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Guide to Method Flexibility and Approval of EPA Water Methods

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In Memory Of

This guide is dedicated to Dr. Baldev Bathija, in memory of his commitment to the improvement of EPA methods, his boundless enthusiasm, and his unwavering support for the streamlining initiative described in this document.

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Acknowledgments

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Foreword

This draft guidance document describes the principles and procedures for a comprehensive initiative to expand method flexibility and expedite approval of analytical methods for wastewater and drinking water at 40 CFR parts 136 and 141. This initiative represents a combined effort of EPA's Office of Science and Technology and Office of Ground Water and Drinking Water to streamline EPA's water methods approval programs.

This guide was prepared by the Engineering and Analysis Division of the Office of Science and Technology within EPA's Office of Water. The guide is for use by EPA Headquarters and Regional personnel, permittees, state and local regulatory authorities, purveyors of new technology, and analytical laboratories in implementing the Office of Water's streamlining initiative.

This guide does not duplicate other Agency guidance and should be supplemented with other guidance for specific topics. Citations for supplemental guidance are included in the guide where applicable.

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Chapter 1

Introduction

1.1 Background and Overview

Within the U.S. Environmental Protection Agency (EPA), the Office of Water (OW) publishes test procedures (analytical methods) for analysis of wastewater and drinking water. Listed at parts 136 and 141 of Title 40 of the *Code of Federal Regulations* (CFR), these methods are authorized for use in data gathering and environmental monitoring under the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA). These methods have been developed by EPA, by consensus standards organizations, and by others. Many of these methods, especially methods published before 1990, are prescriptive with limited ability to modify procedures or change technologies to accommodate specific situations. There has been a growing awareness within EPA and the analytical community that the requirement to use prescriptive measurement methods and technologies to comply with Agency regulations has unintentionally imposed a significant regulatory burden and created a barrier to the use of innovative environmental monitoring technology.

EPA has demonstrated its commitment to reducing unnecessary regulatory burdens by initiating a number of programs that respond to the needs of the regulated community, the technology development community, and the laboratory services community. As part of this new Agency-wide approach, EPA's Office of Science and Technology (OST) and Office of Ground Water and Drinking Water (OGWDW) have coordinated with various Headquarters offices, EPA Regions, States, other governmental agencies, water and wastewater utilities, industry, environmental laboratories, instrument vendors, consensus standards organizations, and other interested parties to define a comprehensive program to streamline OW's water test methods approval program. The streamlining initiative encourages the use of emerging and innovative technologies by (1) increasing method flexibility so that approved methods can be modified without formal EPA approval, (2) providing a mechanism for non-EPA organizations to develop and submit new methods for approval, and (3) expediting the method approval process. EPA believes that streamlining also offers the opportunity to improve the quality of environmental monitoring.

The streamlining initiative seeks to allow laboratories and regulated entities to use professional judgement in modifying and developing alternatives to approved test methods to take advantage of emerging technologies that reduce costs, overcome analytical difficulties, and enhance data quality. A necessary condition of method flexibility is the requirement that a modified method produce results equivalent or superior to results produced by the approved reference method. EPA believes that increasing method flexibility and streamlining the method approval process will provide several benefits. Permittees, permit writers, public water systems, and drinking water laboratories will be allowed the flexibility to select the analytical method that yields improved performance in specific discharge or drinking water monitoring situations. The flexibility to select more appropriate methods provides an opportunity to use new technologies to overcome matrix interference problems, lower

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detection limits, improve laboratory productivity, or reduce the amount of hazardous wastes in the laboratory.

A more flexible method approval program is consistent with President Clinton's Environmental Technology and Reinventing Government initiatives and Congress' National Technology Transfer and Advancement Act of 1995 (NTTAA). It will empower stakeholders while decreasing demands on Agency resources. The streamlined program is intended to accelerate environmental technological innovation as a means of strengthening America's economy and creating jobs while enhancing environmental protection. EPA believes that the incentives provided by a more flexible water test methods approval program will spur the development of new technologies and with it, new jobs. In addition, EPA anticipates that the use of new technologies may lower the cost of environmental measurements, thereby reducing costs of environmental compliance for American industries and municipalities.

1.1.1 Statutory Authority

1.1.1.1 Clean Water Act requirements

The CWA requires the EPA Administrator to promulgate effluent limitations guidelines for specified categories and classes of point sources. Section 301 of the CWA prohibits the discharge of any pollutant into navigable waters unless the discharge complies with a National Pollutant Discharge Elimination System (NPDES) permit issued under Section 402 of the Act. Section 307 requires the EPA Administrator to publish regulations establishing pretreatment standards for introduction of pollutants into publicly owned treatment works (POTWs). Section 401 requires certification for the construction or operation of facilities which may result in any discharge into the navigable waters.

CWA Section 304(h) requires the EPA Administrator to promulgate guidelines establishing test procedures for data gathering and monitoring compliance with published guidelines. EPA's approval of analytical methods is authorized under this section of CWA, as well as the general rulemaking authority in CWA Section 501(a). The Section 304(h) test procedures (analytical methods) are specified at 40 CFR part 136. They include “Methods for Chemical Analysis of Water and Waste” (MCAWW); the 600- and 1600- series methods; methods published by consensus standards organizations such as ASTM and AOAC-International, and the publication “Standard Methods for the Examination of Water and Wastewater” (Standard Methods), which is published jointly by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF); methods used by the U.S. Geological Survey; methods developed by the environmental community; and other methods referenced in CWA regulations. EPA uses these test procedures to support development of effluent limitations guidelines approved at 40 CFR parts 400 - 499, to establish compliance with (NPDES) permits issued under CWA Section 402, for implementation of the pretreatment standards issued under CWA Section 307, and for CWA Section 401 certifications.

1.1.1.2 Safe Drinking Water Act requirements

The SDWA requires the EPA Administrator to promulgate national primary drinking water regulations (NPDWRs) that specify maximum contaminant levels (MCLs) or treatment techniques for listed drinking water contaminants (Section 1412). In addition, Section 1445(a) of SDWA authorizes the Administrator to establish regulations for monitoring to assist in determining whether persons are acting in compliance with the requirements of SDWA. EPA's approval of analytical test procedures is

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authorized under these sections of SDWA, as well as the general rulemaking authority in SDWA Section 1450(a).

SDWA Section 1401(1)(D) specifies that NPDWRs contain criteria and procedures to ensure a supply of drinking water that dependably complies with MCLs, including quality control (QC) and testing procedures to ensure compliance with such levels and to ensure proper operation and maintenance of drinking water supply and distribution systems. These test procedures (analytical methods) are approved at 40 CFR part 141. They include MCAWW methods; the 200, 300 and 500 series methods; and other methods referenced in SDWA regulations. EPA uses these test procedures to establish MCLs under SDWA Section 1412 and to establish monitoring requirements under SDWA Section 1445(a).

1.1.2 Current Office of Water Methods Approval Programs

Requirements for approval of alternate analytical techniques (methods) are specified at 40 CFR 136.4 and 136.5 for wastewater methods and at 40 CFR 141.27 for drinking water methods. These requirements are the basis for the Agency's alternate test procedure (ATP) program for water methods. Under the ATP program, an organization may submit an application for approval of a modified version of an approved method or for approval of a new method to be used as an alternate to an approved method. The submitting organization is responsible for validating the new or modified method. The Agency reviews the ATP validation package and, if required, promulgates successful applications in the CFR. Rulemaking is required when a new or revised method is added to the list of approved methods in the CFR. The ATP and rulemaking processes make heavy demands on stakeholder, contractor, EPA, and *Federal Register* resources. These processes can require several months to approve a minor method modification and a year or more to promulgate a major modification or a new technology. Because advances in analytical technology continue to outpace the capacity of OW's method approval program, the program has been under-utilized and slow to respond to emerging technologies. In the streamlining initiative, which is described below, EPA proposes to amend the procedures at 40 CFR 136.4, 136.5, and 141.27 to specify a more rapid and less resource intensive process for approval of new technologies. The current ATP process is depicted in **Figure 1.1.**

1.2 The Streamlining Initiative

Upon accepting responsibility for the wastewater methods approval program, EPA's EAD undertook a review of the method needs and available resources of EPA; the regulated community; state, regional, and local permitting authorities; and the analytical services community. EAD determined that the methods approval program would best be served by undertaking a streamlining initiative to (1) expand the flexibility to modify approved methods without a cumbersome review and approval process, in order to allow timely introduction of emerging technologies; and (2) expedite the approval of new and modified methods, involving outside organizations in the method development process. During 1995 and 1996, EAD developed and refined a comprehensive initiative to streamline OW's method approval program. This streamlining initiative is a combined effort of EPA's Office of Science and Technology and Office of Ground Water and Drinking Water and applies to approval of wastewater and drinking water methods.

To keep pace with advances in technology, EPA believes that this is an appropriate time to look to organizations outside of EPA to assist in the development of new methods and to find ways to take advantage of emerging technologies to reduce costs, overcome interferences, and enhance data quality. Once the streamlining initiative is in place, EPA expects to increase its reliance on outside

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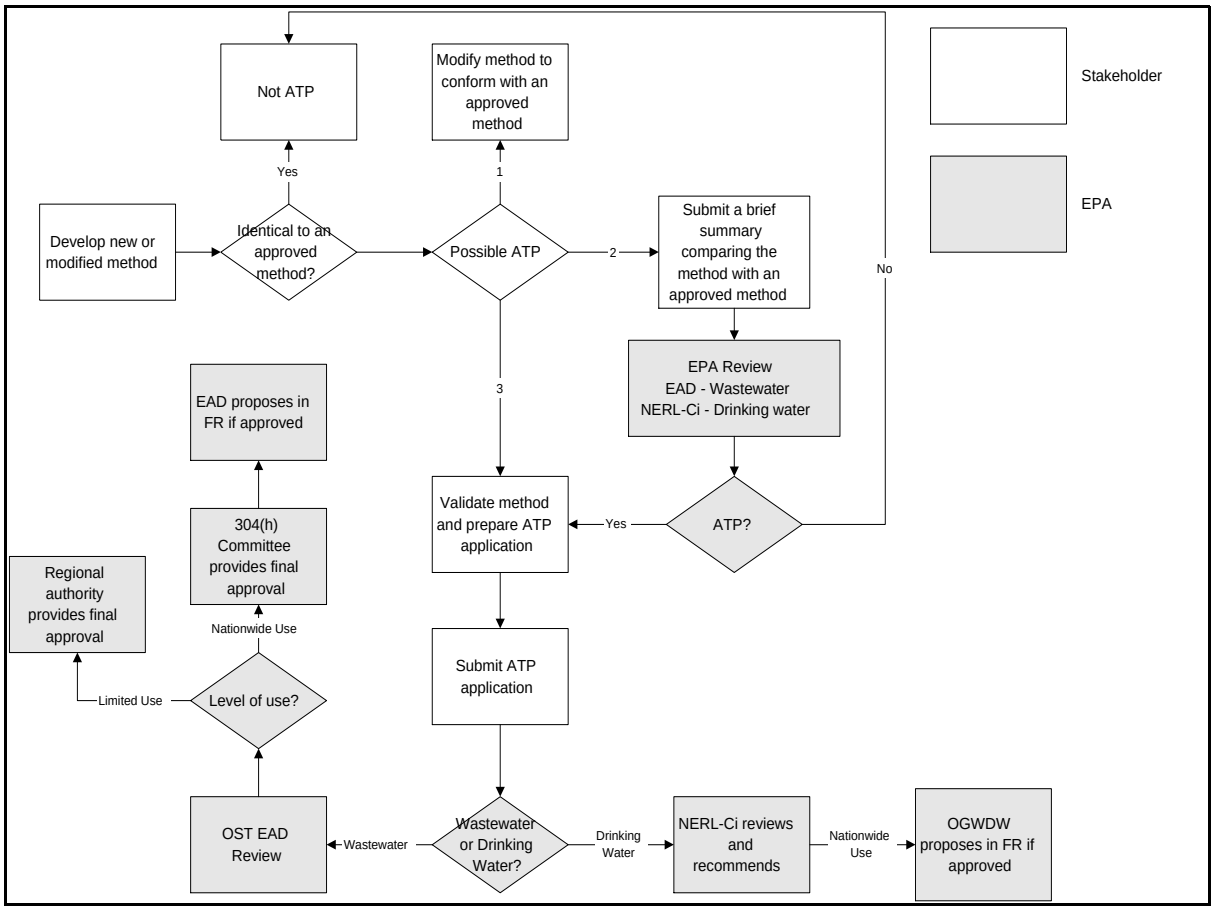
Figure 1-1: The Current Alternate Test Procedure Process



organizations to develop new methods. EPA will focus its methods development efforts on specialized, esoteric, or orphan methods to support regulation development or compliance monitoring.

EPA recognizes that expanded flexibility must be matched with controls to ensure that program quality is maintained. These controls include a system for organizations that modify methods to demonstrate and document equivalency of the modified method to the approved reference method. The requirements for documenting equivalency of modified methods are tiered to reflect the variety of conditions under which a modification will be applied. The requirements for validating newly developed methods are similarly tiered.

An overview of the proposed streamlined method approval program described in this Guide is depicted in **Figure 1.2**. This streamlined program would replace the current ATP process depicted in Figure 1.1.

1.2.1 Streamlining Objectives

The proposed streamlining initiative is designed to improve overall resource use while making the method development process more efficient and accessible to non-EPA organizations. The goals

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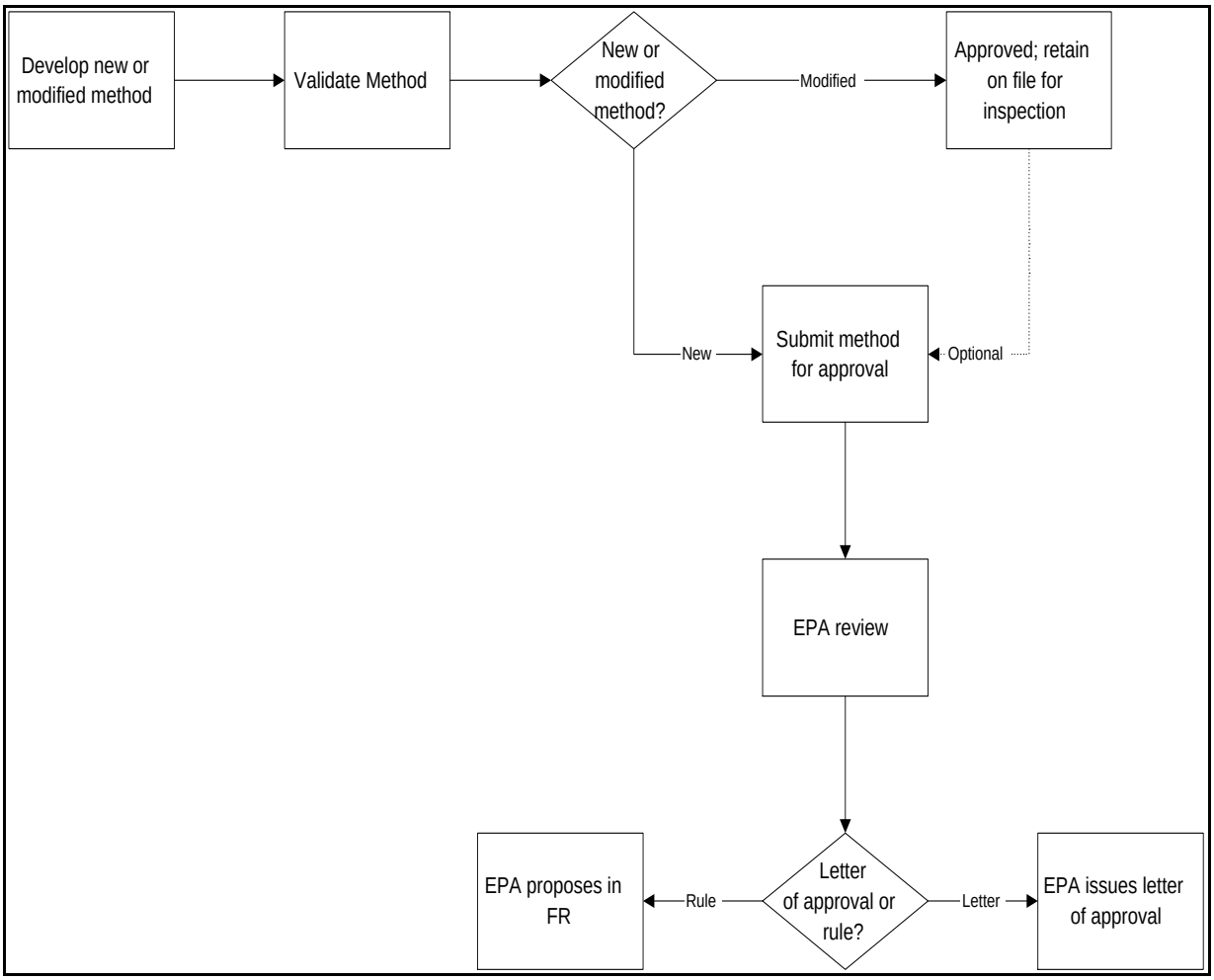
Figure 1-2: Proposed Streamlined Methods Approval Program



of the initiative are to decrease the need for developers of modified methods to use the ATP program and to speedup the approval (or disapproval) of methods subject to ATP review. EPA has defined several specific objectives to meet these goals. The objectives of the streamlining initiative are to:

(1) Increase the current flexibility to modify approved chemical and biological test methods without formal EPA approval; this will allow laboratories to overcome matrix interferences and will facilitate early introduction of innovative technologies.

(2) Designate a reference method for each combination of analyte and determinative technique and establish standardized quality control (QC) tests for approved methods, to ensure data quality while allowing for method flexibility.

(3) Develop QC acceptance criteria for reference methods lacking these criteria, to provide a means whereby a laboratory can demonstrate equivalent or superior performance of a modified method.

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(4) Provide a standard mechanism for validation and approval of new chemical and biological test methods, including a standard method format, to expedite method approval and increase confidence in the validity of the methods and resulting data.

(5) Encourage stakeholder participation in method development, to keep pace with emerging technologies.

(6) Prepare to harmonize the wastewater and drinking water methods by setting the stage for consolidation of the water methods.

(7) Increase standardized data reporting by recommending use of standard data elements for reporting analytical results for environmental and QC samples.

(8) Identify and propose withdrawal of outdated methods from 40 CFR parts 136 and 141, to modernize approved test methods.

1.2.2 Benefits of Streamlining

Advantages of streamlining EPA's water methods approval program are expected to be widely shared by EPA, purveyors of new technology, the regulated community, regulatory authorities, and analytical laboratories. Flexibility in methods is expected to enhance compliance monitoring programs by reducing the need for EPA and state, regional, and local permitting authorities to review and provide formal approval of specific method adaptations. In addition, method flexibility, along with a well-defined program for developing and approving new methods, will provide research laboratories, instrument vendors, and equipment manufacturers with incentives for developing new analytical techniques. This, in turn, will provide the regulated community and their laboratories more flexibility to select analytical methods that yield improved performance in specific wastewater discharge or drinking water monitoring situations.

Expanding method flexibility and streamlining the method approval process will yield several benefits.

(1) Because of increased flexibility to modify methods without formal EPA approval, only new methods require formal EPA approval. Because ATPs for modified methods will be processed only upon request, the number of methods that must pass through the rulemaking process will be significantly reduced. This will reduce demand on Agency resources at the same time that the use of new technologies accelerates.

(2) Allowing more extensive modification of existing methods will make laboratory operations more efficient, reduce analytical costs, reduce the amount of hazardous materials in laboratories, enhance development of new instrumentation, and improve the quality of environmental data.

(3) Non-EPA organizations, including instrument vendors and laboratories, will have a mechanism for gaining timely approval of new methods

(4) Use of direct final rulemaking for approval of noncontroversial method revisions will decrease the time and effort to approve and list a method in the CFR.

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(5) Detailed guidance on the preparation and submission of requests for approval of new methods will ensure that new methods are approved as quickly as possible.

