Surrogates are often used in the analysis for organic analytes. Enter the names of the surrogate compounds in this category.

**#16. Concentrations of surrogates (if applicable).**

Enter the concentration of surrogates once spiked into the sample (i.e., final concentration).

**#17. Recoveries of Surrogates appropriate to the proposed use (if applicable).**

Enter the summary of the surrogate recovery limits and attach a detailed listing if more space is needed.

**#18. Sample Preparation.**

Enter necessary preliminary treatments necessary, e.g., digestion, distillation and/or extraction. A detailed listing may be attached if more space is needed.

**#19. Clean-up Procedures.**

Enter necessary intermediary steps necessary to prior to the determinative step (instrumental analysis), e.g., GPC, copper sulfate, alumina/Florisil treatment, etc.

**#20. Method Blank Result.**

A clean matrix (i.e., does not contain the analytes of interest) that is carried through the entire analytical procedure, including all sample handling, preparation, extraction, digestion, cleanup and instrumental procedures. The volume or weight of the blank should be the same as that used for sample analyses. The method blank is used to evaluate the levels of analytes that may be introduced into the samples as a result of background contamination in the laboratory. Enter the analyte/s and concentration measured in the blank.

**#21. Matrix (reagent water, drinking water, soil, waste solid, air, etc.).**

Refers to the specific sample type within the broader “Medium” that was spiked, e.g., for Medium”: “Hazardous Waste” an example matrix spiked as part of the initial demonstration of method performance might be “solvent waste”.

**ATP Approval Protocol:**

Enter the same matrix type as entered in the header.

**#22. Spiking System, appropriate to the method and application.**

Enter the procedure by which a known amount of analyte/s (“spike”) was added to the sample matrix. This may include the solvent that is employed and the technique to be employed (e.g., permeation tube, or volumetric pipet delivery techniques spiked onto a soil sample and allowed to equilibrate 1 day, etc.). *Solid matrices are often difficult to spike and considerable detailed narrative may be necessary to delineate the procedure. For spikes into aqueous samples, generally a water-miscible solvent is specified.*

**#23. Spike levels (w/units corresponding to final sample concentration).**

Enter the amount of the analyte/s (“spike”) that was added to the sample matrix in terms of the final concentration in the sample matrix.

**ATP Approval Protocol:**

Under the ATP protocol, initial spikes, also known as initial precision and recovery (IPR) standards, shall be performed in reagent water. Using reagent water allows comparison of IPR spike recoveries determined with the modified method against IPR criteria specified in the EPA-designated approved method because approved method IPR specifications are developed from reagent water spikes.

**#24. Source of spiking material.**

Enter the organization or vendor from which the “spiking” material was obtained. This should include specific identification information, e.g., lot#, catalogue number, etc.

**#25. Number of Replicate Spikes.**

The initial demonstration of method performance involves the analyses of replicate spikes into a defined sample matrix category (#21). Enter the number of such replicates. In general at least 4 replicates should be prepared and analyzed independently.

**#26. Precision (analyte by analyte).**

Precision is a measure of agreement among individual determinations. Statistical measures of precision include standard deviation, relative standard deviation or percent difference.

**#27. Bias (analyte by analyte).**

Bias refers to the systematic or persistent distortion of a measurement process which causes errors in one direction. Bias is often measured at the ratio of the measured value to the “true” value or nominal value. Bias is often (erroneously) used interchangeably with “accuracy”, despite the fact that the two terms are complementary, that is, high “accuracy” implies low “bias”, and vice versa. Enter the name of the Bias measure (% recovery, difference from true, etc.), the numeric value with associated units for each analyte obtained for each analyte spiked in the initial demonstration procedure.

**ATP Approval Protocol:**

This field is not applicable.

**#28. Detection Limit (w/units; analyte by analyte).**

A general term for the lowest concentration at which an analyte can be detected and identified. There are various measures of detection which include Limit of Detection and Method Detection Limit. Enter the detection measure (e.g., "MDL") and the analytical result with units for each analyte in the matrix (#21).

**ATP Approval Protocol:**

For ATPs, enter the detection limits specified in the EPA-designated approved method.

**#29. Confirmation of Detection Limit.**

In addition to spikes into the matrix of interest (#21) it may be beneficial to perform the detection measurements in a clean matrix, e.g., laboratory pure water. Results of the spikes in the clean matrix are frequently available in the Agency's published methods. Determining MDLs in a clean matrix using the performance-based method will allow a comparison to the MDLs published in the Agency methods.

Also, the detection limit technique may specify specific procedures to verify that the obtained limit is correct, e.g., the "iterative process" detailed in the 40 CFR Part 136, Appendix B, MDL procedures.

**#30. Quantitation Limit (w/ units; analyte by analyte).**

The lowest concentration that the analyte can be reported with sufficient certainty that an unqualified numeric value is reportable. Measures of Quantitation limits include the Minimum Level (ML), Interim Minimum Level (IML), Practical Quantitation Level (PQL), and Limit of Quantitation (LOQ). Enter the measure of Quantitation limit, and the units for each analyte.

**#31. Qualitative confirmation.**

Enter all relevant criteria used for identification, including such items as: retention time; use of a second chromatographic column; use of second (different) analytical technique; spectral wavelengths; and ion abundance ratios. If the instrumental techniques for the modified method are similar to those of the reference method, use the reference method as a guide when specifying confirmation criteria. If the list of criteria is lengthy, attach it on a separate sheet, and enter "see attached" for this item.

**#32. Frequency (initial Demonstration to be performed.**



Enter the frequency that the initial demonstration has to be repeated, e.g., with each new instrument or once a year, which ever is more frequent.

**#33-#34. Other Criteria.**

Enter other necessary program/project specific method performance categories.

**ATP Approval Protocol:**

Under the ATP approval protocol Categories 33 and 34 are used as follows:

**#33. Matrix Spike/Matrix Spike Duplicate.**

Enter the percent recoveries of analytes spiked into the sample matrix. For method modifications, only one set of matrix spike/matrix spike duplicate (MS/MSD) samples.

**#34. Matrix Spike/Matrix Spike Duplicate Relative Percent Deviation.**

Enter the calculated relative percent deviation between the MS and MSD analyte recoveries.

***Signatures:***

The name, signature and date of each analyst involved in the initial demonstration of method performance is to be provided at the bottom of the check sheet.

## **9.2 Example of Completed Checklists**

This appendix section provides an example of completed checklists and associated laboratory data. The data were obtained from a contract laboratory's testing of Method 1613, "Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS". Method 1613 is approved for use in drinking water (40 CFR 141.24) and wastewater (62 FR 48394, September 15, 1997), and proposed for use in the Pulp, Paper, and Paperboard category at 40 CFR part 430 (58 CFR 66078).

The information is technically detailed, and intended for data reviewers familiar with analytical methods. This example is provided to serve as an additional form of guidance for completing the Checklists.

## Checklist for Initial Demonstration of Method Performance

7/13/96

**For the demonstration of equivalency, provide a checklist for each matrix in each medium.**

**Date:** *February 2, 1994*

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**Laboratory Name & Address:** *ABC Analytical, Inc., Anytown, USA*

**Facility Name:** *Paper Mill #1*

**Discharge Point ID:** *N/A*

**EPA Program and Applicable Regulation:** *CWA Effluent Guidelines*

**Medium:** *Water*

(e.g., water, soil, air)

**Analyte or Class of Analytes:** *Polychlorinated Dioxins and Furans*

(e.g., barium, trace metals, benzene, volatile organics, etc.; Attach separate list, as needed.)

Initial Demonstration of Method Performance (1)				
Category	Performance Criteria (2) Based on		Results Obtained	Perf. Spec. Achieved (✓)
	Measurement Quality Method	Reference Objective		
1. Written method (addressing all elements in the EMMC format) attached				✓
2. Title, number and date/rev. of "reference method", if applicable (3)			<i>EPA Method 1613 Rev. B</i>	✓
3. Copy of the reference method, if applicable, maintained at facility				✓
4. Differences between the PBM and reference method (if applicable) attached				N/A
5. Concentrations of calibration standards	<i>Attach 1</i>		<i>Attach 1</i>	✓
6. %RSD or correlation coefficient of calibration regression	<i>Attach 2</i>		<i>Attach 2</i>	✓
7. Performance range tested (with units)	<i>Attach 3</i>		<i>Attach 3</i>	✓
8. Sample(s) used in initial demonstration have recommended preservative, where applicable.				N/A