(6) Requirements for standard QC tests in all methods will ensure consistency among methods and enhance program and data quality.

(7) Established method validation requirements will facilitate method development as well as ensuring that, prior to approval, all methods undergo levels of testing appropriate to their intended use.

1.2.3 Development of EPA's Streamlining Initiative

Between April and August 1995, EPA developed a “straw man” for streamlining, composed of several draft documents dealing with issues of method flexibility, standardized QC, method validation, and method format. This straw man was provided to and discussed with participants at several public meetings on streamlining held by EPA. As of the publication date of this draft guide, EPA has conducted four public meetings on streamlining its water test methods approval program. These meetings were held in Seattle, Washington on September 28, 1995; Boston, Massachusetts on January 25, 1996; Chicago, Illinois on February 14, 1996; and Denver, Colorado on July 24, 1996. The purpose of these meetings was to present and discuss EPA's straw man for streamlining and to obtain stakeholder suggestions for the purpose of refining the streamlining approach prior to its proposal.

All meetings were announced in the *Federal Register* in advance. The first meeting, held in Seattle, was announced on September 12, 1995, in a *Federal Register* notice titled, "A Public Meeting and Availability of Documents on Streamlining Approval of Analytical Methods at 40 CFR Part 136 and Flexibility in Existing Test Methods" (60 *FR* 47325). That *Federal Register* notice provided supplementary information regarding the streamlining effort and made available several supporting documents. Subsequent public meetings in Boston and Chicago were announced in a *Federal Register* notice dated December 18, 1995 (60 *FR* 65206), and the fourth public meeting in Denver was announced in a *Federal Register* notice on July 10, 1996 (61 *FR* 36328).

Stakeholder comments at the public meetings showed strong support for all of the streamlining objectives. The straw man and summaries of the public meetings were distributed to meeting participants and made available to others in response to requests through OST. Following the first three public meetings, EPA compiled and reviewed preliminary stakeholder advice to assess the initial response to streamlining and revise the approach accordingly. In response to stakeholder suggestions, EPA added seven items to the streamlining initiative:

- Drinking water methods (40 CFR part 141) were included.
- Flexibility was expanded to include changes to the determinative technique.
- Flexibility was qualified to clarify that flexibility in front-end techniques does not apply to sample collection and preservation.
- Tier 1 validation was expanded to allow single-laboratory application of a method modification to multiple matrix types.
- An option to have EPA review Tier 2 and Tier 3 method modifications, upon request, was added.
- An option to have EPA propose and promulgate reviewed Tier 2 and Tier 3 method modifications, upon request, was added.
- An option to submit screening methods for approval as new methods was added.

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This Streamlining Guide and the *Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141* (Method Guidelines and Format) were developed in July 1996, and replaced the supplementary information made available through the September 12, 1995, notice. These documents served as the new straw man discussed at the final public meeting on streamlining held in Denver.

In addition to the public meetings, EPA solicited support and expertise from each of the consensus standards organizations and government agencies that have developed methods already approved for use under the wastewater and drinking water programs. These groups include the American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) as publishers of Standard Methods for the Examination of Water and Wastewater (Standard Methods); ASTM (formerly, American Society for Testing and Materials); AOAC-International (formerly the Association of Official Analytical Chemists); and the U.S. Geological Survey (USGS). EPA also provided the opportunity for individuals, the regulated industry, vendors, laboratories, and laboratory organizations such as the International Association of Environmental Testing Laboratories (IAETL) to voice opinions at these meetings. These groups offered valuable insight concerning problems with the current program and recommended areas of improvement. Also, some of these organizations have developed or are developing standardized procedures for the areas listed above. In these instances, EPA has built upon the experience and efforts of these organizations. For example, EPA recommends use of the method validation protocols developed by ASTM and AOAC-International.

Major stakeholder organizations have participated in and provided input at the public meetings. These organizations include: International Association for Environmental Testing Laboratories American Association for Laboratory Accreditation, American Chemical Society, American Council of Independent Laboratories, American Industrial Hygiene Association, American Water Works Association, Chemical Manufacturers Association, and Water Environment Federation.

To ensure that the streamlining initiative remains current and is responsive to changing policies, OW has committed to support committees such as the Environmental Monitoring Management Council (EMMC) and the National Environmental Laboratory Accreditation Committee (NELAC). OW also is committed to tracking method development efforts by stakeholders such as ASTM, AOAC-International, and the National Council of the Paper Industry for Air and Stream Improvement (NCASI).

EPA has used informal suggestions received at public meetings and through unsolicited correspondence in developing its approach to streamlining that is described in this guide. Formal comments on the streamlining initiative will be requested when streamlining is proposed in the *Federal Register*.

1.2.4 Implementation Issues

Through the public meetings and stakeholder discussions, EPA has identified and is addressing key implementation issues related to streamlining.

1.2.4.1 Legal issues

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Stakeholders expressed concern regarding potential conflicts between regulators and regulated entities when using modified methods. For example, there was wide-spread concern over what would happen if a discharger used a modified method and demonstrated compliance with a regulatory concentration limit whereas a regulatory authority used the unmodified reference method and obtained results suggesting that the discharger was out of compliance.

Representatives from EPA's OST, Office of Wastewater Management, and Office of Enforcement and compliance Assurance met to study this question. Through these discussions it became apparent that the streamlined program would work only if the modified method, once demonstrated to be equivalent to the reference method, carried the same legal force and effect as the reference method. Therefore, the difference in results produced by the modified and unmodified reference methods would be attributable not to the modification, but to differences in results produced by two laboratories. This situation is no different than the situation that currently exists, in that two laboratories can produce different results, one of which is above and the other below a regulatory compliance limit. The legal resolution would therefore remain the same as today -- a decision would be made based on examination of the data.

1.2.4.2 Resource issues

Drinking water laboratory certification officials and pretreatment coordinators have expressed a common concern regarding the expertise and resources needed to adequately assess documentation of method equivalency when modifications are used. To help alleviate this concern, EPA is providing detailed guidance and checklists for assessing method modifications for equivalency with a reference method (see Chapter 6). EPA also may provide training and other types of assistance in this area.

1.2.4.3 The alternate test procedure process

OW anticipates that the flexibility allowed under streamlining will greatly reduce the number of ATPs processed. The ATP process will remain in place as an option to be used for modified methods that are approved and listed in the CFR. Expedited approval procedures, including use of direct final rulemaking for noncontroversial actions, will significantly decrease the time required for approval a method that has received a favorable recommendation from EPA.

1.2.4.4 Pilot testing

OW plans to pilot test the streamlining program prior to implementation. The pilot tests will focus on (1) method flexibility and (2) development and approval of new methods. EPA anticipates conducting several case studies in each of these areas during 1997. The pilot test reports will be reviewed and assessed for changes that should be made to the streamlining program before nationwide implementation.

1.2.4.5 Concerns by consensus standards organizations

Many of the methods approved at 40 CFR parts 136 and 141 are methods developed by consensus standard organizations such as Standard Methods, ASTM, and AOAC-International. In designating reference methods for specific combinations of analytes and determinative techniques, it was EPA’s intent to select as the reference method, the method that contained QC acceptance criteria for the standard QC elements identified in the streamlining initiative, regardless of whether that method was an EPA method or one developed by another organization.

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As envisioned, the streamlining initiative allows modification to the reference method, provided that the QC acceptance criteria are met. Consensus standards organizations have expressed concern that modification of their methods would constitute a legal violation of the method, termed a "standard". Therefore, Standard Methods, ASTM, and AOAC-International have declined to allow any modifications to their designated methods that are not expressly permitted in the methods. Hence, their methods cannot be modified under the procedures outlined in this document and cannot be specified as reference methods in 40 CFR part 136 or 141. This restriction will be noted in the specification of these methods in the CFR tables.

This restriction does not greatly impact the streamlining initiative, because an EPA method exists that can be used as a reference method for nearly all analytes, and because most methods from consensus standards organizations have sufficient explicit internal flexibility to meet the objectives of streamlining and are frequently updated to reflect recent advances in technology. EPA expects to continue relying on consensus standards organizations for the development of future methods as required by the NTTAA and because of limited Agency resources for method development.

1.3 Purpose of Guide

The purpose of this document is to provide detailed guidance to permittees, water utilities, regulatory authorities, purveyors of new technology, and analytical laboratories on implementation of a comprehensive program to expand flexibility and streamline approval of methods under EPA's wastewater and drinking water programs.

1.4 Content and Organization of Guide

The remainder of this document outlines the framework of and provides detailed guidance on EPA's streamlining initiative. Some chapters are procedural and others are descriptive, as appropriate to the topic.

- **Chapter 2 - Method Flexibility**
  This chapter describes the extent of existing method flexibility and outlines the principal concepts of the expanded flexibility that EPA proposes to allow in order to implement a performance-based approach to approving compliance methods in the Office of Water.

- **Chapter 3 - Quality Control Requirements**
  This chapter describes the standard quality control tests that will be required for all methods and specifies procedures for developing performance (i.e. QC acceptance criteria) for new methods.

- **Chapter 4 - Method Validation Requirements**
  This chapter describes the requirements and procedures for validating and documenting validation of a new method or method modification, utilizing a tiered system based on the intended application of the method.

- **Chapter 5 - The Method Approval Process**
  This chapter describes the expedited method approval process that includes a standard method format and procedures for submitting validated methods to EPA for approval.

- **Chapter 6 - Assessing Method Equivalency**

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This chapter provides guidance for assessing whether a method modification produces results equivalent to results produced by a reference method.

- **Chapter 7 - Biological Method Issues**
  The final chapter describes possible future plans to extend flexibility to biological methods. Biological methods include measurement of microbiological parameters as well as methods with biological indicators of toxicity.

The Guide includes several Appendices that contain useful reference materials.

- **Appendix A** provides a comprehensive list of acronyms and abbreviations used in the Guide.
- **Appendix B** is a glossary of terms used in the Guide.
- **Appendix C** contains descriptions of method modifications to 600- and 1600-series EPA methods that have been determined to be within the currently allowed flexibility described in Chapter 2.
- **Appendix D** comprises a list of suggested data elements for reporting, as discussed in Chapter 4.
- **Appendix E** provides the EMMC checklists and certification statement that serve as the basis for proving and evaluating method equivalency, as described in Chapter 6. It also provides an example of a completed method equivalency checklist.
- **Appendix F** specifies QC acceptance criteria for approved inorganic methods that are proposed as reference methods and that do not contain QC acceptance criteria.
- **Appendix G** lists the bibliographic references used in the development of the Guide.

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Chapter 2

Method Flexibility

2.1 Introduction

One of the primary goals of the streamlining initiative is to encourage the use of innovative technologies by increasing method flexibility so that laboratories can modify approved reference methods without formal EPA review. Under the streamlining program, it will no longer be necessary to apply for alternate test procedure (ATP) approval of modified methods. Rather, laboratories will be required to demonstrate and document that the modified method produces results equal or superior to results produced by the unmodified reference method. To ensure data quality, EPA is building in well-defined controls on this increased flexibility. These include designation of a reference method that contains quality control (QC) acceptance criteria for use in demonstrating equivalency, and specific requirements for validating modified methods and documenting equivalency. The purpose of this chapter is to describe the scope of the flexibility that will be offered under streamlining.

This chapter begins by describing the current flexibility in EPA's wastewater and drinking water programs, outlines the increased flexibility offered in the streamlining initiative, and defines the controls that will be used as the foundation for expanded flexibility. The key concepts presented and discussed in this chapter are: *limited flexibility*, *reference methods*, *other approved methods*, *flexibility in front-end and determinative techniques*, *new methods*, *method modifications*, *screening methods*, *method-defined analytes*, and *new target analytes*.

2.2 Existing Flexibility

Methods currently approved at 40 *CFR* parts 136 and 141 under EPA's wastewater and drinking water programs, respectively, allow two types of flexibility: (1) explicit flexibility, which does not require prior EPA approval, and (2) flexibility that requires prior EPA approval through the ATP process.

Method modifications currently are allowed without prior EPA approval only when the modification is explicitly allowed in the approved method. Explicit flexibility is termed **limited flexibility**. Some approved methods provide limited flexibility to substitute specific apparatus with apparatus demonstrated to be equivalent. The areas of currently allowed flexibility are indicated with the terms "should" or the phrase "or equivalent." Substitution of a 500-mL beaker for a 250-mL beaker or use of an "equivalent" chromatographic column are examples of such explicit flexibility. The EPA 600- and 1600- series wastewater methods approved at 40 *CFR* part 136, Appendix A provide limited flexibility to improve separations and reduce the cost of measurements as long as method performance is not sacrificed. Laboratories that choose to exercise explicit flexibility are required to meet the quality control (QC) acceptance criteria of the approved method for certain standardized QC tests. In the development of more recent methods (e.g., Method 1664 and Method 1613), EPA has expanded its definition of allowed flexibility to further encourage the use of new

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techniques that provide equal or better performance at lower costs. However, no approved methods provide unlimited flexibility and few provide the extensive flexibility that EPA proposes in this initiative.

Currently, all modifications not explicitly allowed by the method require prior EPA approval. These modifications must be approved through EPA's alternated test procedure (ATP) program. Historically, the wastewater program has allowed some changes to front-end techniques but not to the determinative technique. The drinking water program has been somewhat less restrictive on changing the determinative technique and has allowed other changes to compliance methods, provided the chemistry of the method is not changed. Some modifications to a front-end technique, such as changing the extraction solvent, are not currently allowed in drinking water methods.

Procedures for requesting ATP approval are specified at 40 CFR 136.4 and 136.5 of the wastewater regulations and at 40 CFR 141.27 of the drinking water regulations. ATP approval requires concurrence by EPA (and sometimes the state) and in some cases, the method must be listed in the CFR via an Agency rulemaking. The current ATP process is described in Chapter 1, Section 1.1.2.

2.3 Scope of Flexibility Provided by Streamlining

The streamlining initiative will allow flexibility to modify approved reference methods without submission of ATPs, provided that a laboratory demonstrates and documents that the modified method produces results equal or superior to those produced by the EPA-designated reference method. Only new methods (or Tier 2 or Tier 3 modified methods for which developers specifically request EPA review) will be subject to the streamlined ATP process. The scope of method flexibility that will be allowed under streamlining is detailed in Sections 2.3.1 - 2.3.5.

It should be noted that the proposed flexibility does not extend to sample collection or preservation conditions. These conditions include, but are not limited to, containers, holding times, preservation procedures or reagents, shipping and storage procedures. Modifications to sample collection and preservation conditions continue to require a variance as specified at 40 CFR 136.3 (c) and 141.27.

2.3.1 Reference Method

The foundation of EPA's flexibility concept is based on the use of a **reference method** against which method modifications can be tested for equivalency. A reference method is a method that has been approved at 40 CFR part 136 or 141, and contains (or is supplemented with) standardized QC procedures and the required QC acceptance criteria for each of these procedures. Using QC acceptance criteria as the performance measure makes the reference methods performance-based without extensive method redevelopment.

Only one reference method will be designated for each combination of regulated analyte and determinative technique. The purpose of specifying a single reference method for a given combination of analyte and determinative technique is to avoid the possible confusion that could be created if two or more reference methods contained differing QC acceptance criteria. The QC acceptance criteria associated with the reference method will be the performance criteria against which method modifications are tested. Method equivalency is demonstrated when results produced by a modification meet or exceed the QC acceptance criteria in the reference method.

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For the streamlining proposal, EPA selected reference methods primarily on the basis of existing QC acceptance criteria and/or the availability of data from which to develop QC acceptance criteria for each of the standardized QC elements described in Chapter 3 of this guide. An important additional consideration was whether or not the organization that developed the method would allow its methods to be subject to the flexibility proposed by the streamlined method approval process. Some external methods organizations, including Standard Methods, ASTM, and AOAC-International, have declined to allow unrestricted modifications to their methods. Their collective decision was based on the need to retain their methods as official "standards," which they have determined cannot be changed. Most of their methods have sufficient explicit flexibility to meet the objectives of streamlining or can be updated rapidly through their respective method approval processes. Because these methods cannot be modified, however, they cannot be designated as reference methods.

A reference method is needed to exercise the increased flexibility offered by the streamlining initiative. However, there are not reference methods for all listed combinations of analyte and determinative technique. In some of these cases (e.g., 40 *CFR* 136 Table ID), reference methods have not been cited because EPA has not yet developed QC acceptance criteria for the methods. In other cases, reference methods are not cited because the data are not yet available. In still others, it is not possible to cite a reference method since there are only Standard Methods, ASTM, or AOAC-International methods for that combination of analyte and determinative technique and these organizations do not allow modification of their methods. EPA has designated most of the reference methods and specified some of the QC acceptance criteria (in the Methods and Criteria document) for chemical analytes listed at 40 CFR parts 136 and 141. In a future rulemaking, EPA plans to designate additional reference methods and develop QC acceptance criteria for all wastewater and drinking water chemical methods, but EPA has not delayed proposal of the streamlining initiative while these activities take place.

Upon implementation of the streamlining initiative, EPA will retain all methods that are approved for use at 40 *CFR* parts 136 and 141, but will re-categorize each method as either a "Reference Method" or an "Other Approved Method". Regardless of whether a method has been designated as a "Reference Method" or as an "Other Approved Method", all approved methods cited at 40 *CFR* parts 136 and 141 will carry equal regulatory status. Reference methods will be cited by adding a column to the tables currently published at 40 *CFR* parts 136 and 141. A partial example of one table format is provided in **Table 2.1**.

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Table 2.1: Example of Proposed 40 *CFR* part 136 Table IB with Reference Methods.

Table IB—List of Approved Inorganic Test Procedures

Parameter/ Methodology	Reference Method[1,35]	Other Approved Methods				
		Standard Methods 18th Ed.[39]	ASTM[39]	USGS[2,39]	AOAC-Intl.[39]	Other
1. Acidity, as $CaCO_3$, mg/L:						
Electrometric endpoint or phenolphthalein endpoint	305.1	2310 B(4a)	D1067-92			
2. Alkalinity, as $CaCO_3$, mg/L:						
Electrometric or Colorimetric titration to pH 4.5, manual or automated	310.1 310.2	2320 B	D1067-92	I-1030-85 I-2030-85	973.43[3]	
3. Aluminum–Total,[4] mg/L; Digestion[4] followed by:						
AA direct aspiration[36]	202.1	3111 D		I-3051-85		
AA furnace	202.2	3113 B				
Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES)[36]	[5]200.7	3120 B				
Direct Current Plasma (DCP)[36]			D4190-82(88)			AES0029[34]
Colorimetric (Eriochrome cyanine R)		3500-AI D				
4. Ammonia (as N), mg/L:						
Manual, distillation (at pH 9.5)[6] followed by	350.2	4500-NH_3 B			973.49[3]	
Nesslerization	350.2	4500-NH_3 C	D1426-93(A)	I-3520-85	973.49[3]	
Titration	350.2	4500-NH_3 E				
Electrode	350.3	4500-NH_3 F or G	D1426-93(B)			
Automated phenate	350.1	4500-NH_3 H		I-4523-85		
Automated electrode						379-75WE[7]
5. Antimony–Total,[4] mg/L; Digestion[4] followed by:						
AA direct aspiration[36]	204.1	3111 B				
AA furnace	204.2	3113 B				
ICP/AES36	[5]200.7	3120 B				

In the future, it is anticipated that new reference methods will be approved at 40 *CFR* parts 136 and 141 only if a new analyte becomes of concern to EPA or if a new determinative technique is developed for an existing analyte of concern. EPA intends to rely on outside organizations to develop most new methods for approval at 40 CFR parts 136 and 141. To be approved (promulgated) as a reference method, the method must meet the following requirements:

- The method submitter must be willing to allow the method to be modified as described in this streamlining initiative.

- The method must be for a combination of analyte of concern and determinative technique for which an approved method does not exist. (This requirement precludes non-unique combinations of analytes and determinative techniques.)

- The combination of analyte and determinative technique must, in EPA's judgement, be useful for determination of an analyte of concern in a matrix of concern to EPA. (This requirement precludes useless combinations of analytes and determinative techniques, e.g., use of a flame ionization detector with EPA Method 508 or 608.)

- The method must pass all criteria set forth in this initiative including requirements for format, QC, QC acceptance criteria, validation, and submittal of supporting documentation.

- The method must pass peer-review and the Agency rulemaking process of proposal, public comment, and final rule.

Based on suggestions and advice received to date, EPA believes that most organizations that modify methods will choose to document the validity of those modifications without seeking formal approval. Therefore, the streamlining initiative will eliminate multiple methods for the same combination of analyte and determinative technique.

After streamlining is implemented, EPA's role in developing methods may be limited to instances where a method is required for monitoring an unusual analyte and/or for monitoring in a specific sample matrix and/or on a schedule that cannot be met by an outside method developer. Regardless of the organization that develops a new method, all new methods considered for approval under 40 CFR part 136 and 141 would continue to be proposed in the *Federal Register* and subject to public comment prior to approval. Additional information concerning the method submission and approval process is provided in Chapter 5.

2.3.2 Modifications to Front-end and Determinative Techniques

Most method modifications allowed under the streamlining initiative fall into one of two categories: (1) modification of a "front-end" technique or (2) modification of the determinative technique. A third category, adding additional analytes, is discussed in Section 2.3.4.

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. Under the streamlining initiative, EPA proposes to allow laboratories the flexibility to modify any and all front-end techniques without notifying EPA, provided the modification is not explicitly prohibited in the reference method and provided the modification can be demonstrated to

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produce results equal or superior to results produced by the reference method. This flexibility includes the ability to modify the chemistry of the front-end of the method. For example, changing the extraction solvent and substituting liquid-liquid for solid-liquid extraction will be allowed. However, if changing the chemistry of the method might affect the extract holding times specified in the reference method, a new extract holding time study must be performed. For example, extracting the water sample with pentane rather than isooctane is not likely to affect extract holding times because the chemical properties of the solvents are very similar. However, replacing ethyl acetate with a chemically dissimilar solvent, acetone, would require a reverification of the holding times for the target analytes in acetone. 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. As noted in Appendix C (issue 26), changes in the sorbent trap in the purge-and-trap volatile organic compound (VOC) methods are allowed, but the methods specifically preclude changes to the purge and desorption times or gas flows. Although these are front-end procedures, the method explicitly disallows modifications because these conditions are independent of the sorbent used and have been optimized for full recovery of the target VOCs.

A **determinative technique** is the physical and/or chemical process by which the measurement of the identity and concentration of an analyte is made. For most methods, the determinative technique consists of an instrumental measurement (i.e., a detector). Examples of determinative techniques are provided in **Table 2-2** at the end of this chapter. Under the refined streamlining initiative, EPA proposes to allow use of an alternate determinative technique that is not explicitly prohibited in the reference method, provided that equivalency is demonstrated and documented as outlined above, and provided that four conditions are met: (1) the alternate determinative technique measures a property similar to the prescribed technique, (2) the alternate technique is demonstrated to be more specific (i.e., identifies the analyte in the presence of interferences) and/or more sensitive (i.e., produces a lower detection limit) for the analyte of concern than the determinative technique in the reference method, (3) there is not another approved method that uses the alternate determinative technique for the determination of that analyte, and (4) use of the alternate determinative technique will not result in a nonsensical combination of analyte, front-end technique, and determinative technique.

Examples of allowed changes to a determinative technique are substitution of a photoionization detector for a flame ionization detector for determination of polynuclear aromatic hydrocarbons, substitution of a nitrogen-phosphorous detector for an electron capture detector (ECD) for determination of analytes containing nitrogen or phosphorous, and substitution of a fluorescence detector for an ultraviolet or visible wavelength detector. Substitution of a mass spectrometer (MS) for an ECD would not be allowed if there is an approved MS method that measures the analyte of concern. Readers are referred to the Streamlining Guide for more guidance on this subject.

Substitution of a photoionization detector (PID) for the flame ionization detector (FID) specified in Method 610 is an excellent example of a useful and allowed modification to the determinative technique because (1) the PID will provide improved sensitivity and specificity for determination of the polynuclear aromatic hydrocarbons (PAHs) determined in Method 610, (2) there are no currently approved methods for PAHs that use the PID as the determinative technique, and (3) use of a PID does not create a nonsensical combination of analyte, front-end techniques, and determinative technique.

Conversely, substitution of a flame ionization detector (FID) for either an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD) for determination of chlorinated pesticides in Method 508 or 608 would not be permitted because the FID is much less sensitive and

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less selective than an ECD or ELCD, and would therefore be nearly useless for compliance determinations of pesticides in an environmental sample. In contrast, use of a high resolution mass spectrometer (HRMS) in place of an ECD or ELCD for determination of pesticides would represent a significant improvement in selectivity (specificity) and/or sensitivity. EPA would accept, and propose for approval, a fully developed method using HRGC/HRMS for determination of chlorinated pesticides.

EPA chose to limit changes to the determinative technique by the four conditions described above to preclude nonsensical combinations of analyte and determinative technique, to encourage a net benefit (increased sensitivity and/or specificity), and to preclude multiple reference methods with the same determinative technique but with different QC acceptance criteria for the same analyte(s) of concern. For example, if a mass spectrometer were substituted for the conventional detectors in EPA methods 601 - 612, all of these methods would become GC/MS methods, but all would contain different QC acceptance criteria. Further, they would all conflict with approved GC/MS Methods 625 and 1625. The proposed restriction on detector substitution also is consistent with EPA's decision in the December 5, 1994 drinking water methods final rule (59 *FR* 62456) not to allow substitution of MS in methods that specify conventional GC detectors. Another reason for limiting changes to the determinative technique is that there are techniques, such as immunoassay, for which EPA has no reference method and therefore no history to insure that the standardized QC proposed in today's rule are germane to, or adequate for, assurance of the quality of data produced by the novel determinative technique. EPA would prefer that a new method be written and submitted for approval when a novel determinative technique is developed. EPA invites public comment on the suitability of the conditions EPA proposes to place on the flexibility to modify determinative techniques in EPA reference methods. EPA would allow limited flexibility to change the determinative technique. An alternate determinative technique can be used provided that (1) the alternate technique is demonstrated to be more specific (i.e., identifies the analyte in the presence of interferences) and/or more sensitive (i.e., produces a lower detection limit) for the analyte(s) of interest than the determinative technique in the reference method, (2) there is not another approved method that uses the alternate determinative technique for determination of that analyte, and (3) use of the alternate determinative technique will not result in a nonsensical combination of analytes, front-end techniques, and determinative techniques.

2.3.3 Method-Defined Analytes

In its initial straw man, EPA expressed concern that some techniques may not produce results equivalent to results produced by techniques employed for "method-defined analytes". A **method-defined analyte** is an analyte that does not have a specific, known composition so that the analytical result depends totally on how the measurement is made. Therefore, a change to either the front-end steps or the determinative technique for a method-defined analyte has the potential of changing the numerical value of the result for a given sample. Examples of method-defined analytes include adsorbable organic halides (AOX), biochemical oxygen demand (BOD), total radioactivity and whole effluent toxicity (WET).

EPA believes that methods for some method-defined analytes will need to have less flexibility than methods for specific chemical substances. EPA believes, however, that some flexibility can and should be allowed in these methods. Therefore, EPA intends to restrict the allowable flexibility in methods for

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Table 2-2
Examples of Determinative Techniques

The following is a partial list of determinative techniques. This list is not all-inclusive; it is merely intended to provide examples of the types of procedures that may be considered subject to modification as determinative techniques under the streamlining initiative.

Alkali Flame Detector (AFD)
Alpha Gas Proportional Counter
Alpha Scintillation Detection
Alpha Spectrometry
Amperometric Detection
Anodic Stripping Voltametry
Atomic Absorption Spectroscopy (AA)
Autoradiaography
Beta Gas Proportional Counter
Beta Scintillation Detection
Bioassay
Capillary Gas Chromatography/Electron Capture Detection (Capillary GC/ECD)
Capillary Gas Chromatography/Electrolytic Conductivity Detection (Capillary GC/ELCD)
Capillary Gas Chromatography/Flame Ionization Detection (Capillary GC/FID)
Capillary Gas Chromatography/Flame Photometric Detection (Capillary GC/FPD)
Capillary Gas Chromatography/High Resolution Mass Spectrometry (Capillary GC/HRMS)
Capillary Gas Chromatography/Low Resolution Mass Spectrometry (Capillary GC/LRMS)
Capillary Gas Chromatography/Nitrogen-Phosphorus Detection (Capillary GC/NPD)
Capillary Gas Chromatography/Photoionization Detection (Capillary GC/PID)
Cold Vapor Atomic Absorption (CVAA)
Cold Vapor Atomic Fluorescence (CVAF)
Conductivity Bridge (a.k.a. "Wheatstone Bridge")
Current Meter
Electret Ionization Chamber
Electrochemical Detector
Electrochemical Sensor
Electron Capture Detection (ECD)
Electrolytic Conductivity Detection (ELCD)
Electromagnetic Current Meter
Emission Spectroscopy
Filter Photometer
Flame Atomic Absorption (FLAA)
Flame Ionization Detection (FID)
Flame Photometric Detection (FPD)
Fluorometry
Fourier Transform Infrared Spectrometer (FTIR)
Gamma Ray Counter

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Table 2-2 (Continued)
Examples of Determinative Techniques

Gamma Spectrometry
Gas Chromatography (GC)
GC/Alkali Flame Detector (GC/AFD)
GC/ECD
GC/ELCD
GC/FID
GC/FPD
GC/FTIR
GC/Halogen Specific Detector (HSD)
GC/Mass Spectrometry (GC/MS)
GC/Nitrogen Phosphorus Detector (GC/NPD)
GC/Photoionization Detector (GC/PID)
GC/Thermal Conductivity Detector (GC/TCD)
GC/Thermionic Detector
Graphite Furnace Atomic Absorption (GFAA)
High Resolution Gamma Spectrometry
High Resolution Gas Chromatography (HRGC)
High Resolution Mass Spectrometry (HRMS)
HPLC/Electrochemical Detector
HPLC/Fluorescence Detector
HPLC/FTIR
HPLC/Thermospray-Mass Spectrometry Detector
HPLC/Refractive Index Detector
HPLC/Ultraviolet Detector (HPLC/UV)
Human eye
Human nose
Human tongue
Hydrometer
Inductively Coupled Plasma/Atomic Emission spectroscopy (ICP/AES)
Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)
Infrared Spectrophotometer (IR)
Ion-Selective Electrode
Laser Phosphorimeter
Liquid Scintillation Counter
Mass Spectrometer (MS)
Microscopy
Neutron Activation Analysis
Nitrogen-Phosphorus Detector (NPD)
Non-dispersive Infrared (NDIR)

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Table 2-2 (Continued)
Examples of Determinative Techniques

Nephelometer
Particle Beam Mass Spectrometry
pH Meter
Photoacoustic Infrared Detector
Photoionization Detector
Photometer
Polarograph
Potentiometer
Pressure Meter
Quartz Furnace AA
Spectrophotometer
Stabilized Temperature Graphite Furnace AA (STGFAA)
Thermal Conductivity Detector
Thermal Chromatography/Mass Spectrometry
Transmission Electron Microscopy (TEM)
Tensiometer
Titration
Toxic Gas Vapor Detector Tube
Turbidimeter
X-Ray Diffraction
X-Ray Fluorescence

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method-defined analytes and establish more stringent requirements for exercising this flexibility and for demonstrating equivalency. To implement this proposal, EPA would either not designate a reference method for a method-defined analyte or would footnote the tables in 40 *CFR* parts 136 and 141 for those analytes that are method-defined and either update or supplement these methods with explicit guidance concerning areas of allowed flexibility.

EPA will accept and review new or modified methods that produce results significantly different from results produced by approved methods for method-defined analytes. The Agency cannot guarantee, however, that such methods will ever be used in regulation development or monitoring. For example, methods currently approved at 40 *CFR* part 136 for determination of oil and grease are based on separatory funnel extraction using CFC-113 or hexane, drying, concentration, and weighing (gravimetry). Other methods based on GC, infrared spectroscopy (IR), or immunoassay techniques have been or are being developed for determination of oil and grease, but it is not expected that any of these other determinative techniques will produce results equivalent to results produced by gravimetry. EPA will accept application for approval of a new method that employs a different determinative technique from gravimetry, and will propose and attempt to approve such a method on request by the method developer; however, EPA will need to create a separate category within the tables in 40 *CFR* part 136 for such methods. This table will apply only to methods for method-defined analytes that produce results significantly different from results produced by the approved methods.

Given this limitation and the potential negative connotation that may be associated with methods in such a table, purveyors of new technology for determination of method-defined analytes may choose to avoid submitting a new method to EPA for approval and promulgation. Instead, they may find it preferable to exercise the flexibility provided in this initiative and demonstrate that the new technique produces results equivalent to the reference method on a matrix-by-matrix basis. EPA will work with method developers to determine that a combination of analyte and determinative technique is new and to assess whether a new method for a method-defined analyte is desirable.

2.3.4 Flexibility to Add New Target Analytes

In today's proposed rule, EPA has also given details for modifying 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, 1194; 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 rather than develop a new one 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, 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 the proposed flexibility procedures for modified and new methods, developers can obtain approval for adding analytes to an approved method as an allowed method modification if the conditions below are met.

Laboratories may add a new target analyte to approved methods provided (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 and employed for determination of the target analyte, (3) there is not another approved method that uses the same determinative technique for that

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analyte and (4) the that 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. The third and fourth criteria preclude method shopping whereby a user might add analytes to a reference method with less rigid QC acceptance, sample collection or holding time criteria. For example, if an approved method for an analyte of concern requires acidification of the sample, a user does not have the flexibility to modify a method that does not require sample acidification to include analysis of the analyte of concern. Modifications of this type require EPA approval as a new method.

If QC acceptance criteria do not exist for a new analyte, the guidelines contained in Chapter 3 should be followed to develop and obtain approval for these criteria. Alternatively, under conditions described in Chapters 4 and 5, QC acceptance criteria for the new analyte may be transferred from the criteria for an analyte with similar chemical characteristics. Other requirements for obtaining approval of QC acceptance criteria for additional target analytes are described in Chapters 4 and 5.

2.3.5 New Methods, Screening Methods, and Modified Methods

A critical aspect of the streamlining initiative is to provide flexibility to modify an existing approved method provided that results obtained using the modified method meet the QC acceptance criteria of the reference method. Following release of its initial straw man, EPA received several requests to clarify the differences between new and modified methods and the requirements that pertain to each. Many reviewers also asked EPA if the procedures for developing, proposing and approving methods for use in the wastewater and drinking water programs would be applicable to screening methods. Clarifications that address these issues are as follows.

A **new method** is a set of procedures that:

(1) Is documented in accordance with the requirements detailed in the *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141*,
(2) Contains the standardized QC elements detailed in Chapter 3,
(3) Contains QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3,
(4) Employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141, and
(5) Employs a determinative technique that is more sensitive and/or selective (specific) than the determinative techniques in all methods previously approved for the analyte.

A method that meets all five of these characteristics is considered to be a **confirmatory method** if the method also is sufficiently selective and quantitative that <u>most</u> positive results do not have to be verified by analysis with another method. The term “confirmatory” is used to distinguish this type of method from a screening method (described below). All methods currently approved at 40 *CFR* parts 136 and 141 are confirmatory methods.

Methods with disparate characteristics have been developed and marketed as screening methods. Some are inexpensive and easy to use; others require expensive equipment and training to conduct complex procedures. Some screening methods are designed to be used at the sample collection site; others require a well-equipped laboratory. In this Guide, a **screening method** is defined as a method that meets the first four of the five conditions described above for new methods

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and that has been demonstrated to produce a false negative probability of no more than one percent (1%) at the limit(s) of regulatory concern. Methods can fail the fifth condition for a new method, if they are non-selective or not quantitative for the target analyte. A non-selective method is a method in which the determinative (or other step) technique in the method may produce a result for any one of several analytes that share common physical or chemical characteristics with the target analyte. For example, an atrazine immunoassay might respond to any triazine (atrazine, simazine, cyanazine) pesticide in the sample.

Screening methods may be quantitative, but are often semi-quantitative or presence-absence. For example, if the same water sample containing a free chlorine residual of 1.3 mg/L were analyzed with several methods, a quantitative titrimetric method might provide a result such as 1.2 ± 0.2 mg/L. A semi-quantitative colorimetric method might indicate that the free chlorine residual concentration was in the range of 1.0 to 1.5 mg/L. Analysis with a presence-absence method that had a minimum sensitivity of 0.5 mg/L would produce a presence reading indicating that a free chlorine residual was present at 0.5 mg/l or more.

When using a screening method, <u>all</u> positive results must be verified by re-analysis with a confirmatory method because screening methods can be less selective and therefore more subject to false positives than confirmatory methods. Historically, EPA has not considered screening methods for approval at 40 *CFR* part 136 or part 141. Under the streamlining initiative, EPA proposes to consider the approval of these methods for compliance monitoring provided: (1) the method meets all the requirements described in the Streamlining Guide and in the regulations at 40 CFR 136.5 and 141.27, (2) all positive sample results obtained with the method are confirmed and reported using an approved confirmatory method, and (3) the probability of the method producing a false negative result at concentrations of regulatory interest is no more than one percent (1%). EPA notes that, for part 141 approval, these criteria may be when the Agency implements the requirements for screening methods that are in the August 2, 1996 amendments to the SDWA. When the streamlining initiative is promulgated, a separate table will be published at 40 *CFR* parts 136 and 141 to list screening methods that have been approved for compliance monitoring.

The definitions of confirmatory and screening methods in this section are deliberately narrow to preclude them from being considered as method modifications under the concept of method flexibility. A **modified method** is an approved method that has been modified to change a front-end technique or the determinative technique, either using explicit flexibility or expanded flexibility allowed under streamlining. Under the streamlining initiative, there will be two forms of method modifications:

- Modifications to approved methods may be made as specified within those methods. This explicit flexibility existed prior to the streamlining initiative and will continue to exist. Explicit flexibility exists for all approved methods including EPA, Standard Methods, ASTM, AOAC-International, and other methods approved at 40 *CFR* parts 136 and 141.

- Modifications to approved methods designated as reference methods. This flexibility does not exist prior to implementation of the streamlining initiative. After streamlining has been promulgated, modifications may be made to reference methods provided that the modification
  - Meets the requirements detailed in 40 *CFR* 136 or 141, and
  - Meets the requirements detailed in this Streamlining Guide which is being incorporated into the CFR by reference as part of the streamlining rule

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These modifications may not be made to Standard Methods, ASTM, and AOAC-International methods, and none of these methods have been designated as a reference method under this initiative.

2.4 Controls on Flexibility

EPA has established a number of controls that provide the foundation for the increased flexibility allowed under streamlining. These controls are:

- A requirement to demonstrate and document equivalency when method modifications are used.
- Designation of a reference method that contains QC acceptance criteria for use in demonstrating equivalency.
- Standard procedures for validating new methods and demonstrating equivalency of method modifications, based on the intended use of the method.
- A requirement for all new methods to contain standardized QC and specify QC acceptance criteria.
- Detailed requirements for preparing the method validation package and supporting data when new or modified methods are validated.
- Guidance for regulatory authorities' use in assessing equivalency of method modifications.

These controls are described in the appropriate chapters of this guide, as described in Chapter 1, Section 1.4.

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Chapter 3

Quality Control Requirements

3.1 Introduction

As the foundation for method flexibility, EPA will designate an approved method as the "reference method" for each combination of analyte and determinative technique. Any newly developed method that contains a unique combination of analyte and determinative technique would be considered a new method and, when approved, could be designated as the reference method for that unique combination of analyte and determinative technique. Any approved method not designated as a reference method will be designated as an "other approved method." All methods must contain standardized quality control (QC) tests. All reference methods must contain standardized QC tests and specify QC acceptance criteria for each test. The QC acceptance criteria of the reference method must be met when using other approved methods or method modifications. The QC acceptance criteria in the reference method are the performance measures for demonstrating equivalency of method modifications.