Initial Demonstration of Method Performance (1)				
Category	Performance Criteria (2) Based on		Results Obtained	Perf. Spec. Achieved (✓)
	Measurement Quality Method	Reference Objective		
9. Samples(s) used in initial demonstration met recommended holding times, where applicable				✓
10. Interferences	<i>Attach 4</i>		<i>Attach 4</i>	✓
11. Qualitative identification criteria used	<i>Attach 5</i>		<i>Attach 5</i>	✓
12. Performance Evaluation studies performed for analytes of interest, where available: Latest study sponsor and title: Latest study number:			<i>John Doe, PE Study, 1234</i>	✓
13. Analysis of external reference material				N/A
14. Source of reference material				N/A
15. Surrogates used, if applicable	<i>Attach 6 &amp; 8</i>		<i>Attach 6 &amp; 8</i>	✓
16. Concentrations of surrogates, if applicable	<i>Attach 6 &amp; 8</i>		<i>Attach 6 &amp; 8</i>	✓
17. Recoveries of surrogates appropriate to the proposed use, if applicable	<i>Attach 6 &amp; 8</i>		<i>Attach 6 &amp; 8</i>	✓
18. Sample preparation	<i>Extraction</i>		<i>Extraction</i>	✓
19. Clean-up procedures				N/A
20. Method Blank Result	<i>Attach 8</i>		<i>Attach 8</i>	✓
21. Matrix (reagent water, drinking water, sand, waste solid, ambient air, etc.)			<i>Paper Mill Effluent</i>	✓
22. Spiking system, appropriate to method and application	<i>volumetric pipet</i>		<i>volumetric pipet</i>	✓
23. Spike concentrations (w/ units corresponding to final sample concentration)	<i>Attach 6</i>		<i>Attach 6</i>	✓
24. Source of spiking material			<i>Acme Standards lot #105 cat #41</i>	✓
25. Number of replicate spikes	<i>at least four</i>		<i>four</i>	✓

Initial Demonstration of Method Performance (1)				
Category	Performance Criteria (2) Based on		Results Obtained	Perf. Spec. Achieved (✓)
	Measurement Quality Method	Reference Objective		
26. Precision (analyte by analyte)	Attach 7		Attach 7	✓
27. Bias (analyte by analyte)				N/A
28. Detection Limit (w/ units; analyte by analyte)				N/A
29. Confirmation of Detection Limit, if applicable				N/A
30. Quantitation Limit (w/ units: analyte by analyte)	Attach 9		Attach 9	✓
31. Qualitative Confirmation	Attach 5		Attach 5	✓
32. Frequency of performance of the Initial Demonstration	Annual		Annual	✓
33. Other criterion (specify)				N/A
34. Other criterion (specify)				N/A

<sup>1</sup> Provide a detailed narrative description of the initial demonstration.

<sup>2</sup> For multi-analyte methods, enter "see attachment" and attach a list or table containing the analyte-specific performance criteria from the reference method or those needed to satisfy measurement quality objectives.

<sup>3</sup> If a reference method is the source of the performance criteria, the reference method should be appropriate to the required application, and the listed criteria should be fully consistent with that reference method.

**Name and signature of each analyst involved in the initial demonstration of method performance (includes all steps in the proposed method/modification):**

John Doe \_\_\_\_\_ 2/2/94  
Name Signature Date

\_\_\_\_\_  
Name Signature Date

\_\_\_\_\_  
Name Signature Date

**The certification above must accompany this form each time it is submitted.**

**Certification Statement**

**Date:** *February 2, 1994*

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**Laboratory Name & Address:** *ABC Analytical, Inc., Anytown, USA*

**Facility Name:** *Paper Mill #1*

**Discharge Point ID:** *N/A*

**EPA Program and Applicable Regulation:** *CWA Effluent Guidelines*

**Medium:** *Water*

**(e.g., water, soil, air)**

**Analyte or Class of Analytes:** *Polychlorinated Dioxins and Furans*

**(e.g., barium, trace metals, benzene, volatile organics, etc.; Attach separate list, as needed.)**

We, the undersigned, CERTIFY that:

1. The method(s) in use at this facility for the analysis/analyses of samples for the programs of the U.S. Environmental Protection Agency have met the Initial and any required Continuing Demonstration of Method Performance Criteria specified by EPA.

2. A copy of the method used to perform these analyses, written in EMMC format, and copies of the reference method and laboratory-specific SOPs are available for all personnel on-site.

3. The data and checklists associated with the initial and continuing demonstration of method performance are true, accurate, complete and self-explanatory (1).

4. All raw data (including a copy of this certification form) necessary to reconstruct and validate these performance related analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized inspectors.

*Jane Doe, Laboratory Manager*  
Facility Manager's Name and Title

\_\_\_\_\_  
Signature

*2/2/94*  
Date

*John Doe, Chemist*  
Quality Assurance Officer's Name

\_\_\_\_\_  
Signature

*2/2/94*  
Date

This certification form must be completed when the method is originally certified, each time a continuing demonstration of method performance is documented, and whenever a change of personnel involves the Facility Manager or the Quality Assurance Officer.

(1) True: Consistent with supporting data.

Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.

Complete: Includes the results of all supporting performance testing.

Self-Explanatory: Data properly labeled and stored so that the results are clear and require no additional explanation.

### **9.3 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 electronic versions of data can be very helpful in expediting the review of an ATP. Data files should be in IBM-PC compatible format, suitable for input directly into statistical analysis software, such as the Trimmed Spearman-Kärber, Probit, Dunnett, and ICP programs.

ATP Data Form<sup>†</sup>

ATP Method Title*		Revision Date	___/___/___
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\*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							
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## Initial Precision Recovery (IPR) Data

Spiking Concentration used for IPR Study (include units): \_\_\_\_\_

IPR Data				
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## 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			
Points	Lin	Conc	Low	High	Precision	Low	High	Low	High	RPD	MDL	ML

<sup>†</sup> 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.



## 10.0 APPENDIX E - QUALITY CONTROL ACCEPTANCE CRITERIA

Table IF- Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1

No	Analyte-Detector	Reference Method	Spike conc.	Calibration point	lin	Specification								RPD	ML
						IPR			OPR		MS/MSD				
						% Recovery and Precision			% Recovery		% Recovery				
Low	High	SD	Low	High	Low	High	Low	High							
1.	Aluminum - Flame	202.1	500 ug/L	3	10 %	81	117	18	79	119	79	119	20	15 ug/L	
	" - Furnace	202.2	500 ug/L	5	25 %	71	127	28	68	130	68	130	31	20 ug/L	
	" - ICP	200.7	500ug/L	3	10 %	81	121	20	79	123	79	123	22	50 ug/L	
2.	Ammonia - distill														
	" - Nessler	350.2	1 mg/L	3	10 %	81	121	20	79	123	79	123	22	50 ug/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 ug/L	
	" - Phenate	350.1	1 mg/L	1	---	87	115	14	86	116	86	116	15	10 ug/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 ug/L	5	25 %	70	118	24	68	120	68	120	26	20 ug/L	
	Antimony - ICP	200.7	200 ug/L	3	10 %	71	121	25	68	124	68	124	28	20 ug/L	
4.	Arsenic														
	" - Hydride	206.3	100 ug/L	3	10 %	71	127	28	68	130	68	130	31	2.0 ug/L	
	" - Furnace	206.2	100 ug/L	3	10 %	82	118	18	80	120	80	120	20	5.0 ug/L	
	" - ICP	200.7	100 ug/L	3	10 %	73	129	28	70	132	70	132	31	20 ug/L	
	" - Color (SDDC)	206.4	40 ug/L	3	10 %	72	128	28	69	131	69	131	31	10 ug/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 ug/L	
	" - ICP	200.7	1 mg/L	3	10 %	90	110	10	89	111	89	111	11	2 ug/L	
6.	Beryllium - Flame	210.1	100 ug/L	3	10 %	85	109	12	84	110	84	110	13	50 ug/L	
	" - Furnace	210.2	50 ug/L	5	25 %	79	119	20	77	121	77	121	22	1.0 ug/L	
	" - ICP	200.7	100 ug/L	3	10 %	79	119	20	77	121	77	121	22	1.0 ug/L	
7.	Boron - Color	212.3	240 ug/L	5	25 %	54	146	46	49	151	49	151	51	100 ug/L	
	" - ICP	200.7	1 mg/L	3	10 %	76	126	25	74	128	74	128	27	10 ug/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 ug/L	3	10 %	88	110	11	87	111	87	111	12	50 ug/L	
	Cadmium - Furnace	213.2	100 ug/L	3	10 %	84	114	15	83	115	83	115	16	0.5 ug/L	
	Cadmium - ICP	200.7	100 ug/L	3	10 %	84	118	17	83	119	83	119	18	2 ug/L	
10.	Calcium - Flame	215.1	200 ug/L	3	10 %	82	120	19	80	122	80	122	21	200 ug/L	
	Calcium - ICP	200.7	10 mg/L	3	10 %	86	120	17	84	122	84	122	19	20 ug/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 ug/L	3	10 %	84	112	14	83	113	83	113	15	10 ug/L	
14.	Chromium - Flame	218.1	100 ug/L	3	10 %	67	123	28	64	126	64	126	31	15 ug/L	
	Chromium - Furnace	218.2	100 ug/L	3	10 %	83	117	17	82	118	82	118	18	5 ug/L	
	Chromium - ICP	200.7	100 ug/L	3	10 %	84	118	17	82	119	82	119	18	10 ug/L	
15.	Cobalt - Flame	219.1	500 ug/L	3	10 %	85	113	14	84	114	84	114	15	500 ug/L	
	Cobalt - Furnace	219.2	100 ug/L	3	10 %	85	113	14	83	115	83	115	16	5 ug/L	
	Cobalt - ICP	200.7	100 ug/L	3	10 %	86	116	15	84	118	84	118	17	5 ug/L	
16.	Copper - Flame	220.1	100 ug/L	3	10 %	90	110	10	89	111	89	111	11	100 ug/L	
	Copper - Furnace	220.2	100 ug/L	5	25 %	86	112	13	84	114	84	114	15	5 ug/L	