The person or organization that develops a reference method for a particular combination of analyte and determinative technique will be responsible for validating the method and for developing the QC acceptance criteria.. QC acceptance criteria will be based on data generated during the method validation study. Under the streamlining initiative, EPA is proposing to require a method validation study that reflects the level of intended use for a method. This three-tiered approach to method validation is explained in Chapter 4. EPA believes that the tiered approach will minimize the validation requirements of limited-use methods (single-laboratory and single-industry use) and will focus resources on validation of methods that are intended for nationwide use. Because QC acceptance criteria will be developed from validation studies and because the validation requirements vary with each tier, the statistical procedures used to develop the criteria will vary by tier.

Some methods presently approved at 40 CFR parts 136 and 141 do not contain acceptance criteria for all standardized QC tests. In the streamlining proposal, EPA has provided supplementary QC acceptance criteria for methods proposed as reference methods that do not already contain QC acceptance criteria. QC acceptance criteria must be developed for and specified in all new methods that will be approved as reference methods.

This chapter describes the three method validation tiers, lists and describes the standardized QC tests required in all approved methods, and outlines procedures for developing QC acceptance criteria for new methods at Tiers 1, 2, and 3. The key concepts presented and discussed in this chapter are: *standardized QC tests*, *calibration linearity*, *calibration verification*, *absolute and relative retention time precision*, *initial precision and recovery*, *ongoing precision and recovery*, *analysis of blanks*, *surrogate or labeled compound recovery*, *matrix spike and matrix spike duplicate*, *method detection limit demonstration*, *reference sample analysis*, and *QC acceptance criteria*.

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3.2 Description of Tiers

Tier 1 refers to new methods or method modifications that will be used by a single laboratory for one or more matrix type(s). As used in streamlining, a matrix type is a sample medium (e.g., air, water, soil) with common characteristics across a given industrial category or subcategory. Validation requirements for Tier 1 reflect this limited use and correspondingly require single-laboratory testing in the matrix type(s) in which the method will be used. In response to comments received during public meetings, EPA has refined requirements for this tier to allow single laboratories to apply new or modified methods to an unlimited number of matrix types after the method has been validated in nine discrete matrix types. If results of Tier 1-Multiple Matrix Type validation studies are to be applied to a different medium, each medium must be represented in the samples tested in the validation study. Procedures for developing QC acceptance criteria for Tier 1 methods are given in Section 3.4.1.

Tier 2 refers to new methods or method modifications that will be used by multiple laboratories analyzing samples of one matrix type from a single industrial category or subcategory. Validation at Tier 2 requires a three-laboratory interlaboratory study in the matrix type(s) in which the method will be used. Procedures for developing QC acceptance criteria for Tier 2 methods are given in Section 3.4.2.

Tier 3 refers to new methods or method modifications that will be used on a nationwide basis by all laboratories for all matrix types. Validation at Tier 3 requires a nine-laboratory interlaboratory study on nine matrix types. Validation must be performed on a minimum of nine matrix types in each sample medium to which the method will be applied. Procedures for developing QC acceptance criteria for Tier 3 methods are given in Section 3.4.3.

3.3 Standardized Quality Control Tests

Under this initiative, standardized QC tests are required for use with currently approved methods and are a mandatory component of all new methods. The standardized QC tests are as follows:

- calibration linearity
- calibration verification
- absolute and relative retention time precision (for chromatographic analyses)
- initial precision and recovery
- ongoing precision and recovery
- analysis of blanks
- surrogate or labeled compound recovery
- matrix spike and matrix spike duplicate precision and recovery (for non-isotope dilution analyses)
- method detection limit demonstration
- analysis of a reference sample

These tests are described in Sections 3.3.1 - 3.3.10 below.

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3.3.1 Calibration Linearity

The calibration linearity specification establishes a break point between a straight line through the origin and a straight line not through the origin or a curved calibration line. This break point is specified as a maximum relative standard deviation (RSD=100s/$\overline{X}$, expressed as percent) of the:

- relative response (RR) for isotope dilution calibration,
- response factor (RF) for internal standard calibration, or
- calibration factor (CF) for external standard calibration,

below which an averaged RR, RF, or CF may be used. The number of calibration points is dependent on the error of the measuring technique. Measurement technique error is determined by (1) calibrating the instrument at the minimum level (ML) of quantitation and a minimum of two additional points, and (2) determining the RSD of the RR, RF, or CF. For most analyses, such as the determination of semi-volatile organic compounds by extraction, concentration, and gas chromatography, the measuring instrument is calibrated, and sample preparation processes are excluded from the calibration process; for others, such as the determination of purgeable organic compounds by purge-and-trap gas chromatography, calibration encompasses the entire analytical process. Table 3-1 below gives the number of calibration points required depending on the calibration linearity.

Table 3-1: Minimum Number of Points Required for Calibration[1]

Percent RSD[2]	Minimum Number of Calibration Points
0 - <2	1[3]
2 - <10	3
10 - <25	5
>25	7

[1] Based on Rushneck et al. 1987. Effect of number of calibration points on precision and accuracy of GC/MS, in Proceedings of Tenth Annual Analytical Symposium, USEPA: Washington, DC.

[2] Percent RSD shall be determined from the calibration linearity test.

[3] Assumes linearity through the origin (0,0). For analytes for which there is no origin (such as pH), a two-point calibration shall be performed.

The ideal calibration is a straight line that intersects the origin (zeroth order). In practice, no calibration line constructed from three or more calibration points will intersect the exact origin (0.000 ..., 0.000 ...). If, however, an error band is constructed around the calibration line, the error band will include the origin for most calibrations. The use of an averaged RR, RF, or CF is an attempt to represent the calibration with a single value that includes all of the points, including the origin, within the error represented by the RSD.

The maximum RSD specification is applicable to calibration with three or more calibration points. For some methods, a least-squares regression and correlation coefficient have been used. However, an unweighted least-squares regression that covers a large range will inappropriately weight the highest calibration point(s). Equally weighing each point in a least-squares regression produces the same result as an averaged RR, RF, or CF. Therefore, unless the method specifies use of a least-

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squares regression and/or correlation coefficient, the RSD of the RR, RF, or CF must be used to establish calibration linearity.

Calibrations higher than zeroth order calibration (straight line through the origin) are required when the linearity criterion cannot be met. For most instruments and analytical systems, these calibrations are first order (linear not through the origin; $y = mx + b$) and second order ($y = ax^2 + bx + c$). A second or higher order calibration may be justified when an analyte can only be determined with a method that uses a determinative technique with a nonlinear response over the calibration range. A second order or higher order calibration may be used, provided that the calibration increases monotonically. Monotonically means that the response is successively greater at successively higher concentrations. For example, an immunoassay typically requires a third ($y = ax^3 + bx^2 + cx + d$) or fourth ($y = ax^4 + bx^3 + cx^2 + dx + e$) order calibration, although not all of the terms in these equations may be needed.

EPA believes that most instruments and analytical systems are linear over a range large enough to preclude the need for second order or higher calibration. If the linear range of any of these systems is limited, sample dilution and reanalysis should be performed to bring the concentration within the linear range, rather than extend the calibration into a nonlinear region of the instrument response. EPA discourages use of higher than first-order calibration because responses in the nonlinear region of the instrument response can mask curvature in the response that may be attributable to preparation of an inaccurate standard. EPA requires that all calculations of concentrations of analytes in blanks, field samples, QC samples, and samples prepared for other purposes be based on an averaged RR, RF, or CF, or on a calibration curve.

3.3.2 Calibration Verification

This test is used to periodically verify that instrument performance has not changed significantly from calibration. Verification is based on time (e.g., working day; 12-hour shift) or on the number of samples analyzed in a batch (e.g., after every 10th sample). The terms "shift" and "batch" should be specified in the method. If not, the general rule has been that calibration verification is performed every 12-hour shift on instruments used for determination of organic analytes and every 10th sample on instruments used for determination of metals. However, the over-riding rule should be that verification is performed frequently enough to assure that the response of the instrument or analytical system has not drifted significantly from calibration.

Calibration verification tests are typically performed by analyzing a single standard in the concentration range of interest for the target analyte(s). In most methods, this standard is in the range of 1 - 5 times the minimum level (ML) of quantitation and is at the same level as one of the standards used for calibration. The calibration verification standard concentration should be within 1 - 5 times the ML rather than at a "midpoint" concentration because specifying the midpoint can be interpreted as one-half (½) the highest calibration point. Using a concentration this high when the calibration covers orders of magnitude may lead to erroneous results, because this midpoint standard may be far removed from the range where most measurements will be made.

If the calibration is linear through the origin (as defined by linearity criteria in Table 3-1), specifications for calibration verification are developed to define the allowable deviation of the RR, RF, or CF of the calibration verification standard from the averaged RR, RF, or CF of the calibration. If linearity criteria for calibration are not met, specifications for calibration verification are developed

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to define the allowable deviation of the RR, RF, or CF of the calibration verification standard from a specific point on the calibration curve.

For calculation of analyte concentrations, the averaged RR, RF, or CF, or the calibration curve is always used; i.e., the calibration is not updated to the RR, RF, CF or the single point verification. Updating the calibration to a single point after establishing an averaged RR, RF, or CF, or a calibration curve is equivalent to performing a single-point calibration. This updating procedure, which is sometimes termed "continuing calibration," is unacceptable and shall not be used because it nullifies the statistical power of the full calibration.

3.3.3 Absolute and Relative Retention Time Precision

Absolute retention time (RT) and relative retention time (RRT) are the QC criteria used in chromatographic analyses to aid in the identification of each detected analyte and to confirm that sufficient time was allowed for the chromatographic separation of the analytes in complex mixtures. These criteria also prevent laboratories from accelerating the analysis in an effort to reduce costs, only to find that complex mixtures cannot be adequately resolved.

A minimum RT specification is developed for those methods in which a minimum analysis time must be established to ensure separation of the analytes in complex mixtures including known or expected interferences. An RT precision specification is developed for identification of an analyte by external standard measurements, and an RRT precision specification is developed for (1) each analyte relative to its labeled analog by isotope dilution measurements, (2) each labeled compound relative to its internal standard for isotope dilution measurements, and (3) each analyte relative to an internal standard for internal standard measurements.

3.3.4 Initial Precision and Recovery

The initial precision and recovery (IPR) test, also termed a "startup test," is used for initial demonstration of a laboratory's capability to produce results that are at least as precise and accurate as results from practice of the method by other laboratories. The IPR test also is used to demonstrate that a method modification will produce results that are as precise and accurate as results produced by the reference method. The IPR test consists of analyzing at least four replicate aliquots of a reference matrix spiked with the analytes of interest and with either surrogate compounds or, for isotope dilution analysis, labeled compounds. The concentration of the target analytes in the spike solution may vary between one and five times the concentration used to establish the lowest calibration point (e.g., one to five times the ML). The spiked aliquots are carried through the entire analytical process. The IPR test is performed by the laboratory before it utilizes a method or a method modification for analysis of actual field samples. Specifications are developed for the permissible range of recovery for each analyte and for an upper limit on the standard deviation or RSD of recovery.

3.3.5 Ongoing Precision and Recovery

The ongoing precision and recovery (OPR) test, sometimes termed a "laboratory control sample," "quality control check sample," or "laboratory-fortified blank," is used to ensure that the laboratory remains in control during the period that samples are analyzed, and it separates laboratory performance from method performance in the sample matrix. The test consists of a single aliquot of reference matrix spiked with the analyte(s) of interest and carried through the entire analytical process with each batch of samples. Typically, the concentration of the target analyte(s) in the same as the

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concentration used in the IPR test. Specifications are developed for the permissible range of recovery for each analyte.

3.3.6 Analysis of Blanks

Blanks are analyzed either periodically or with each sample batch to demonstrate that no contamination is present that would affect the analysis of standards and samples for the analytes of interest. The period or batch size is defined in each method. Typical periods and batch sizes are one per shift or one for every 10 or 20 samples, but more or fewer may be required, depending upon the likelihood of contamination.

For most methods, QC acceptance criteria for blanks are given in each method and are specified as the concentration or amount of the analyte allowed in each type of blank. The source of contamination in a blank must be identified and eliminated before the analysis of standards and samples may begin. Samples analyzed with an associated contaminated blank must be reanalyzed. Methods for which blank contamination cannot be eliminated should specify blank-subtraction procedures.

3.3.7 Surrogate or Labeled Compound Recovery

The surrogate or labeled compound recovery is used to assess the performance of the method on each sample. For this test, surrogates or stable, isotopically labeled analogs of the analytes of interest are spiked into the sample and the recovery is calculated. Specifications are developed for the permissible range of recovery for each surrogate and/or labeled compound from each sample.

3.3.8 Matrix Spike and Matrix Spike Duplicate

The matrix spike and matrix spike duplicate (MS/MSD) test is used in non-isotope dilution methods to assess method performance in the sample matrix. In most cases, analytes of interest are added to a field sample aliquot that is then thoroughly homogenized and split into two spiked replicate aliquots.[1] One of these replicates is identified as the matrix spike sample and the other is identified as the matrix spike duplicate sample. The recoveries of the analytes, relative to the spike, are determined in each sample. The precision of the determinations also is assessed by measuring the relative percent difference (RPD) between the analyte concentrations measured in the MS and MSD. The MS and MSD samples should each be spiked at a level that results in the concentration of the target analyte(s) being

- At the regulatory compliance limit or
- One to five times the background concentration of unspiked field sample, or
- At the level specified in the method, whichever is greater.

If the background concentration in the field sample is so high that the spike will cause the calibration range of the analytical system to be exceeded, the sample is spiked after the field sample is diluted by the minimal amount necessary for this exceedance not to occur. This dilution of the sample to stay within the calibration range of the analytical system for the target analyte is necessary to verify that

[1] For analytes, such as oil and grease, that adhere to container walls and cannot be adequately homogenized, it is not possible to divide a spiked aliquot into two replicate aliquots. In these cases, two field samples are collected and each field sample is spiked with identical concentrations of the analytes of interest to produce an MS and MSD sample.

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the sample matrix has not prevented reliable determination of the analyte. Specifications are developed for the permissible range of recovery and RPD for each analyte.

3.3.9 Demonstration of Method Detection Limit

Nearly all of the 40 *CFR* part 136, Appendix A methods contain method detection limits (MDLs), although few of the methods explicitly require laboratories to demonstrate their ability to achieve these MDLs. Under the streamlining initiative, EPA will develop MDLs for each analyte in each existing reference method, and organizations developing new reference methods will be required to develop analyte-specific MDLs applicable to those methods. The MDLs published for each reference method will be used as an indicator of method performance. Each laboratory that intends to practice a method will be required to demonstrate achievement of an MDL that meets the criteria specified in the reference method. The MDL must be determined according to the procedures specified at 40 CFR part 136, Appendix B. The Appendix B MDL calculation and analytical procedure is described in Section 3.4.1.1.

3.3.10 Reference Sample Analysis

The most common reference sample is a Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST). The reference sample and the period for its use are specified in each method. EPA is considering setting acceptance criteria for standard reference materials to be within some percentage of the stated value based on the variability of measurement for that analyte. One possible indicator of that variability is the relative standard deviation calculation for the initial precision and recovery samples. Corrective action to be taken when the acceptance criteria are not met should involve identifying the samples affected, determining the amount of the effect, and if the effect is significant, determining the impact of the effect on the environmental samples analyzed.

3.4 Development of Quality Control Acceptance Criteria

The procedures for developing QC acceptance criteria at Tier 1, Tier 2, and Tier 3 methods are described in Sections 3.4.1, 3.4.2, and 3.4.3, respectively. Under the streamlining initiative, interlaboratory study data are required to develop QC acceptance criteria for Tier 2 and Tier 3 methods. Although these studies are not necessary for Tier 1 methods, interlaboratory study data may be available. If interlaboratory data are available for a Tier 1 method, these data should be used to develop QC acceptance criteria for Tier 1 methods by following the Tier 2 or Tier 3 procedures described in Section 3.4.2 or 3.4.3, respectively. Where possible, interlaboratory study data used for development of QC acceptance criteria should be derived from study designs that follow the basic principles outlined in *Guidelines for Collaborative Study Procedures to Validate Characteristics of a Method of Analysis*, JAOAC *72* No. 4, 1989, *Use of Statistics to Develop and Evaluate Analytical Methods* (published by AOAC-International), ASTM Standard D-2777 (published by ASTM), or other well-established and documented principles.

The statistical procedures described in Sections 3.4.1 and 3.4.2 for Tier 1 and Tier 2 are based on the use of interlaboratory multipliers. These multipliers were derived from a comparison of

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intralaboratory versus interlaboratory variability in the development of EPA Method 1625.[2] The variation in the interlaboratory multiplier used is directly related to the number of laboratories used at each of the two tiers. The general relationship follows the concept that an increase in the number of laboratories used results in a decrease in the interlaboratory multiplier.

If the method being developed is applicable to a large number of compounds, the organization responsible for developing QC acceptance criteria for the method may wish to consider the use of statistical allowances for simultaneous compound testing. Procedures associated with simultaneous compound testing and the develoment of applicable QC acceptance criteria can be found at 49 FR 43242 and in the Method 1625 validation study report.[3]

3.4.1 Quality Control Acceptance Criteria Development for New Methods at Tier 1

Method validation at Tier 1 consists of (1) using the new method to perform an MDL study in accordance with the MDL procedure described at 40 *CFR* part 136, Appendix B, (2) using the results of this MDL study to establish an ML, and (3) running, in a single laboratory, a test of four spiked reference matrix samples and four spiked samples of the sample matrix (or matrices) to which the method is to be applied. The spike level of these reference matrix and real-world matrix IPR samples must be in the range of one to five times the ML, or at the regulatory compliance level, whichever is higher.

3.4.1.1 Method detection limit and minimum level

An MDL must be determined for each target analyte using the procedure detailed at 40 *CFR* part 136, Appendix B. This procedure involves spiking seven replicate aliquots of reference matrix or the sample matrix with the analytes of interest at a concentration within one to five times the estimated MDL. The seven aliquots are then carried through the entire analytical process, and the standard deviation of the seven replicate determinations is calculated. The standard deviation is multiplied by 3.14 (the Student's *t* value at 6 degrees of freedom) to form the MDL. If the spike level is greater than five times the determined MDL, the spike level must be reduced and the test repeated until the MDL is within a factor of five of the spike level. The precautions concerning blanks and the effect of the matrix, and the detailed steps in 40 *CFR* part 136, Appendix B must be observed to arrive at a reliable MDL. In addition, if the analytical system or instrument fails to produce a positive response for any of the seven replicates (i.e., produces a zero or negative result), the MDL procedure must be repeated at a higher spike level.

The ML is established by multiplying the MDL by 3.18 and rounding to the number nearest to (1, 2, or 5) x 10^n, where n is positive or negative integer. The purpose of rounding is to allow instrument calibration at a concentration equivalent to the ML without the use of unwieldy numbers. The use of 3.18 results in an overall standard deviation multiplier of 10, which is consistent with the American Chemical Society's (ACS) limit of quantitation (LOQ) (P. S. Porter et al., *Environ. Sci. Technol.*, 22, 1988).

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[2] Appendix I, “Estimation of Variance Components”, of the *Interlaboratory Validation of U.S. Environmental Protection Agency Method 1625A*, available from the EPA Sample Control Center operated by DynCorp, Alexandria, VA 22314, 703/519-1140.

[3] *Interlaboratory Validation of U.S. Environmental Protection Agency Method 1625A*. See above.

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Once established, the ML is used as the lowest calibration point. The instrument or analytical system is then calibrated at the ML and a minimum of two additional points to assess calibration linearity (Section 3.4.1.2) and to determine the number of calibration points required and how these points are spaced (Section 3.3.1).