Table IF- Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1

No	Analyte-Detector	Reference Method	Spike conc.	Specification										
				Calibration		IPR			OPR		MS/MSD			ML
						% Recovery and Precision	% Recovery	% Recovery	Low	High	RPD			
point	lin	Low	High	SD	Low	High	Low	High	Low	High	RPD	ML		
	Copper - ICP	200.7	100 ug/L	3	10 %	86	116	15	84	118	84	118	17	10 ug/L
17.	Cyanide - Spectro	335.2	250 ug/L	3	10 %	65	129	32	62	132	62	132	35	60 ug/L
18.	Fluoride - Elec/man	340.2	1 mg/L	3	10 %	85	115	15	84	116	84	116	16	100 ug/L
	Fluoride - SPADNS	340.1	1 mg/L	3	10 %	79	127	24	77	129	77	129	26	100 ug/L
	Fluoride - Auto	340.3	1 mg/L	3	10 %	87	117	15	85	119	85	119	17	50 ug/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 ug/L	3	10 %	87	113	13	86	114	86	114	14	300 ug/L
	Iron - Furnace	236.2	100 ug/L	5	25 %	80	124	22	78	126	78	126	24	5 ug/L
	Iron - ICP	200.7	500 ug/L	3	10 %	88	116	14	86	118	86	118	16	100 ug/L
22.	TKN - Digest	351.3	2 mg/L	5	25 %	49	153	52	44	158	44	158	57	50 ug/L
	TKN - Titr	351.3	5 mg/L	3	10 %	82	118	18	80	120	80	120	20	50 ug/L
	TKN - Nessler	351.3	5 mg/L	5	25 %	78	122	22	76	124	76	124	24	50 ug/L
	TKN - Electrode	351.3	5 mg/L	5	25 %	69	129	30	66	132	66	132	33	50 ug/L
	TKN - Phenate	351.1	5 mg/L	5	25 %	78	122	22	76	124	76	124	24	50 ug/L
	TKN - Block/color	351.2	5 mg/L	3	10 %	79	119	20	77	121	77	121	22	100 ug/L
23.	Lead - Flame	239.1	300 ug/L	3	10 %	87	113	13	86	114	86	114	14	40 ug/L
	Lead - Furnace	239.2	100 ug/L	3	10 %	84	116	16	82	118	82	118	18	5 ug/L
	Lead - ICP	200.7	300 ug/L	3	10 %	84	118	17	82	120	82	120	19	20 ug/L
24.	Magnesium - Flame	242.1	2 mg/L	3	10 %	83	115	16	81	117	81	117	18	20 ug/L
	Magnesium - ICP	200.7	2 mg/L	3	10 %	84	120	18	82	122	82	122	20	50 ug/L
25.	Manganese - Flame	243.1	100 ug/L	3	25 %	86	112	13	85	113	85	113	14	100 ug/L
	Manganese - Furnace	243.2	100 ug/L	3	10 %	83	113	15	81	115	81	115	17	1 ug/L
	Manganese - ICP	200.7	100 ug/L	3	10 %	86	114	14	84	116	84	116	16	2 ug/L
26.	Mercury - CV/Man	245.1	4 ug/L	5	25 %	84	126	26	71	129	71	129	29	0.2 ug/L
	Mercury - CV/Auto	245.2	4 ug/L	3	10 %	77	121	22	75	123	75	123	24	0.2 ug/L
27.	Molybdenum - Flame	246.1	300 ug/L	3	10 %	67	131	32	64	134	64	134	35	300 ug/L
	Molybdenum - ICP	200.7	100 ug/L	3	10 %	80	118	19	78	120	78	120	21	10 ug/L
28.	Nickel - Flame	249.1	100 ug/L	3	10 %	83	117	17	81	119	81	119	19	0.2 ug/L
	Nickel - Furnace	249.2	100 ug/L	3	10 %	84	116	16	83	117	83	117	17	5 ug/L
	Nickel - ICP	200.7	100 ug/L	3	10 %	82	120	19	80	122	80	122	21	20 ug/L
29.	Nitrate	352.1	1 mg/L	5	25 %	77	125	24	75	127	75	127	26	0.1 mg/L
30.	NO2-NO3 - Cd/Man	353.3	1 mg/L	3	10 %	79	119	20	77	121	77	121	22	10 ug/L
	NO2-NO3 - Cd/Auto	353.2	1 mg/L	3	10 %	88	110	11	87	111	87	111	12	50 ug/L
	NO2-NO3 - Cd/Hydra	353.1	1 mg/L	3	10 %	88	110	11	87	111	87	111	12	10 ug/L
31.	O-phosphate - Auto	365.1	300 ug/L	3	10 %	86	112	13	84	114	84	114	15	10 ug/L
	O-phosphate - Man 1	365.2	300 ug/L	3	10 %	89	113	12	87	115	87	115	14	10 ug/L
32.	DO - Winkler	360.2	1 mg/L	3	10 %	98	102	2.0	98	102	98	102	2.2	50 ug/L
	DO - Electrode	360.1	1 mg/L	3	10 %	98	102	2.0	98	102	98	102	2.2	50 ug/L
33.	Phenol - Color/Man	420.1	500 ug/L	3	10 %	59	123	32	56	126	56	126	35	5 ug/L

Table IF- Standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table 1

No	Analyte-Detector	Reference Method	Spike conc.	Calibration		Specification									ML
						IPR			OPR		MS/MSD				
						% Recovery and Precision			% Recovery		% Recovery				
point	lin	Low	High	SD	Low	High	Low	High	RPD						
	Phenol - Color/Auto	420.2	500 ug/L	3	10 %	41	121	40	37	125	37	125	44	2 ug/L	
34.	Phosphorus - Asc/Man	365.2	1 mg/L	3	10 %	82	112	15	81	113	81	113	16	10 ug/L	
	Phosphorus - Asc/Man	365.3	1 mg/L	3	10 %	79	115	18	77	117	77	117	20	10 ug/L	
	Phosphorus - Asc/Auto	365.1	1 mg/L	3	10 %	81	111	15	80	112	80	112	16	10 ug/L	
	Phosphorus - Block	365.4	1 mg/L	3	10 %	80	112	16	79	113	79	113	17	10 ug/L	
35.	Potassium - Flame	258.1	10 mg/L	3	10 %	84	116	16	82	118	82	118	18	100 ug/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 ug/L	3	10 %	77	117	20	75	119	75	119	22	5 ug/L	
	Selenium - ICP	200.7	300 ug/L	5	25 %	80	120	20	78	122	78	122	22	50 ug/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 ug/L	
38.	Silver - Flame	272.1	100 ug/L	3	10 %	88	112	12	86	114	86	114	14	100 ug/L	
	Silver - Furnace	272.2	100 ug/L	3	10 %	83	115	16	82	116	82	116	17	1 ug/L	
	Silver - ICP	200.7	100 ug/L	3	10 %	83	117	17	82	118	82	118	18	5 ug/L	
39.	Sodium - Flame	273.1	30 ug/L	3	10 %	90	116	13	88	118	88	118	15	30 ug/L	
	Sodium - ICP	200.7	10 mg/L	3	10 %	86	122	18	85	123	85	123	19	100 ug/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 ug/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 ug/L	
42.	Thallium - Flame	279.1	100 ug/L	3	10 %	85	115	15	83	117	83	117	17	600 ug/L	
	Thallium - Furnace	279.2	100 ug/L	3	10 %	81	115	17	80	116	80	116	18	5 ug/L	
	Thallium - ICP	200.7	100 ug/L	3	10 %	73	127	27	70	130	70	130	30	50 ug/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 ug/L	3	10 %	82	118	18	80	120	80	120	20	10 ug/L	
	Vanadium - ICP	200.7	200 ug/L	3	10 %	87	113	13	86	114	86	114	14	10 ug/L	
46.	Zinc - Flame	289.1	100 ug/L	3	10 %	87	113	13	85	115	85	115	15	50 ug/L	
	Zinc - Furnace	289.2	100 ug/L	3	10 %	81	119	19	79	121	79	121	21	0.2 ug/L	
	Zinc - ICP	200.7	100 ug/L	3	10 %	83	121	19	81	123	81	123	21	5 ug/L	

## Legend for acronyms and abbreviations in Table IF:

Reference Method: QC acceptance criteria are for modifications to the reference method specified in Table IB.

CAL points: the number of points required for calibration

CAL 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.

Spike conc. : the concentration at which the QC acceptance criteria were determined.