3.4.1.2 Calibration linearity

Establish the RSD of the response factors (RFs), calibration factors (CFs), or relative responses (RRs) based on the precision of the determinative technique, as described in Section 3.3.1, and as determined in Section 3.4.1.1. If the RSD is < 2%, a one- or two-point calibration is employed (see Section 3.1.1) and it is unnecessary to establish a limit for calibration linearity.

If three or more calibration points are required, the RSD for the RFs, CFs, or RRs is determined as follows:

(1) Determine the average response factor ($\overline{RF}$), calibration factor ($\overline{CF}$), or relative response ($\overline{RF}$) for each analyte from the initial calibration:

$$\overline{RF} = (RF_1 + RF_2 + ... + RF_n)/n$$

where n is the number of calibration points.

(2) Determine the RSD using $\overline{RF}$, $\overline{CF}$,or $\overline{RF}$ and the standard deviation (s) of the RF ,CF, or RR for each analyte from the initial calibration. The RSD is determined by:

$$RSD = 100s/(\overline{RF})$$

(3) Develop a maximum RSD as follows:

$$RSD_{max} = kRSD$$

where k is the square root of the 95th percentile of an F distribution with degrees of freedom corresponding to the number of points in the initial calibration minus 1 in both numerator and denominator. For a three point calibration, the value of k is 4.4, and for a five-point calibration, the value of k is 2.5.

Note: In the above equations, the $\overline{RF}$ and RF terms should be replaced by $\overline{CF}$ and CF or $\overline{RR}$ and RR terms where appropriate.

3.4.1.3 Calibration verification

Using the average response factor ($\overline{RF}$), calibration factor ($\overline{CF}$), or relative response ($\overline{RR}$) from the initial calibration, calculate the upper and lower QC acceptance criteria for the calibration verification as follows:

(1) Calculate a multiplier, k, as the 97.5th percentile of a Student's *t* distribution with n - 1 degrees of freedom times the square root of (1 + 1/n), where there are n points in the calibration. For a three point calibration, the n - 1 Student's *t* value is 4.3, and for a five point

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calibration, the Student's *t* value is 2.8, resulting in values for k of 5.0 for a three point and 3.0 for a five point calibration.

(2) Calculate the upper and lower QC acceptance criteria for the response or calibration factors for each analyte by developing a window around the average response factor found in the initial calibration by:

$$\text{Lower limit} = \overline{\mathbf{RF}} - ks$$
$$\text{Upper limit} = \overline{\mathbf{RF}} + ks$$

where k is the multiplier determined in Step 1 and s is the standard deviation determined in 3.4.1.2, Step 2.

Note: In the above equations, the $\overline{\mathbf{RF}}$ terms should be replaced by $\overline{\mathbf{CF}}$ or $\overline{\mathbf{RR}}$ terms where appropriate.

3.4.1.4 Initial and ongoing precision and recovery

For Tier 1 methods, an IPR test must be performed in both a reference matrix (usually, reagent water) and the sample matrix of interest. Results of the reference matrix IPR tests are used to generate QC acceptance criteria for IPR and OPR tests as described in this subsection. Results of the sample matrix IPR test are used to develop QC acceptance criteria for the MS/MSD tests (see Section 3.4.1.5 below). The reference matrix IPR test is performed by analyzing four aliquots of the reference matrix spiked with the target analyte(s) at the concentration determined in Section 3.3.4.

Calculate the QC acceptance criteria for the IPR and OPR tests using results of the test of the reference matrix per the following steps:

(1) Calculate the average percent recovery ($\overline{X}$), the standard deviation of recovery (s), and the relative standard deviation (RSD=100s/$\overline{X}$) of the four IPR results.

(2) IPR QC acceptance criterion for precision - To approximate a 95% confidence interval for precision, the RSD is multiplied by the square root of the 95th percentile of an F distribution with 3 degrees of freedom in the numerator and denominator. The resulting multiplier on the RSD will then be 3.0. The QC acceptance criterion for precision in the IPR test (RSD_{max}) is calculated as follows:

$$RSD_{max} = 3.0RSD.$$

(3) IPR QC acceptance criteria for recovery - Calculate the QC acceptance criteria for recovery in the IPR test by constructing a ± 5.3s window around the average percent recovery ($\overline{X}$). This factor comes from the 97.5th t percentile for 3 degrees of freedom, multiplied by $\sqrt{1.15(1+1)+(1/4+1/4)}$ to account for interlaboratory variability and the estimation of the mean:

$$\text{Lower limit (\%)} = \overline{X} - 5.3s$$
$$\text{Upper limit (\%)} = \overline{X} + 5.3s$$

(Based on EPA's interlaboratory validation study of Method 1625, the additional variance due to interlaboratory variability is estimated as $1.15s^2$.)

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(4) OPR QC acceptance criteria for recovery - A similar miltiplier is used as for the IPR test but the second factor is $\sqrt{1.15(1+1) + (1 + 1/4)}$, so the multiplier is 6.0. Calculate the QC acceptance criteria for recovery in the OPR test by constructing a ± 6.0s window around the average percent recovery $\overline{X}$:

$$\text{Lower limit (\%)} = \overline{X} - 6.0s$$
$$\text{Upper limit (\%)} = \overline{X} + 6.0s$$

Note: For highly variable methods, it is possible that the lower limit for recovery for both the IPR and OPR analyses will be a negative number. In these instances, the data should either be log-transformed and the recovery window recalculated, or the lower limit established as "detected," as was done with some of the 40 CFR part 136, Appendix A methods (49 FR 43234).

3.4.1.5 Matrix spike and matrix spike duplicate

As noted above, an IPR test must be performed in both an appropriate reference matrix and the sample matrix of interest for Tier 1 new methods. The results of the sample matrix IPR test are used to develop acceptance criteria MS/MSD analyses. Sample matrix IPR tests are performed by: (1) determining the background concentration of the sample matrix, (2) spiking four replicate aliquots of the sample matrix at a concentration equal to the regulatory compliance limit, one to five times the ML determined in Section 3.4.1.1, or one to five times the background concentration of the sample, whichever is greater, and (3) analyzing each of these spiked replicate samples.

Calculate the QC acceptance criteria for the recovery of MS and MSD samples as follows:

(1) Calculate the average percent recovery ($\overline{X}$) and the standard deviation of recovery (s) of each target analyte in the sample matrix IPR aliquots.

(2) Calculate the QC acceptance criteria for recovery in the MS and MSD tests by constructing a ± 6.0s window around the average percent recovery ($\overline{X}$) (derived the same as for the OPR test above):

$$\text{Lower limit (\%)} = \overline{X} - 6.0s$$
$$\text{Upper limit (\%)} = \overline{X} + 6.0s$$

Note: For highly variable methods, it is possible that the lower limit for recovery for both IPR and OPR analysis will be a negative number. In these instances, the data should either be log-transformed and the recovery window recalculated, or the lower limit established as "detected," as was done with some of the 40 CFR part 136, Appendix A methods (49 FR 43234).

Calculate the QC acceptance criteria for the relative percent difference between the MS and MSD as follows:

(1) Calculate the relative standard deviation (RSD) of the recoveries of each target analyte in the sample matrix IPR aliquots as follows:

$$RSD = 100s/\overline{X}$$

(2) Calculate the relative percent difference (RPD) criterion as follows:

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$$RPD_{max} = 4.5RSD$$

This multiplier is calculated as $\sqrt{2}$ times the square root of the 95th percentile of an F distribution with 1 and 3 degrees of freedom.

3.4.1.6 Absolute and relative retention time

Determine the average retention time, $\overline{RT}$ (and/or average relative retention time, $\overline{RRT}$), and the standard deviation (s) for each analyte and standard. Determine the upper and lower retention time (or relative retention time) limits using the following:

$$\text{Lower limit} = \overline{RT} - ts\sqrt{1 + \frac{1}{n}}$$

$$\text{Upper limit} = \overline{RT} + ts\sqrt{1 + \frac{1}{n}}$$

The relative retention time upper and lower limits are determined by replacing $\overline{RT}$ with $\overline{RRT}$ in the equations above. The t value is the 97.5th percentile of a t distribution with n - 1 degrees of freedom, where n is the number of retention time or relative retention time values used.

3.4.1.7 Blanks

Establish the QC acceptance criteria for blanks. The usual requirement is that the concentration of an analyte in a blank must be below the ML or below one-third (1/3) the regulatory compliance level, whichever is higher. In instances where the level of the blank is close to the regulatory compliance level or the level at which measurements are to be made, it may be necessary to require multiple blank measurements and establish the QC acceptance criteria based on the average of the blank measurements plus two standard deviations of the blank measurements.

3.4.1.8 Reference sample

Establish the QC acceptance criteria for the reference sample based on the error provided with the reference sample.

3.4.2 Quality Control Acceptance Criteria Development for New Methods at Tier 2

Method validation at Tier 2 consists of running tests on a single matrix type collected from three different facilities in the same industrial subcategory, with the sample being analyzed in three separate laboratories (see 40 *CFR* parts 405 - 503 for industrial categories and subcategories). If the matrix type being validated is drinking water, then tests shall be run on a drinking water matrix collected from three different sources or on three drinking water samples that each have different characteristics (see Section 4.4.2).

Each of the three laboratories will need to run a full suite of tests, beginning with an MDL study to determine the appropriate ML, followed by calibration, IPR, OPR, and blank analyses, along

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with a pair of MS/MSD analyses for each sample matrix. Results from each laboratory will be submitted to the organization responsible for developing the method. That organization will use the laboratory results to develop QC acceptance criteria as described in the following subsections.

3.4.2.1 Method detection limit and minimum level

Each laboratory participating in the MDL study must perform an MDL test as described in Sections 3.4.1.1 and 6.3.2.9. The organization responsible for developing the new method must establish an MDL for the method, using a pooled MDL from the three laboratories. The precautions concerning blanks and the effect of the matrix, and the detailed steps in 40 *CFR* part 136, Appendix B must be observed to arrive at a reliable MDL.

A pooled MDL is calculated from m individual laboratory MDLs by comparing the square root of the mean of the squares of the individual MDLs and multiplying the result by a ratio of t-values to adjust for the increased degrees of freedom.

$$MDL_{pooled} = \sqrt{\frac{d_1\left(\frac{MDL_{(Lab\,1)}}{t_{(0.99,d_1)}}\right)^2 + d_2\left(\frac{MDL_{(Lab\,2)}}{t_{(0.99,d_2)}}\right)^2 + \ldots d_m\left(\frac{MDL_{(Lab\,m)}}{t_{(0.99,d_m)}}\right)^2}{d_1 + d_2 + \ldots d_m}}\; t_{(0.99,d_1+d_2+\ldots d_m)} \quad ,$$

where m = the number of laboratories, and d_i = the number of replicates used by lab i to derive the MDL. In the case of 3 laboratories with 7 replicates per laboratory, the equation simplifies to:

$$MDL_{pooled} = \sqrt{\frac{MDL^2_{(Lab\,1)} + MDL^2_{(Lab\,2)} + MDL^2_{(Lab\,3)}}{3}}\;\frac{2.55}{3.14}$$

The organization responsible for developing the method also must use this pooled MDL to develop an ML. Procedures for determining the ML are given in Section 3.4.1.1. Once established, the ML is used as the lowest calibration point. The instrument or analytical system is then calibrated at the ML and a minimum of two additional points to assess calibration linearity (Section 3.4.1.2) and to determine the future number of calibration points required and how these points are spaced (Section 3.3.1).

3.4.2.2 Calibration linearity

Establish the RSD of the response factors (RFs), calibration factors (CFs),or relative responses ($\overline{\mathbf{RR}}$s) based on the precision of the determinative technique, as described in Section 3.3.1 and as determined in Section 3.4.2.1. If the RSD is < 2%, a one- or two-point calibration is employed (see Section 3.1.1) and it is unnecessary to establish a limit for calibration linearity.

If three or more calibration points are required, the upper limit on the RSD of the RFs or CFs is determined as follows:

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(1) Calculate the overall average RF ($\overline{RF}$), overall average CF ($\overline{CF}$), or overall average RR ($\overline{RR}$) for each analyte using the individual results from all three laboratories. For example, for a 3-point calibration using RFs:

$$\overline{RF} = (RF_{1(lab\ 1)} + RF_{2(lab\ 1)} + RF_{3(lab\ 1)} + RF_{1(lab\ 2)} + RF_{2(lab\ 2)} + RF_{3(lab\ 2)} + RF_{1(lab\ 3)} + RF_{2(lab\ 3)} + RF_{3(lab\ 3)})/9$$

(2) Calculate the pooled within-laboratory standard deviation (s_w) of the RF, CF, or RR for each analyte from all three laboratories. The pooled within-laboratory standard deviation is calculated as the square root of the mean of the squares of the sample standard deviations of the calibration results at each individual laboratory.

$$s_w = \sqrt{\frac{s^2_{(lab\ 1)} + s^2_{(lab\ 2)} + s^2_{(lab\ 3)}}{3}}$$

(3) Calculate the relative standard deviation of the RF, CF, or RR for each analyte as:

$$RSD = \frac{100 s_w}{\overline{RF}}$$

(4) Calculate the maximum RSD of the RF, CF, or RR for each analyte as follows:

$$RSD_{max} = kRSD$$

where k is the square root of the 95th percentile of an F distribution with n - 1 degrees of freedom in the numerator and m(n - 1) degrees of freedom in the denominator, where m is the number of laboratories and n is the number of calibration points. For three laboratories using a three point calibration, (m=3, n = 3), the value of k is 2.3, and for three laboratories using a five point calibration (m=3, n = 5), the value of k is 1.8.

Note: In the above equations, the $\overline{RF}$ and RF terms should be replaced by $\overline{CF}$ and CF or $\overline{RR}$ and RR terms where appropriate.

3.4.2.3 Calibration verification

Using the average response factor, calibration factor, or relative response from the initial calibration, calculate the upper and lower QC acceptance criteria for calibration verification as follows:

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(1) Determine "k" by multiplying the 97.5th percentile of a Student's *t* distribution with m(n-1) degrees of freedom times the square root of (1 + 1/mn), where there are n points in the calibration and m laboratories:

$$k = t\sqrt{(1 + \frac{1}{mn})}$$

For a three point calibration with three laboratories, the m(n - 1) Student's *t* value is 2.4, and for a five point calibration, the Student's *t* value is 2.2, resulting in combined multipliers of 2.5 for a three point calibration, and 2.3 for a five point calibration.

Multiply k by the pooled standard deviation, s_w ,found in Section 3.4.2.2.

(2) Calculate the upper and lower QC acceptance criteria for the response factors, calibration factors, or relative responses for each analyte by developing a window around the average response factor, calibration factor, or relative response by:

$$\text{Lower limit} = \overline{RF} - ks_w$$
$$\text{Upper limit} = \overline{RF} + ks_w$$

Note: In the above equations, the $\overline{RF}$ terms should be replaced by $\overline{CF}$ or $\overline{RR}$ terms where appropriate.

3.4.2.4 Initial and ongoing precision and recovery

For the IPR and OPR tests, QC acceptance criteria are calculated using the average percent recovery and the standard deviation of recovery from the IPR tests on four aliquots of the reference matrix and the OPR test of one aliquot of the reference matrix (for a total of five samples) in the three laboratories, as follows:

(1) Calculate the average percent recovery ($\overline{X}$) for each analyte based on all data points from all laboratories, the between-laboratory standard deviation (s_b) of the mean results for each of the three laboratories (standard deviation of the three lab means $\overline{X}_{(lab\ 1)}$, $\overline{X}_{(lab\ 2)}$, $\overline{X}_{(lab\ 3)}$), and the pooled within-laboratory standard deviation (s_w) of the 5 samples calculated as in 3.4.2.2. Note: the organization responsible for developing the method must ensure that all laboratories are spiking IPR and OPR samples at the same concentration.

(2) IPR QC acceptance criterion for precision - To calculate a 95% confidence interval for precision, the RSD (computed as s_w divided by $\overline{X}$) is multiplied by the square root of a 95th percentile F value with 3 degrees of freedom in the numerator and 4m degrees of freedom in the denominator, where m = the number of laboratories. The resulting multiplier on the RSD for three laboratories will then be 1.9. The QC acceptance criterion for precision in the IPR test (RSD_{max}) is calculated as follows:

$$RSD_{max} = 1.9RSD$$

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(3) IPR QC acceptance criteria for recovery -Calculate the combined standard deviation for interlaboratory variability and estimation of the mean (s_c) as:

$$s_c = \sqrt{(1+\frac{1}{m})s_b^2 + (\frac{1}{4} - \frac{1}{n})s_w^2} \quad ,$$

where m = the number of laboratories, and n = the number of data points per laboratory. For 3 laboratories and 5 data points per laboratory,

$$s_c = \sqrt{\frac{4}{3}s_b^2 + \frac{1}{20}s_w^2} \quad .$$

(4) Calculate the QC acceptance criteria for recovery in the IPR test by constructing a ± 3.2 s_c window around the average percent recovery ($\overline{X}$, where 3.2 is the 97.5th percentile Student's *t* value for 3 degrees of freedom (an estimated degrees of freedom based on the variance ratios observed with EPA Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 3.2s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 3.2s_c$$

If more than 3 laboratories are used, the degrees of freedom for *t* will increase, but a complete calculation is beyond the scope of this document. An approximation of degrees of freedom equal to the number of laboratories will serve for most situations.

(5) OPR QC acceptance criteria for recovery - Calculate the combined standard deviation for interlaboratory variability and estimation of the mean (s_c) as:

$$s_c = \sqrt{(1+\frac{1}{m})s_b^2 + (1 - \frac{1}{n})s_w^2} \quad ,$$

where m = the number of laboratories, and n = the number of data points per laboratory. For 3 laboratories and 5 data points per laboratory,

$$s_c = \sqrt{\frac{4}{3}s_b^2 + \frac{4}{5}s_w^2} \quad .$$

(6) Calculate the QC acceptance criteria for recovery in the OPR test by constructing a ± 2.6 s_c window around the average percent recovery ($\overline{X}$, where 2.6 is the 97.5th percentile Student's *t*

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value for 5 degrees of freedom (an estimated degrees of freedom based on the variance ratios observed with EPA Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 2.6s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 2.6s_c$$

If more than 3 laboratories are used, the degrees of freedom for *t* will increase, but a complete calculation is beyond the scope of this document. An approximation of degrees of freedom equal to twice the number of laboratories will serve for most situations.

3.4.2.5 Matrix spike and matrix spike duplicate

Results of the MS/MSD analyses performed in the validation study are used to develop the MS/MSD QC acceptance criteria for Tier 2. Each laboratory will measure MS and MSD in each of the three samples. Calculate the MS and MSD performance criteria as follows.

(1) Calculate the mean and sample standard deviation of the recoveries of each MS/MSD pair, and then compute the overall mean recovery ($\overline{X}$), the between-laboratory/matrix standard deviation of the 9 pairwise means (s_b), and the pooled within-laboratory/matrix standard deviation (s_w, as calculated in 3.4.2.2) for each target analyte.

(2) In order to allow for interlaboratory variability, calculate the combined standard deviation (s_c) for interlaboratory variability and estimation of the mean. For 3 laboratories and 3 matrices,

$$s_c = \sqrt{\frac{4}{3}s_b^2 + \frac{5}{6}s_w^2}$$

Derivation of the formula for other than 3 laboratories and 3 matrices is beyond the scope of this text.

(3) MS/MSD QC acceptance criteria for recovery - Calculate the QC acceptance criteria for recovery in the MS/MSD test by constructing a ± $2.2s_c$ window around the average percent recovery ($\overline{X}$) using the combined standard deviation. This factor comes from a *t* value for an estimated 7 degrees of freedom (based on this experimental design and variance ratios observed in Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 2.2s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 2.2s_c$$

Note: For highly variable methods, it is possible that the lower limit for recovery will be a negative number. In these instances, the data should either be log-transformed and the recovery

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window recalculated, or the lower limit established as "detected," as was done with some of the 40 CFR part 136, Appendix A methods.