%Recovery: the amount of analyte recovered expressed as a percent.

SD: the standard deviation of the % recovery.

IPR SD : the upper limit on the QC acceptance criterion for precision of the determination of % recovery expressed as the SD at the spike concentration, it is not an RSD.

IPR recovery (low/high): the lower and upper QC acceptance criteria for % recovery in the initial precision and recovery test.

OPR recovery (low/high): the lower and upper QC acceptance criteria for % recovery in the ongoing precision and recovery test.

MS/MSD recovery (low/high): the lower and upper QC acceptance criteria for % recovery of the matrix spike and matrix spike duplicate.

RPD = relative percent difference (RPD) is the absolute value of the difference between two measurements expressed as a percent. For the MS/MSD test  $RPD = 100\% \times \frac{|MS - MSD|}{\frac{1}{2}(MS + MSD)}$ .

MS/MSD RPD: the upper limit on the QC acceptance criterion for precision expressed as the RPD for the MS/MSD test.

ML value: The minimum level (ML) as the lowest calibration point

Table I Standardized QC and QC Acceptance Criteria for Modifications to Methods in 40 CFR 141.23(k)(1)

No.	Analyte - Detector	Reference Method	Spike conc.	Specification										MDL
				Calibration point lin		IPR			OPR		MS/MSD			
						% Recovery and Precision			% Recovery		% Recovery			
						Low	High	SD	Low	High	Low	High	RPD	
1.	Antimony -	200.8	10 ug/L	3	10 %	81	117	18	80	118	80	118	19	0.4 ug/L
	Antimony - STGFAA	200.9	10 ug/L	3	10 %	72	132	30	69	135	69	135	33	0.8 ug/L
2.	Arsenic - ICP	200.7	50 ug/L	3	10 %	87	113	13	86	114	86	114	14	0.008 mg/L
	Arsenic - ICP/MS	200.8	50 ug/L	3	10 %	91	111	10	90	112	90	112	11	1.4 ug/L
	Arsenic - STGFAA	200.9	50 ug/L	3	10 %	86	114	14	84	116	84	116	16	0.5 ug/L
3.	Barium - ICP	200.7	1 mg/L	3	10 %	91	107	7.6	91	107	91	107	8.4	0.001 mg/L
	Barium - ICP/MS	200.8	1 mg/L	3	10 %	92	106	7.2	91	107	91	107	7.9	0.8 ug/L
4.	Beryllium - ICP	200.7	4 ug/L	3	10 %	84	112	14	83	113	83	113	15	0.0003 mg/L
	Beryllium - ICP/MS	200.8	4 ug/L	3	10 %	87	115	14	85	117	85	117	16	0.3 ug/L
	Beryllium - STGFAA	200.9	4 ug/L	3	10 %	82	118	18	80	120	80	120	20	0.02 ug/L
5.	Cadmium - ICP	200.7	5 ug/L	3	10 %	82	118	18	81	119	81	119	19	0.001 mg/L
	Cadmium - ICP/MS	200.8	5 ug/L	3	10 %	89	109	10	88	110	88	110	11	0.5 ug/L
	Cadmium - STGFAA	200.9	5 ug/L	3	10 %	80	118	19	78	120	78	120	21	0.05 ug/L
6.	Calcium - ICP	200.7	100 mg/L	3	10 %	93	110	8.6	92	112	92	112	9.5	0.01 mg/L
7.	Chromium - ICP	200.7	100 ug/L	3	10 %	90	108	9.4	89	109	89	109	10	0.003 mg/L
	Chromium - ICP/MS	200.8	100 ug/L	3	10 %	90	106	8.4	89	107	89	107	9.2	0.9 ug/L
	Chromium - STGFAA	200.9	50 ug/L	3	10 %	85	115	15	84	116	84	116	16	0.1 ug/L
8.	Copper - ICP	200.7	1 mg/L	3	10 %	93	109	8	92	110	92	110	8.8	0.003 mg/L
	Copper - ICP/MS	200.8	1 mg/L	3	10 %	92	110	9.4	91	111	91	111	10	0.5 ug/L
	Copper - STGFAA	200.9	100 ug/L	3	10 %	86	114	14	85	115	85	115	15	0.7 ug/L
9.	Cyanide - Spectro/Auto	335.4	200 ug/L	3	10 %	66	118	26	63	121	63	121	29	5 ug/L
10.	Fluoride - IC	300.0	2 mg/L	3	10 %	85	109	12	84	110	84	110	13	0.01 mg/L
11.	Lead - ICP/MS	200.8	15 ug/L	3	10 %	92	111	9.8	91	113	91	113	11	0.6 ug/L
	Lead - STGFAA	200.9	15 ug/L	3	10 %	84	118	17	82	120	82	120	19	0.7 ug/L
12.	Mercury - CV/Man	245.1	2 ug/L	3	10 %	66	122	28	63	125	63	125	31	0.2 ug/L
	Mercury - CV/Auto	245.2	2 ug/L	3	10 %	67	119	26	64	122	64	122	29	0.2 ug/L
	Mercury - ICP/MS	200.8	2 ug/L	3	10 %	54	138	42	50	142	50	142	46	0.2 ug/L
13.	Nickel - ICP	200.7	100 ug/L	3	10 %	87	109	11	86	110	86	110	12	0.005 mg/L
	Nickel - ICP/MS	200.8	100 ug/L	3	10 %	91	107	8.4	90	108	90	108	9.2	0.5 ug/L
	Nickel - STGFAA	200.9	50 ug/L	3	10 %	85	115	15	83	117	83	117	17	0.6 ug/L
14.	Nitrate - IC	300.0	5 mg/L	3	10 %	90	110	9.6	89	111	89	111	11	0.002 mg/L
	Nitrate - Cd/Auto	353.2	5 mg/L	3	10 %	88	114	13	87	115	87	115	14	10 ug/L
15.	Nitrite - IC	300.0	1 mg/L	3	10 %	83	111	14	81	113	81	113	16	0.004 mg/L
	Nitrite - Cd/Auto	353.2	1 mg/L	3	10 %	92	108	8.0	91	109	91	109	8.8	10 ug/L
16.	O-phosphate - IC	300.0	1 mg/L	3	10 %	84	114	15	83	115	83	115	16	0.003 mg/L
	O-phosphate - Asc/Auto	365.1	1 mg/L	3	10 %	90	110	9.8	89	111	89	111	11	1 ug/L
17.	Selenium - ICP/MS	200.8	50 ug/L	3	10 %	82	110	14	80	112	80	112	16	7.9 ug/L
	Selenium - STGFAA	200.9	50 ug/L	3	10 %	76	112	18	75	113	75	113	19	0.6 ug/L
18.	Silica - ICP	200.7	5 mg/L	3	10 %	87	121	10	84	124	84	124	12	0.02 mg/L
19.	Sodium - ICP	200.7	5 mg/L	3	10 %	92	116	12	91	117	91	117	13	0.03 mg/L
20.	Thallium - ICP/MS	200.8	5 ug/L	3	10 %	89	115	13	88	116	88	116	14	0.3 ug/L
	Thallium - STGFAA	200.9	5 ug/L	3	10 %	68	128	30	65	131	65	131	33	0.7 ug/L