(4) MS/MSD QC acceptance criteria for relative percent difference (RPD) - To evaluate a 95% confidence interval for precision, the RSD (computed using the pooled within laboratory standard deviation s_w of the MS/MSD samples divided by $\overline{X}$) is multiplied by the square root of the 95th percentile F value with 1 degrees of freedom in the numerator and 3m degrees of freedom in the denominator multiplied by $\sqrt{2}$, where m is the number laboratories. The resulting multiplier on the RSD for 3 laboratories and 3 samples will then be 3.2. The QC acceptance criterion for precision in the MS/MSD test (RPD_{max}) is calculated as follows:

$$RPD_{max} = 3.2RSD.$$

3.4.2.6 Absolute and relative retention time

Establishing QC acceptance criteria for RT and RRT precision is problematic when multiple laboratories are involved because laboratories have a tendency to establish the chromatographic conditions that suit their needs. Calculating average RTs and RRTs based on different operating conditions will result in the establishment of erroneously wide windows. It is advised, therefore, that the organization developing the method specify to the participating laboratories the chromatographic conditions and columns to be used. Any future laboratories operating under different conditions will need to develop new acceptance criteria for RT and RRT precision.

Determine the average retention time, $\overline{RT}$, (or average relative retention time, $\overline{RRT}$), and the corresponding standard deviation (s) for each analyte and standard. Determine the upper and lower retention time (or relative retention time) limits using the following:

$$\text{Lower limit} = \overline{RT} - ts_{avg}\sqrt{1 + \frac{1}{n}}$$

$$\text{Upper limit} = \overline{RT} + ts_{avg}\sqrt{1 + \frac{1}{n}}$$

where the t value is the 97.5th percentile of a t distribution with n - 1 degrees of freedom and where n is the number of retention time or relative retention time data values to be used.

3.4.2.7 Blanks

Establish the QC acceptance criteria for blanks. The usual requirement is that the concentration of an analyte in a blank must be below the ML or below one-third (1/3) the regulatory compliance level, whichever is higher. In instances where the level of the blank is close to the regulatory compliance level or the level at which measurements are to be made, it may be necessary to require multiple blank measurements and establish the QC acceptance criteria based on the average of the blank measurements plus two standard deviations of the blank measurements.

3.4.2.8 Reference sample

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Establish the QC acceptance criteria for the reference sample based on the error provided with the reference sample.

3.4.3 Quality Control Acceptance Criteria Development for New Methods at Tier 3

In Tier 3, a single sample collected from each of a minimum of nine industrial categories is analyzed in nine separate laboratories (one sample analyzed by each laboratory). Details for the characteristics and definitions of these samples are given in Chapter 4 of this guide. Because data gathered from nine laboratories lends itself to the statistical procedures used for interlaboratory method validation studies, the procedures suggested by ASTM and AOAC-International are particularly applicable and those procedures are preferred for development of QC acceptance criteria. However, QC acceptance criteria may also be developed for the Tier 3 methods in ways that are analogous to development of these criteria at Tiers 1 and 2, with minor modifications described below.

3.4.3.1 Method detection limits and minimum levels

Each laboratory participating in the validation must perform an MDL study as described in Section 3.4.1.1. The organization responsible for developing the new method must establish an MDL for the method, using a pooled MDL from the nine laboratories. A pooled MDL is calculated from m individual laboratory MDLs by computing the square root of the mean of the squares of the individual MDLs and multiplying the result by a ratio of *t*-values to adjust for the increased degrees of freedom.

$$MDL_{pooled} = \sqrt{\frac{d_1\left(\frac{MDL_{(Lab\,1)}}{t_{(0.99,d_1)}}\right)^2 + d_2\left(\frac{MDL_{(Lab\,2)}}{t_{(0.99,d_2)}}\right)^2 + \ldots d_m\left(\frac{MDL_{(Lab\,m)}}{t_{(0.99,d_m)}}\right)^2}{d_1 + d_2 + \ldots d_m}}\; t_{(0.99,d_1+d_2+\ldots d_m)} \quad ,$$

where m = the number of laboratories, and d_i = the number of replicates used by lab i to derive the MDL. In the case of 9 laboratories with 7 replicates per laboratory, the equation simplifies to:

$$MDL_{pooled} = \sqrt{\frac{MDL^2_{(Lab\,1)} + MDL^2_{(Lab\,2)} + \ldots MDL^2_{(Lab\,m)}}{9}}\;\frac{2.41}{3.14}$$

The organization responsible for developing the method must also use this MDL to develop an ML. Procedures for determining the ML are given in Section 3.4.1.1. Once established, the ML is used as the lowest calibration point. The instrument or analytical system is then calibrated at the ML and a minimum of two additional points to assess calibration linearity (Section 3.4.1.2) and to determine the number of calibration points required and how these points are spaced (Section 3.3.1).

3.4.3.2 Calibration linearity

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Establish the RSD of the response factor, calibration factor or relative response based on the precision of the determinative technique, as described in Section 3.3.1. The RSD and the RSD limit for the response factor, calibration factor, or relative response is determined as follows:

(1) Calculate the average response factor ($\overline{RF}$), average calibration factor ($\overline{CF}$), or average relative response ($\overline{RR}$) and pooled within-laboratory standard deviation (s_w) of the RF, CF, or RR determined for each analyte from each of the nine laboratories. The pooled standard deviation is computed as the square root of the mean of the squares of the sample standard deviations among the calibration results at each individual laboratory.

$$s_w = \sqrt{\frac{s^2_{(lab\ 1)} + s^2_{(lab\ 2)} + \ldots s^2_{(lab\ 9)}}{9}}$$

(2) Calculate the relative standard deviation (RSD) for each compound:

$$RSD = 100\frac{s_w}{\overline{RF}}$$

(3) Calculate the maximum RSD for each analyte by the following:

$$RSD_{max} = kRSD,$$

where k is the square root of the 95th percentile of an F distribution with n - 1 degrees of freedom in the numerator and m(n - 1) degrees of freedom in the denominator, where m is the number of laboratories and n is the number of calibration points. For nine laboratories using a three-point calibration (n = 3), the value of k is 1.9, and for nine laboratories using a five-point calibration (n = 5), the value of k is 1.6.

Note: In the above equations, the $\overline{RF}$ and RF terms should be replaced by $\overline{CF}$ and CF or $\overline{RR}$ and RR terms where appropriate.

3.4.3.3 Calibration verification

Using the average response factor or calibration factor from the initial calibration, calculate the upper and lower QC acceptance criteria for the calibration verification as follows:

(1) Determine “k” by multiplying the 97.5th percentile of a Student’s *t* distribution with m(n-1) degrees of freedom times the square root of (1 + 1/mn), where there are n points in the calibration and m laboratories:

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$$k = t\sqrt{(1 + \frac{1}{mn})}$$

For a three-point calibration with nine laboratories, the m(n - 1) Student's *t* value is 2.1 and for a five-point calibration, the Student's *t* value is 2.0, resulting in combined multipliers of 2.1 for both a three-point calibration and a five-point calibration.

Multiply k by the pooled standard deviation s_w found in Section 3.4.3.2.

(2) Calculate the upper and lower QC acceptance criteria for the response factors, calibration factors, or relative responses for each analyte by developing a window around the average response factor, calibration factor, or relative response by:

$$\text{Lower limit} = \overline{RF} - ks_w$$
$$\text{Upper limit} = \overline{RF} + ks_w$$

Note: In the above equations, the $\overline{RF}$ terms should be replaced by $\overline{CF}$ or $\overline{RR}$ terms where appropriate.

3.4.3.4 Initial and ongoing precision and recovery

For the IPR and OPR tests, QC acceptance criteria are calculated using the average percent recovery and the standard deviation of recovery from the IPR tests of four aliquots of the reference matrix and the OPR test of one aliquot of the reference matrix (for a total of five samples) in nine laboratories. The QC acceptance criteria are developed using the following steps:

(1) Calculate the average percent recovery ($\overline{X}$) for each analyte based on all data points from all laboratories, the between-laboratory standard deviation (s_b) of the mean results for each of the m laboratories (the standard deviation of the m laboratory averages $\overline{X}_{lab1}$, $\overline{X}_{lab2}$, ..., $\overline{X}_{labm}$), and the pooled within-laboratory standard deviation (s_w) of the five samples calculated as in 3.4.3.2. Note: the organization responsible for developing the method must ensure that all laboratories are spiking IPR and OPR samples at the same concentration.

(2) IPR QC acceptance criteria for precision - To calculate a 95% confidence interval for precision, the RSD (computed as s_w divided by $\overline{X}$) is multiplied by the square root of the 95th percentile F value with 3 degrees of freedom in the numerator and 4m degrees of freedom in the denominator. The resulting multiplier for nine laboratories will be 1.7. The QC acceptance criterion for precision in the IPR test (RSD_{max}) for 9 laboratories is calculated as follows:

$$RSD_{max} = 1.7RSD$$

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(3) IPR QC acceptance criteria for recovery -Calculate the combined standard deviation for interlaboratory variability and estimation of the mean (s_c) as:

$$s_c = \sqrt{(1+\frac{1}{m})s_b^2 + (\frac{1}{4} - \frac{1}{n})s_w^2} \quad ,$$

where m = the number of laboratories, and n = the number of data points per laboratory. For 9 laboratories and 5 data points per laboratory,

$$s_c = \sqrt{\frac{10}{9}s_b^2 + \frac{1}{20}s_w^2} \quad .$$

(4) Calculate the QC acceptance criteria for recovery in the IPR test by constructing a ± 2.3 s_c window around the average percent recovery ($\overline{X}$, where 2.3 is the 97.5th percentile Student's *t* value for 10 degrees of freedom (an estimated degrees of freedom based on the variance ratios observed with EPA Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 2.3s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 2.3s_c$$

If more than 9 laboratories are used, the degrees of freedom for t will increase, but a complete calculation is beyond the scope of this document. An approximation of degrees of freedom equal to the number of laboratories will serve for most situations.

(5) OPR QC acceptance criteria for recovery - Calculate the combined standard deviation for interlaboratory variability and estimation of the mean (s_c) as:

$$s_c = \sqrt{(1+\frac{1}{m})s_b^2 + (1 - \frac{1}{n})s_w^2} \quad ,$$

where m = the number of laboratories, and n = the number of data points per laboratory. For 9 laboratories and 5 data points per laboratory,

$$s_c = \sqrt{\frac{10}{9}s_b^2 + \frac{4}{5}s_w^2}$$

(6) Calculate the QC acceptance criteria for recovery in the OPR test by constructing a ± 2.1 s_c window around the average percent recovery ($\overline{X}$, where 2.1 is the 97.5th percentile Student's *t*

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value for 19 degrees of freedom (an estimated degrees of freedom based on the variance ratios observed with EPA Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 2.1 s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 2.1 s_c$$

If more than 9 laboratories are used, the degrees of freedom for *t* will increase, but a complete calculation is beyond the scope of this document. An approximation of degrees of freedom equal to twice the number of laboratories will serve for most situations.

3.4.3.5 Matrix spike and matrix spike duplicate

Results of the MS/MSD analyses performed in the Tier 3 validation study are used to develop the MS/MSD QC acceptance criteria for Tier 3. Calculate the MS and MSD performance criteria as follows.

(1) Calculate the percent recovery ($\overline{X}$) and the between-laboratory standard deviation (s_b) of the mean results for each of the nine laboratories and also the pooled within-laboratory standard deviation (s_w as calculated as in 3.4.3.2) for each target analyte using the MS and MSD analyses.

(2) In order to allow for interlaboratory variability, calculate the combined standard deviation (s_c) for interlaboratory variability and estimation of the mean as:

$$s_c = \sqrt{(1 + \frac{1}{m}) s_b^2 + \frac{1}{2} s_w^2}.$$

where m = the number of laboratories. For nine labs,

$$s_c = \sqrt{\frac{10}{9} s_b^2 + \frac{1}{2} s_w^2}$$

(3) MS/MSD QC acceptance criteria for recovery - Calculate the QC acceptance criteria for recovery in the MS/MSD test by constructing a ± 2.2 s_c window around the average percent recovery $\overline{X}$ using the combined standard deviation. This factor comes from a t value for an estimated 11 degrees of freedom (based on this experimental design and variance ratios observed in Method 1625):

$$\text{Lower limit}(\%) = \overline{X} - 2.2 s_c$$
$$\text{Upper limit}(\%) = \overline{X} + 2.2 s_c$$

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Note: For highly variable methods, it is possible that the lower limit for recovery will be a negative number. In these instances, the data should either be log-transformed and the recovery window recalculated, or the lower limit established as "detected," as was done with some of the 40 CFR part 136, Appendix A methods.

(4) MS/MSD QC acceptance criterion for relative percent difference (RPD) - To calculate a 95% confidence interval for precision, the RSD (computed using the pooled within-laboratory standard deviation, s_w, of the MS/MSD samples divided by $\overline{X}$) is multiplied by the square root of the 95% percentile F value with 1 degree of freedom in the numerator and m degrees of freedom in the denominator multiplied by $\sqrt{2}$. The resulting multiplier on the RSD for nine laboratories will be 3.2. The QC acceptance criterion for precision in the MS/MSD test (RPD_{max}) is calculated as follows:

$$RPD_{max} = 3.2RSD.$$

3.4.3.6 Absolute and relative retention time

Establishing QC acceptance criteria for RT and RRT precision is problematic when multiple laboratories are involved because laboratories have a tendency to establish the chromatographic conditions that suit their needs. Calculating average RTs and RRTs based on different operating conditions will result in the establishment of erroneously wide windows. It is advised, therefore, that the organization developing the method specify to the participating laboratories the chromatagraphic conditions and columns to be used. Any future laboratories operating under different conditions will need to develop new acceptance criteria for RT and RRT precision.

(1) Using replicate RT and/or RRT data, calculate the upper and lower QC acceptance criteria for each analyte using the procedures in the calibration verification test in Section 3.4.1.3.

(2) Determine the average retention time, $\overline{RT}$ (or average relative retention time, $\overline{RRT}$), and the corresponding standard deviation (s) for each analyte and standard. Determine the upper and lower retention time (or relative retention time) limits using the following:

$$\text{Lower limit} = \overline{RT} - ts\sqrt{1 + \frac{1}{n}}$$

$$\text{Upper limit} = \overline{RT} + ts\sqrt{1 + \frac{1}{n}}$$

where the t value is the 97.5th percentile of a t distribution with n - 1 degrees of freedom, where n is the number of retention time or relative retention time data values to be used.

3.4.3.7 Blanks

Establish the QC acceptance criteria for blanks. The usual requirement is that the concentration of an analyte in a blank must be below the ML or below one-third (1/3) the regulatory compliance level, whichever is higher. In instances where the level of the blank is close to the regulatory compliance level or the level at which measurements are to be made, it may be necessary to require

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multiple blank measurements and establish the QC acceptance criteria based on the average of the blank measurements plus two standard deviations of the blank measurements.

3.4.3.8 Reference sample

Establish the QC acceptance criteria for the reference sample based on the error provided with the reference sample.

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Chapter 4

Method Validation Requirements

4.1 Introduction

Method validation is the process by which a laboratory or vendor establishes the performance of a new method or substantiates the performance of a method modification. New and modified methods must be validated to prove that they accurately measure the concentration of an analyte in an environmental sample. In keeping with the intent of streamlining and flexibility, EPA proposes to establish validation requirements that reflect the level of intended use of the method. This is accomplished through a three-tiered approach, as shown in Table 4-1.

Table 4-1: Application of Method Tiers

Tier Level	Laboratory Use	Applicable to . . .
Tier 1	Single Laboratory	One or more matrix types from any industry; or one or more PWSs
Tier 2	All Laboratories	One or more matrix types within one industrial category or subcategory; or all PWSs
Tier 3	All Laboratories	All matrix types from all industrial categories and subcategories

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

All new and modified methods must be validated to demonstrate that the method is capable of yielding reliable data for compliance monitoring purposes under the Clean Water Act or Safe Drinking Water Act. The same tests are performed to validate new and modified methods; however, the results are used differently. Test results from validation of a new method are used to develop quality control (QC) acceptance criteria for that method, whereas test results from validation of a modified method are used to demonstrate that the modified method produces results equivalent or superior to results produced by the reference method.

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Method modifications are considered to be approved by EPA and may be used after successful validation and documentation at the appropriate tier. For new methods, the validation study must be submitted to EPA and the new method must be approved by EPA before the method can be used for compliance monitoring. Requirements for submitting validation documentation and seeking method approval are provided in Chapter 5.

Although many compliance monitoring analyses are performed by contract laboratories on behalf of a regulated entity, the responsibility for maintaining validation documentation for new and modified methods rests with the regulated entity. Regulated entities, therefore, must inform their contract laboratories about the requirements for detailed documentation of method modifications that are specified in this chapter.

The key concepts presented and discussed in this chapter are: *method validation, Tiers 1-3, industrial category, industrial subcategory, matrix type, matrix effect, sample matrix effect validation, facility, public water system, sample medium,* and *sample matrix*.

4.2 Summary of Validation Requirements

Requirements for validation depend on the tier to which the new or modified method will be applied. Validation requirements are summarized in Table 4-2. Table 4-2 specifies the numbers of matrix types and facilities or PWSs that must be tested and the numbers and types of analyses required to validate a new or modified method at each tier. To clarify the use of the term “matrix type,” as compared to the terms “sample medium” and “sample matrix,” a **sample medium** is the common name for the physical phase of a sample matrix. Air, water, soil, and sludge are sample media. A **matrix type** is a sample medium with common characteristics across a given industrial category or subcategory. For example, C-stage effluents from chlorine bleach mills, effluent from the continuous casting subcategory of the iron and steel industrial category, POTW sludge, and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory are each a matrix type. For the purposes of this initiative, all drinking waters constitute a single matrix type. A **sample matrix** is the component or substrate that contains the analytes of interest. For purposes of sample collection, "sample matrix" is synonymous with "sample".

As used in Table 4-2, a **facility** is a plant or group of plants within a single location that is regulated under a single National Pollutant Discharge Elimination System (NPDES) permit and/or SDWA. A single facility may have multiple water supplies, discharges, waste streams, or other environmental media that are subject to compliance monitoring. For example, a single facility within the Pulp, Paper, and Paperboard industrial category may have a direct discharge, an indirect discharge, and an in-process waste stream that are all subject to compliance monitoring.

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Table 4-2. Summary of Validation Requirements for New Methods and Method Modifications[1]

Method Application	Number of			Number of Analyses Required			
	Labs	Matrix types	Facilities/ PWSs	IPR- reagent water[2]	IPR- sample matrix [3]	MS/MSD	MDL[4]
Tier 1-Single-lab WW/DW- First matrix type or first PWS	1	1	1	4	4	2[5]	7
WW- Each addt'l matrix type (8 max.) from any industrial category	1	1	1	0[6]	0[6]	2[5]	0[6]
DW- Each addt'l PWS (2 max.)	1	1	1	0[6]	0[6]	2[5]	0[6]
Tier 2-Multi-lab, single matrix type WW/DW- Each matrix type in a single industrial category	3	1	3	12	0	6[7]	21
Tier 3-Multi-lab, multiple matrix types WW only- All matrix types, all industrial categories	9[8]	9	9	36	0	18[7]	63

(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. Method application would be designated by tier for wastewater (WW) and drinking water (DW) programs. Three would be the maximum number of public water systems (PWSs) that would be required to validate a new or modified drinking water method at Tier 1 or 2. Nine would be the maximum number of matrix types (or facilities) that would be required to validate a new or modified wastewater method at Tier 1 or 3; at Tier 2 the number would be three matrix types.

(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, except as noted under footnote 7, would be four times the number of laboratories required to validate a method modification or new method because each laboratory would perform a 4-replicate IPR test.

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(3) IPR sample matrix analyses would be used to establish QC acceptance criteria for matrix spike/matrix spike duplicate (MS/MSD) recovery and precision for a Tier 1 new method only. Would not be required for validation of Tier 2 or 3 new methods because this variability data would be obtained from MS/MSD tests. Would not be required for validation of a method modification because MS/MSD data from the reference method would be used.