**Legend for acronyms and abbreviations in Table I:**

Reference Method: QC acceptance criteria are for modifications to the reference method specified at 141.23(k)(1).

Calibration: the number of points required for calibration and the linearity of the 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.

Spike conc. : the concentration at which the QC acceptance criteria were determined.

%Recovery: the amount of analyte recovered expressed as a percent.

SD: the standard deviation of the % recovery also expressed as a percent.

IPR SD : the upper limit on the QC acceptance criterion for precision of the determination of % recovery expressed as the SD at the spike concentration, it is not an RSD.

IPR recovery (low/high): the lower and upper QC acceptance criteria for % recovery in the initial precision and recovery test.

OPR recovery (low/high): the lower and upper QC acceptance criteria for % recovery in the ongoing precision and recovery test.

MS/MSD recovery (low/high): the lower and upper QC acceptance criteria for % recovery of the matrix spike and matrix spike duplicate.

RPD: relative percent difference (RPD) is the absolute value of the difference between two measurements expressed as a percent. For the MS/MSD test  $RPD = 100\% \times [(MS - MSD) / \frac{1}{2} (MS + MSD)]$ .

MS/MSD RPD: the upper limit on the QC acceptance criterion for precision expressed as the RPD for the MS/MSD test.

MDL: the method detection limit from table at 141.23(a)(4)(i) or the reference method against which to evaluate the MDL of the modified method.

Asc/Auto Ascorbic Acid Automated

Cd/Auto Cadmium Automated

CV Man/Auto Cold Vapor Manual/Automated

IC Ion Chromatography

ICP Inductively Coupled Plasma as in ICP Atomic Emission Spectrometry

ICP/MS ICP/Mass Spectrometry

STGFAA Stabilized Temperature Graphite Furnace Atomic Absorption

Spectro/Auto Spectrophotometric Semi-Automated