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Table 4-2. Summary of Validation Requirements for New Methods and Method Modifications[1] (cont'd)

(4) A method detection limit (MDL) test would be performed in each laboratory using the new or modified method. 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 regulations at 40 CFR parts 136 and 141 and/or in chapter 6 of the Streamlining Guide (EPA 1996a).

(5) MS/MSD analyses would be required only for a method modification because, for new methods, the MS/MSD QC acceptance criteria would be established by the 4-replicate sample matrix IPR test. For modified methods, the MS/MSD test would demonstrate that the reference method MS/MSD QC acceptance criteria have been met.

(6) The MDL, reagent water IPR, and sample matrix IPR tests would not have to be repeated after the first matrix type, facility, or PWS was validated.

(7) For validation of a new method, the MS/MSD analyses would establish QC acceptance criteria for MS/MSD recovery and precision. For validation of a method modification, the MS/MSD analyses would demonstrate that reference method MS/MSD recovery and precision have been met. The required number of MS/MSD analyses would be two times the number of facilities, PWSs or matrix types tested.

(8) The number of laboratories and samples would vary if a conventional interlaboratory study is used.

The tiered approach to validating new and modified methods, presented in Table 4-2, accommodates variability in the analytical performance of a method that can be attributed to the type of sample analyzed. This variability is termed a **matrix effect** and can be observed in samples taken at different locations in matrices of the same type (intramatrix) or in samples from different locations and in different matrix types (intermatrix). Under the streamlining initiative, each successive tier addresses matrix effects to a greater degree through increasing levels of **sample matrix effect validation**, broadly defined as a test of the extent to which differences, if any, in method performance could be attributed to variability between samples obtained from different industrial matrices, facilities, or PWSs. Matrix effects need to be tested by the IPR sample matrix and MS/MSD analyses listed in Table 4-2. Intramatrix effects need to be tested in water samples taken from different PWSs or from different waste streams. Intermatrix effects need to be validated on a group of samples taken from discharge samples collected from several different industrial categories. In all cases, the laboratory must try to determine if the measurement result for the target analyte using a new or modified method differs from the result obtained in a reagent water matrix or in a previously validated matrix type or PWS sample.

As shown in Table 4-2, a **Tier 1** new or modified method is validated in a single laboratory on one or more matrix types obtained from one or more facilities, or on samples obtained from one or more PWSs. Validation of additional facilities or PWSs requires analysis of MS/MSD samples for each additional facility or PWS. However, in response to stakeholder requests that there should be

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some maximum number of single-laboratory validations after which further validation would be unnecessary because sample matrix effects would have been sufficiently addressed, EPA has included a provision for a maximum number of matrix type, facility, or PWS analyses for Tier 1 methods. For a wastewater method, the maximum number of matrix types or facilities tested under Tier 1 is nine, each from a different industrial category or subcategory. For a drinking water method, the maximum number of PWS samples tested under Tier 1 is three samples, each from a PWS with different water quality characteristics. Validation in three PWSs, rather than nine, is required because three is consistent with the validation data in many EPA drinking water methods and because the variability in drinking water samples (and therefore the probability of matrix effects) is usually less in drinking water samples than in wastewater samples.

Tier 2 validation is applicable to one or more matrix types within a single industrial category or subcategory. Because Tier 2 new and modified methods apply to each matrix across all laboratories, EPA developed Tier 2 validation requirements to incorporate intramatrix variability. Tier 2 requires validation of the method in drinking water samples obtained from three PWSs, or wastewater samples of one or more matrix types obtained from three or more facilities within a single industrial category or subcategory. Because the drinking water program regulates only one matrix type, drinking (potable) water, Tier 2 results in nationwide approval for a drinking water method.

Tier 3 validation is applicable to the wastewater program and applies to all matrix types in all industrial categories. Consequently, Tier 3 validation requirements include provisions to account for both intramatrix and intermatrix variability. Tier 3 requires validation of the method in wastewater samples of up to nine matrix types obtained from nine different facilities. Tier 3 validation applies to the wastewater program which regulates several industrial categories, each of which may contain more than one matrix type. Tier 3 does not apply to the drinking water program because the drinking water program regulates only one matrix type.

For all multi-matrix tiers, it is extremely important to select suitable samples and matrix types for validation. The matrix types, facilities, or PWSs selected for validation need to have sufficiently different water quality characteristics so that the matrix effects, if any, can be observed. Proposed criteria for selecting matrix types, facilities, or PWSs from which to obtain samples for validation are specified in section 4.4.1.

4.3 Description of Tier 1, 2, and 3 Validation Studies

Ideally, a method modification or a new method should be validated through a classical interlaboratory method validation study of the type used historically by EPA, ASTM, AOAC-International, and other organizations. EPA recognizes, however, that a formal interlaboratory method validation 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. 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, and improve overall laboratory productivity without undertaking costly and time-consuming interlaboratory studies.

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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** is expected to be used by water supply laboratories, dischargers, and state and municipal laboratories repetitively testing samples from multiple sites within the same industrial category on a routine basis. **Tier 3** is expected to be used by vendors, commercial laboratories, dischargers, and state and municipal laboratories testing a wide variety of sample matrices from diverse sites. Vendors seeking approval of a new technology would also be expected to use Tier 3.

4.3.1 Tier 1 Validation Studies

The primary intent of Tier 1 is to allow use of a new or modified method by a single laboratory. Tier 1 can be applied to a single matrix type or, for drinking water, a single PWS. It also can be applied to multiple matrix types or multiple PWSs.

Tier 1 - Single matrix type/single PWS

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

Tier 1 - Multiple matrix types

For wastewater, if a laboratory intends to apply the method to more than one matrix type, the laboratory must validate the method on each matrix type, to a limit of nine matrix types. Table 4-2 specifies the specific requirements for the first matrix type and those for each additional matrix type. Some laboratories may be testing multiple matrix types for the same analytes using the same modified method. This raises the question of the number of matrix types to which the modification must be applied to demonstrate that it will likely be successful for all other matrix types. In responding to this question, EPA believes that the number certainly cannot be greater than the number required for validation of a method for nationwide use (nine) and has, therefore, established nine different matrix types as the number after which a test on each subsequent matrix type is not required. The matrices that must be tested for validation of a method for wastewater are given in Table 4-3.

As with a Tier 1-Single matrix type/PWS 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 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 4-3, the validation is applicable to all other matrix types.

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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.

Table 4-3

Wastewater Matrices Required for Multiple-Matrix Validation Studies

1. Effluent from a publicly owned treatment works (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
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
- $CaCO_3$ greater than 140 mg/L

Tier 1 - Multiple PWSs

For drinking water, if a laboratory intends to apply the method to more than one PWS, the laboratory must validate the method on each PWS, to a limit of three PWSs. Table 4-2 specifies the specific validation requirements for the first PWS and those for each additional PWS. EPA proposes to require validation in three rather than nine PWSs, because three is consistent with the validation data in many EPA drinking water methods and because the variability in drinking water samples (and therefore the probability of matrix effects) is usually less in drinking water samples than in wastewater samples.

As with a Tier 1-Single matrix type/PWS validation study, Tier 1 - Multiple PWS validation studies are performed in a single laboratory and, therefore, cannot be transferred to another laboratory. If a method is validated by a single laboratory in one or two PWSs, the validation is applicable to those PWSs only. However, once a laboratory has validated the method in three PWSs and those

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PWSs possess different water quality characteristics, as described below, the validation is applicable to all other PWSs.

To test the modified method for potential matrix effects, the three PWS samples must be collected from PWSs with water quality characteristics that are sufficiently different that sample matrix effects, if any, can be observed. In all cases, the laboratory must try to determine if the measurement result for the target analyte using a new or modified method differ from the result obtained in a reagent water matrix or in a previously validated matrix type or PWS sample. 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 new or modified method. 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.

4.3.2 Tier 2 Validation Studies

The primary intent of Tier 2 is to allow all regulated entities and laboratories to apply a new or modified method 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 new or modified drinking water method.

EPA believes that implementation of Tier 2 will encourage the development and application of techniques that overcome matrix interference problems, lower detection limits, improve the reliability of results, lower the costs of measurements, and improve overall laboratory productivity when analyzing samples from a given industry. For example, the National Council of the American Paper Industry for Air and Stream Improvement, Inc. (NCASI) has suggested a large number of improvements to EPA's proposed and approved methods, with the specific objective of improving method performance in samples from the Pulp, Paper, and Paperboard industrial category. EPA believes that NCASI's suggestions have merit and result in improvements in the reference methods. Through Tier 2, EPA is codifying the ability of NCASI and other industry organizations and associations to improve the approved methods within their respective industries.

Significant industries within Tier 2 are: PWSs, publicly-owned treatment works (POTWs), and individual industrial categories and subcategories that are defined in the regulations at 40 *CFR* parts 405 - 503. At present, there are approximately 42 industrial categories and 650 industrial subcategories defined in the Part 405 - 503 regulations, each of which constitutes an individual industry under the streamlining initiative.

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 a minimum of three separate facilities in the same industrial category or subcategory. A sample from each facility will be sent to each of the laboratories, for a total of nine sample analyses.

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For POTWs, if a new or modified method is validated on final effluent only, that method is 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 will be monitored, the method must be validated separately on these sample matrix types.

In contrast to Tier 1, once a new or modified method 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 matrix types from within the industrial category or subcategory for which the method has been validated, and as long as the other laboratories meet all of the method's QC acceptance criteria. If the new or modified method is to be applied to another industrial category or subcategory, or to other media or matrix types in the same category or subcategory, the modification must be validated on media/matrix types in each category/subcategory.

4.3.3 Tier 3 Validation Studies

The primary intent of Tier 3 is to allow nationwide use of a new or modified method by all regulated entities and laboratories. 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 a variety of matrices, matrix types, and media.

Tier 3 validation studies are performed in a minimum of nine laboratories, each with a different matrix type at minimum, for a total of nine samples. The minimum requirements for sample matrices that must be used in the validation study are given in Table 4-3. 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 4-3. For example, if a modification 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 purveyor of a method modification in identifying sources for samples of such discharges.

4.4 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 a detailed study plan. For a simple method modification made at Tier 1, a detailed study plan may be unnecessary if the modification is straightforward and easily understood by the analyst and regulatory authority. In such a case, a simplified study statement may suffice.

The validation study plan should contain the elements described in sections 4.4.1 through 4.4.6.

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4.4.1 Background

The Background section of the validation study plan must:

- Identify the method as a new method or a modification of a reference method.
- Include a method summary.
- If a modification, cite the organization and method number (given in 40 CFR parts 136, 141, and 405 - 503) for the reference method.
- If a modification, describe the reasons for and extent of the modification, the logic behind the technical approach to the modification, and the result of the modification.
- If a new method, describe the rationale for developing the method and explain how the method meets the criteria for a new method specified in section 2 of this guide.
- Identify the matrices, matrix types, and/or media to which the method is believed to be applicable.
- List the analytes measured by the method or modification 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.)

4.4.2 Objectives

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

4.4.3 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.

4.4.4 Technical Approach

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The Technical Approach section of the validation study plan should:

- Indicate at which Tier level 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.

4.4.5 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.

4.4.6 Limitations

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

4.5 Detailed Procedures for Conducting Tier 1, 2, and 3 Validation Studies

When validating new or modified methods, laboratories must adhere to the standardized QC described in Chapter 3 and detailed in the new or modified method. Laboratories must use a reference matrix (usually, reagent water) and field samples for the validation study.

4.5.1 Optional Preliminary Testing

Although preliminary testing of the new or modified method is not required, many users may wish to conduct such studies prior to performing all of the required tests outlined in Sections 4.6.3-4.6.11 below. Performance of preliminary testing may help organizations identify and correct problems with the method prior to the more extensive and costly method validation study. Typical preliminary performance testing may include a determination of the method detection limit (MDL), analysis of initial precision and recovery (IPR) samples, and ruggedness tests. If such preliminary tests are performed and yield results that suggest further revision of the method is unnecessary, the preliminary test results may be used to fulfill the MDL or IPR test requirements described in Sections 4.6.3 and 4.6.5. If, however, changes are made to the procedures as a result of the preliminary tests, those tests must be repeated as part of the full validation study described below.

4.5.2 Method Compilation

Prior to conducting a complete validation study, the organization responsible for developing or modifying the method should detail the full method in accordance with EPA's *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141*. If the organization that develops a new method is a consensus standards organization or government organization with a standardized format, that format may be used. The documented method should be distributed to each laboratory

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

4.5.3 Method Detection Limit Study

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

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate an MDL that meets the criteria specified in the reference method or in Section 6.3.2.9 of this Guide. For wastewater methods, the MDL must be equal to or less than the MDL of the reference method or less than 1/10 the regulatory compliance limit, whichever is greater. This 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 reference method but is potentially more valuable in allowing determination of the analyte(s) of interest at the regulatory compliance limit in a complex sample matrix.

- If the validation study is of a new wastewater method, the organization responsible for development of the new method must use the results of the MDL study to determine a minimum level (ML) of quantitation as described in Chapter 3. Determination of an ML for new drinking water methods is encouraged but not required, because the regulations at 40 CFR part 141 specify detection and sometimes quantitation limits for all regulated analytes.

Each laboratory must perform its MDL study on an instrument that is calibrated at a range that will encompass the ML.

4.5.4 Calibration

Following completion of the MDL study, each laboratory participating in the study must perform a multi-point calibration in accordance with the procedures specified in the new or modified method. However, a single-point calibration is allowed if the < 2% relative standard deviation (RSD) criteria at Section 3.3.1 of this guide are met.

- If the validation study is of a modified method, 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 reference method or, as may often be the case for drinking water methods, in the applicable regulations.

- If the validation study is of a new method, the organization responsible for development of the method must use the results of the validation study to develop a linearity criterion as described in Chapter 3.

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4.5.5 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 to analyze four spiked reagent water replicates.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the IPR precision and recovery criteria given in the reference method.

- If the validation study is of a new method, the organization responsible for development of the method must use the results of these IPR analyses to develop precision and recovery criteria as described in Chapter 3.

For a new method, the concentration of the IPR samples must be stated in the method. As described in Chapter 3, this concentration should be between one and five times the ML.

4.5.6 Field Sample Analyses

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

4.5.6.1 Tier 1 - Single Matrix Type/Single PWS Validation Studies

In a Tier 1-Single matrix type/PWS study performed to validate a method modification, the laboratory must determine the background concentration of an unspiked sample prior to analyzing an MS/MSD pair for the matrix being tested, for a total of three field sample analyses (background, MS, and MSD). Each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery criteria given in the reference method.

In a Tier 1 - Single matrix type/PWS study performed to validate a new method, the laboratory must analyze four spiked replicates of the matrix type to which the new or modified method will be applied. The replicate samples must be spiked with the analyte(s) of interest at either the concentration specified in the reference method, at a concentration one to five times the background concentration of the analyte(s) in the sample, or at two to five times the ML, whichever is greater. In other words, the laboratory will perform an IPR test in the matrix type of interest. Prior to spiking the replicate samples, the laboratory must determine the background concentration of an unspiked aliquot. In all, Tier 1-Single matrix type/PWS validation studies of new methods will require analysis of five field samples (one background and four matrix). The organization responsible for developing the method must use the results of these sample analyses to develop MS/MSD precision and recovery criteria as described in Chapter 3.

4.5.6.2 Tier 1 - Multiple Matrix Type Validation Studies

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In Tier 1-Multiple matrix type studies performed to validate new or modified methods, 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. 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, a Tier 1-Multiple matrix type validation study will require analysis of 6 - 27 samples.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery criteria given in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop MS/MSD precision and recovery criteria as described in Chapter 3.

4.5.6.3 Tier 1 - Multiple PWSs

In Tier 1-Multiple PWSs studies performed to validate new or modified methods, the laboratory must determine the background concentration and analyze an MS/MSD pair for each PWS sample being tested, up to a total of three PWS samples. Since three field sample analyses are required for each PWS sample (one background, one MS, and one MSD), and between two and three PWS samples may be tested, a Tier 1-Multiple PWSs validation study will require analysis of 6 - 9 samples.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery criteria given in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop MS/MSD precision and recovery criteria as described in Chapter 3.

4.5.6.4 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 for each of the three samples received. Because there are three laboratories, each of which performs three analyses (one background, one MS, and one MSD) on each of the three samples received, Tier 2 validation studies will require analysis of 27 samples.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery criteria given in the reference method.

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- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop MS/MSD precision and recovery criteria as described in Chapter 3.

4.5.6.5 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.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the MS/MSD precision and recovery criteria given in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop MS/MSD precision and recovery criteria as described in Chapter 3.

4.5.7 Ongoing Precision and Recovery

If the field samples discussed in Section 4.6.6 are analyzed as a batch with the IPR samples, analysis of an OPR sample is unnecessary in the validation study. If, however, field samples are analyzed in a different batch or batches, then each laboratory participating in the Tier 1, 2, or 3 validation study must analyze an OPR sample with each batch. The concentration of the OPR sample must be as stated in the method being validated.

- If the validation study is of a modified method, each laboratory participating in the study laboratory that analyzes an OPR sample must demonstrate that it can meet the OPR recovery criteria given in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of the IPR tests described above in Section 4.6.5 to develop OPR recovery criteria as described in Chapter 3.

4.5.8 Calibration Verification

If the field samples discussed in Section 4.6.6 are analyzed on the same shift or in the same set of instrumental determinations as the initial calibration sequence, calibration verification is unnecessary. However, if field samples are analyzed on a different shift or in a different instrument batch, each laboratory participating in the Tier 1, 2, or 3 validation study must verify calibration as described in the method.

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- If the validation study is of a modified method, each laboratory participating in the study and verifying calibration must demonstrate that it can meet the acceptance criteria given in the reference method for calibration verification.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of the calibration sequence described above in Section 4.6.4 to develop QC acceptance criteria for the calibration verification analyses as described in Chapter 3.

4.5.9 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.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the QC acceptance criteria for blanks that are specified in the method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop QC acceptance criteria for allowable blank contamination as described in Chapter 3.

4.5.10 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.

- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the surrogate or labeled compound recovery criteria specified in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop surrogate or labeled compound recovery QC acceptance criteria as described in Chapter 3.

4.5.11 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.

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- If the validation study is of a modified method, each laboratory participating in the study must demonstrate that it can meet the absolute and relative retention time criteria that are specified in the reference method.

- If the validation study is of a new method, the organization responsible for developing the method must use the results of these sample analyses to develop absolute and relative retention time criteria as described in Chapter 3.

4.5.12 New Analytes

As described in Chapter 2, EPA proposes to consider the addition of new analytes to approved methods as acceptable performance-based method modifications under the streamlining initiative. Because these method modifications are performance-based, laboratories will be required to demonstrate equivalency in accordance with the requirements summarized above for other Tier 1, 2, and 3 method modifications. In addition, laboratories are required to either develop QC acceptance criteria for the added analyte, transfer QC acceptance criteria from an analyte with similar chemical characteristics, or transfer QC acceptance criteria from another method with the same analyte.

4.5.13 Further Validation Studies for New Methods

After completing the Tier 1, 2, or 3 validation studies of new methods, the organization responsible for developing the method must document the study results in accordance with Section 4.7 below and submit the results and the method to EPA for review and approval, as described in Chapter 5. If, based on its review of the method, EPA concludes that the method is not sufficiently rugged or reliable for its intended use, EPA may require further method development and further testing to define the stability and reliability of the method. The tests and studies that must be performed in this case are dependent upon the analyte(s) and the analytical system, and will be determined on a case-by-case basis as these situations arise.

4.6 Validation Study Report

Laboratories or other organizations responsible for developing a new or modified method at Tier 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 method modifications, the completed Checklists (*Checklist for Initial Demonstration of Method Performance*, *Checklist for Continuing Demonstration of Method Performance*, and *Certification Statement*), along with the raw data and example calculations, are considered adequate to document method equivalency; a full validation study report is not necessary.

The information and supporting data required in the validation study report are sufficient to enable EPA to evaluate a new method for adequacy or to support a claim of equivalent performance for a method modification. Some items are required only for a modification; these are clearly identified below. If data are collected by a contract laboratory, the organization responsible for using the method (i.e. permittee, POTW, PWS, or other regulated entity) is responsible for ensuring that all

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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 4.6.1 through 4.6.11.

4.6.1 Background

The Background section of the validation study report must describe the method (new method or method modification) that was validated and identify the organization responsible for developing the method. This section must:

- Identify the method as a new method or a modification of a reference method.
- Include a method summary.
- If a modification, cite the organization and method number (given in 40 CFR parts 136, 141, and 405 - 503) for the reference method.
- If a modification, describe the reasons for and extent of the modification, the logic behind the technical approach to the modification, and the result of the modification.
- If a new method, describe the rationale for developing the method and explain how the method meets the criteria for a new method specified in section 2 of this guide.
- Identify the matrices, matrix types, and/or media to which the method is believed to be applicable.
- List the analytes measured by the method or modification 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.)

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- State the purpose of the study.

4.6.2 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 4.4 for required elements of the study design).

4.6.3 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.
- Describes how analyses were performed.
- Identify any problems encountered or deviations from the study plan and their resolution/impact on study performance and/or results.

4.6.4 Data Reporting and Validation

This section of the validation study report must describe the procedures that were used to report and validate study data. Although EPA will not establish a standard format for analytical data submission because of the large variety of formats currently in use, EPA strongly recommends the Department of Energy Environmental Management Electronic Data Deliverable Master Specification (DEEMS) because it will expedite processing of the data review. The DEEMS list contains all of the

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data elements that laboratories should submit to document method validation. A DEEMS data element dictionary is provided in Appendix D of this guide.

4.6.5 Results

This section of the validation study report presents the study results. Results must be presented on the Checklists *(Checklist for Initial Demonstration of Method Performance*, *Checklist for Continuing Demonstration of Method Performance*, and *Certification Statement)*, 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 4.6.10).

The Checklists, instructions for their completion, and an example set of completed Checklists are provided in Appendix E to this guide. 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 all QC requirements of the method were met. For modified methods, the Checklists verify that the modified method met all QC acceptance criteria of the reference method, for purposes of assessing method equivalency.

4.6.6 Development of QC Acceptance Criteria

For new methods, the validation study report must contain a section that describes the basis for development of QC acceptance criteria for all of the required QC tests. The requirements for developing QC acceptance criteria are detailed in Chapter 3.

4.6.7 Data Analysis/Discussion

This section of the validation study report must provide a statistical analysis and discussion of the study results. For validation of modified methods, the discussion must address any discrepancies between the results and the QC acceptance criteria of the reference method.

4.6.8 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).

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4.6.9 Appendix A - The Method

For new methods, the method, prepared in EPA format (i.e., in accordance with EPA's *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141*), must be appended to the validation study report. All new methods must contain QC acceptance criteria for all required QC elements (see Chapter 3).

For modified methods, the modified portion of the reference method, prepared in EPA format, must be appended to the validation study report.

4.6.10 Appendix B - Validation Study Plan

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

4.6.11 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.

4.6.11.1 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 the 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.)

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- 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 reference 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.

4.6.11.2 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.

4.7 Reporting Validation Study Results

Only validation study results for new methods are required to be reported to EPA, although entities can request EPA review of method modification validation study results at Tier 2 and 3. Chapter 5 describes procedures for submitting validation study results for EPA review and approval of new methods and Tier 2 and 3 method modifications.

4.7.1 Reporting Validation Study Results for New Methods

Validation study results for all new methods, regardless of tier, must be submitted to EPA for approval. Guidance for submitting validation study results to EPA and a description of the approval process are provided in Chapter 5. The organization responsible for developing the method also must maintain on file complete records of all validation study documentation, including the study plan, validation study report, completed Checklists, and all other information submitted to EPA.

4.7.2 Reporting Validation Study Results for Method Modifications

Validation study results for modified methods, regardless of tier, need not be submitted to EPA for approval. Rather, the organization responsible for developing the method modification must

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maintain on file complete records of all validation study documentation, including the study plan, validation study report, completed Checklists, supporting data, and other information required in section 4.6. Laboratories using the modification also should provide a copy of the validation study report with appendixes to all regulated entities whose samples have been analyzed by the modified method.

Regulated entities must retain validation study reports on file and make the files available for review on request by a permitting authority. All records must be available for review by auditors.

Submission of validation study results for Tier 1, 2, and 3 method modifications is not required because EPA does not intend to formally approve such modifications. Tier 1, 2, and 3 modifications are considered to be approved by EPA as long as all validation study and documentation requirements have been met. For entities wishing to seek public recognition that their procedures have been demonstrated to be acceptable for use, EPA proposes to provide an option for submission of Tier 2 and Tier 3 method modificationsfor EPA approval as described in Chapter 5.

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Chapter 5

Method Approval Process

5.1 Introduction

Two principal objectives of the streamlining initiative are to encourage organizations external to EPA to develop and submit for approval new analytical methods and to expedite method approval at 40 CFR parts 136 and 141. The key to the success of these efforts is to define procedures and provide guidance to the public on how to develop, validate, and submit a method to EPA for approval. This guidance is intended to encourage participation of external organizations in method development. Additionally, it will expedite the method approval process by ensuring that methods submitted to EPA for approval are in the correct format, have been appropriately validated, and are accompanied by the necessary supporting documentation.

This chapter details the procedures for preparing and submitting method documentation under the streamlining initiative, and describes the rulemaking process required to approve a new method or method modification. By providing increased method flexibility as described in Chapter 2 of this guide, EPA expects to significantly reduce the number of modified methods that must undergo rulemaking as alternate test procedures (ATPs), while increasing the number of new methods submitted for approval. Under the streamlining initiative, all new methods will be subject to EPA review and approval. Modified methods at validation Tiers 2 and 3 will be reviewed and approved by EPA only if requested. EPA approval may take the form of a letter of approval or a rulemaking to propose the method at 40 CFR part 136 or part 141, as described in this chapter.

The key concepts presented and discussed in this chapter are*: method development, standard EPA method format, rulemaking process, direct final rulemaking, proprietary reagents, proprietary instruments, and proprietary methods*.

5.2 Pre-Submission Procedures

Under streamlining, EPA must review all new methods, and will review Tier 2 and Tier 3 method modifications upon request. Prior to submitting a method to EPA for review, a party developing a new or modified method will undertake several preparatory activities: method development, method validation, and, if a rulemaking will occur, compilation of preamble information. Method developers also may wish to publish their method independently.

5.2.1 Method Development

Any party who identifies a new or improved procedure or technique for analyzing an analyte of interest can develop a new method or method modification. A new method must be a unique combination of analyte and determinative technique, as discussed in Chapter 2. Otherwise, it would

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qualify as a modification of an existing method. In addition, the determinative technique in a new method must be more sensitive and/or selective (specific) than the determinative techniques in all methods previously approved for the analyte. Further, a new method must include the standardized QC elements and specify QC acceptance criteria for each required QC element. The QC acceptance criteria must be developed from data gathered in the method validation study, as described in Chapter 3 of this guide.

The **method development** process will typically include drafting the method, and checking, modifying, and rechecking testing procedures. If an interlaboratory study is required to validate the method, generally a single-laboratory study is done during the method development phase to identify method revisions needed preceding the interlaboratory study. The method should be written in the **standard EPA method format**. EPA method format requirements are specified in *Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141* (Guidelines and Format). The Guidelines and Format document incorporates the analytical methods format prescribed by EPA's Environmental Monitoring Management Council (EMMC). An objective of the EMMC format is to standardize all Agency analytical methods.

A standardized method format used by a government agency such as the U.S. Geological Survey or a consensus standards organization such as Standard Methods, ASTM, or AOAC-International can be used by those organizations, in lieu of the EPA format. However, these formats may be used only by these organizations to avoid possible confusion over authorship. Other parties are required to use the standard EPA format. EPA will review and approve standardized formats from governmental authorities and industrial associations upon request, but will not approve miscellaneous formats written by instrument manufacturers, individual laboratories, and others, because of the potential proliferation of different method formats. EPA believes that the format provided in Guidelines and Format is more than adequate to meet the needs of the analtyical community.

5.2.2 Method Validation

Each new method or method modification must be tested to assess its performance. The process of establishing or substantiating method performance is called validation. Method validation requirements are described in Chapter 4. The method developing organization is responsible for performing the validation study at the appropriate validation tier, according to the procedures described in Chapters 4. A validation study plan should be prepared prior to the study; the results of the study must be detailed in a method validation report. The contents of the method validation report and the supporting Checklists and data that must accompany the report are specified in Chapter 4.

5.2.3 Compilation of Information to Support Development of Preamble

When methods will undergo the rulemaking process, the method submitter must compile information on the method that will facilitate EPA preparation of a draft preamble for proposal of the method at 40 CFR parts 136 or 141. Information that should be provided includes: a detailed 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.

When preparing method information, the method submitter must:

- Define the purpose and intended use of the method.

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- State what the method is based upon, noting any relationship of the method to other existing analytical methods. Indicate whether the method is associated with a sampling method.

- List analytes that can be measured by the method, including each analyte's Chemical Abstracts Service Registry Number (CASRN). If regulations cite other than the most commonly used analyte name, refer to the regulation. For pesticides, use "acceptable common names." The use of registered trade names is permitted.

- Identify the matrix(ces) for which the method has been found satisfactory.

- Indicate the statistically determined method detection limit (MDL) and the analyte concentration range over which the method is applicable. State the matrix(ces) in which MDL was determined. If the MDL is not available, report an instrumental detection limit and define how it was derived. Indicate the minimum level (ML) and water quality criteria if appropriate to the analyte and method.

- Describe method limitations, such as "This method is not applicable to saline water," or "This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities." Indicate any means of recognizing cases where the method may not be applicable to the sample under test.

- Outline, specifying amounts of sample and reagent, the procedure that is followed to determine the presence or absence of the listed analytes. Include any sample pretreatment, such as filtration or digestion. In this description, identify the basic steps involved in performing the method, but omit the details that are a necessary part of the complete statement of procedure.

- State the type of procedure (colorimetric, electrometric, volumetric, etc.) and describe the source of color, major chemical reaction, including pertinent chemical equations, etc. For instrumental methods, state the technique.

- Identify the determinative step in the method.

- List options to the method, if applicable.

- Discuss in a summary fashion how quality is assured in the method. For new methods, describe and discuss the development of QC acceptance criteria for all of the standard QC elements. For modified methods, include a discussion that compares the method results to the QC acceptance criteria of the reference method.

- Describe and discuss the method validation study and the study results, including study design and objectives, study limitations, study management, technical approach, data reporting and validation, results, data analysis discussion, and conclusions.

- Describe and discuss any MDL studies or other method studies that were conducted during method development and validation

Looking at previous method rules provides an idea of the type of method information and the appropriate level of detail for submitting method information to EPA. Examples of preambles for

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method rules 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.

5.2.4 Method Publication

An objective of the streamlining initiative is to incorporate methods by reference in proposals. EPA is working with the Office of the Federal Register (OFR) to accomplish this objective. Incorporation by reference would facilitate method updates, increase the accessibility of the method, and save on publication costs. To support incorporation by reference, it would be helpful if the method developing organization published the method. Method approval requests submitted by governmental authorities or industrial associations should meet this requirement without difficulty. Vendors, laboratories and other small parties may be unable to undertake direct publication. A possible solution for small parties wishing to incorporate their methods by reference is to have the methods published by the National Technical Information Service (NTIS) or the Educational Resources Information Center (ERIC). If suitable means of publication are not available, particularly to small business submitters, EPA may assist in having the method published by NTIS or ERIC.

5.3 Submission of Method Approval Applications to EPA

When the pre-submission steps are completed, the method submitter must compile and submit to EPA a method approval application package. The method approval application package will be submitted to the Analytical Methods Staff (AMS), within EPA's Office of Water. The application package will contain the method validation study report, including the formatted method and supporting data. Requirements for the method validation study report and supporting documentation are specified in section 4.6. If the method will undergo rulemaking, the application package also must include information to facilitate EPA preparation of a draft preamble as described in section 5.2.3.

5.4 EPA Review of Method Approval Applications

EPA will review all new methods, and will review Tier 2 and Tier 3 method modifications if requested. When a method package is submitted for review, EPA will first check the documentation for completeness. If all of the documentation is in order, EPA will begin an internal review of the method for scientific merit, consistency, and appropriateness. If documentation is incomplete, EPA will contact the submitter and request submission of missing documentation before proceeding with its review.

The internal review at EPA may involve multiple programs and workgroups. Should any problems or questions arise, EPA will communicate with the submitter to resolve the outstanding issues. Depending on the circumstances, EPA may return the application to the submitter for revision.

If internal reviewers recommend approval of the new method or method modification, EPA will issue a letter of acceptance for a Tier 1 new method. For Tier 2 and Tier 3 new methods, EPA will begin the rulemaking process. For Tier 2 and Tier 3 method modifications, the method submitter has the option of receiving a letter of approval or proceeding with the rulemaking process.

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Table 5-1: EPA Review and Action for New and Modified Methods

	New Method	Modified Method
Tier 1 Single-lab, single matrix type/single PWS	• EPA review required • EPA issues a letter of approval	• No EPA review
Tier 2 Multi-lab, single matrix type/all PWSs	• EPA review required • Approved through rulemaking	• If requested, EPA reviews and - issues letter of approval, or - conducts rulemaking
Tier 3 Multi-lab, all matrix types	• EPA review required • Approved through rulemaking	• If requested, EPA reviews and - issues letter of approval, or - conducts rulemaking

5.5 Tier 1/Single-Laboratory Use Methods

Under the streamlining initiative, EPA proposes to allow use of single-laboratory, limited-use methods as Tier 1 methods for both wastewater and drinking water. This will provide the means by which (1) a new technology can be introduced, and (2) specific matrix interference problems can be overcome. Further, additional single laboratories can use the technology until a sufficient number of devices are available for interlaboratory validation.

Currently, EPA reviews single-laboratory, limited-use methods only for special applications. Examples of special circumstances could include procedures to remove sulfate interferences in drinking water matrices and, as described below, technologies that can eliminate total cyanide false positives in some wastewater measurements. Under streamlining, EPA will review and issue letters of approval for Tier 1 new methods. Tier 1 modified methods can be used once they are validated and documented in accordance with EPA guidelines (see method validation guidelines in Chapter 4). EPA will not review Tier 1 method modifications.

EPA recognizes that allowing single-laboratory use of a new technology for regulatory compliance carries with it the risk that results produced with the new technology may not agree with results produced by an approved method. However, EPA believes that there can be a net benefit to the regulated community by allowing new technologies that can overcome matrix interference problems. For example, it is known that methods that measure total cyanide are susceptible to interferences from thiosulfates and other substances, and certain members of the regulated industry have pointed out to EPA that they have been faced with permit violations caused by these interferences. A new technology involving flow-injection and ligand-exchange has been demonstrated to overcome many of the matrix interferences in the determination of cyanide. Upon application by a discharger, and provided that the method could be demonstrated by the discharger to overcome the matrix interference problem, EPA would grant approval for use of the method on the particular discharge. After a sufficient number of dischargers utilized the new technology, the method employing the technology could be validated in an interlaboratory study then proposed for listing in Table IB at 40 CFR part 136.3.

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Although method modifications do not require formal approval, Tier 1 new methods must be submitted to EPA for review. Upon recommendation for approval, a letter of approval will be issued. Tier 1 modified methods can be used directly upon verification. EPA will not review Tier 1 method modifications.

5.6 Rulemaking Process

The customary **rulemaking process** consists of four phases: 1) proposal of the rule, 2) public comment, 3) response to comments, and 4) publication of the final rule. The proposed rule requests public comment and allows a specified comment period, for example 30 to 90 days depending on the magnitude of the proposed change. At the end of the comment period, EPA will forward any significant comments to the method submitter. The submitter would then provide technical assistance to EPA in drafting responses to comments. All comments that have scientific or legal merit, or raise substantive issues with the proposed rule, must be answered to complete the rulemaking process.

EPA will review the comment responses and complete a response-to-comments document that must be included in the final rule. EPA will prepare 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 date, the method is approved.

EPA plans to use a **direct final rulemaking** process to expedite the approval of noncontroversial updates to methods, such as revisions to currently approved methods published by EPA, other government agencies, and consensus standards organizations. Direct final rules are warranted when it is not in the public interest to delay approval of the action and when the action is not expected to elicit public comment to which the Agency would be required to respond.

The direct final rulemaking process was designed to accelerate the approval of noncontroversial rules. In this process, the rule is published only once, because the proposed and final rules are considered to be published simultaneously as a “direct final rule” in the Federal Register. The proposed rule has a specific comment period (typically 60 days after FR publication) and the final rule has a later effective date (typically 120 days after FR publication). If no comments that would normally require an official Agency response are received during the comment period, the final rule becomes effective.

If comments requiring a response are received during the comment period, the Agency must take one of two actions before the effective date. The Agency can publish a Federal Register notice withdrawing all or part of the action, or the Agency can publish another final rule within the 120-day period. This final rule would include the Agency's response to comments and final action on the proposed action with a new effective date for updating the CFR. If a second final rule must be prepared, the submitting party (e.g., consensus standards organization) would be required to provide EPA with technical assistance in preparing the response to comments before the final rule could be published.

Direct final rulemaking saves time and Agency resources. For example, based on the example time periods given in this section, if no adverse comments are received, a direct final rule would become effective within 120 days of publication (i.e., the CFR tables would be updated on the 120-day effective date).

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5.7 Proprietary Reagents, Instruments, and Methods

EPA separates proprietary components into three categories: proprietary reagents, proprietary instruments, and proprietary methods. EPA intends to attempt to accommodate the inclusion of **proprietary reagents** and **proprietary instruments** in the approval of analytical methods for compliance purposes to the extent that such inclusion still provides an adequate opportunity for public review and comment under the Administrative Procedure Act. EPA does not anticipate, however, that it could approve the use of **proprietary methods** for determining compliance with regulatory requirements where the entire method is claimed as "confidential business information" because the opportunity for public review and comment might be restricted too severely. If a proprietary method is patented, the method would be considered for approval as a compliance method because the public would be able to comment on the patented method. EPA believes the restriction on approval of proprietary methods is not serious because reagents or instruments, not complete methods, will continue to be the most common proprietary components used in compliance methods.

Proprietary reagents and instruments are currently included for use in approved methods and would continue to be allowed in approved methods. The details of the proprietary elements would need to be disclosed to EPA, but would be withheld from the public if the person requesting protection for the confidential business information (CBI) demonstrates that the information is entitled to confidential treatment under 40 CFR part 2. Examples of proprietary components may include immunoassay reagents and antibodies and liquid phases in GC columns; e.g., DB-1®, SPB-octyl, Dexsil®, etc. A new or modified method submitted for EPA approval would need to include language stating that the proprietary reagent or instrument could be replaced by an equivalent. Changes made to the method after EPA approval would require the manufacturer to demonstrate, through supporting documentation, that the new proprietary equipment, substance, or reagent would produce results equal or superior to results produced with the material originally tested and on which the method approval is based. Additionally, EPA would not propose a method containing a proprietary reagent without accurate, specific instructions for handling the reagent and for safe disposal of each spent proprietary reagent and/or reaction product. When a material safety data sheet (MSDS) would need to accompany the proprietary material, the MSDS would be the appropriate vehicle to provide these instructions. Submission of a complete MSDS with a new method would satisfy EPA's need for instructions for safe handling and disposal of the reagent.

EPA recommends that developers of new methods that are proprietary consider Tier 1 validation because EPA cannot propose or promulgate (i.e., list in the CFR) new methods for nationwide use (i.e., Tier 2 or 3) in which all or a portion of the procedures used to determine the identity and concentration of the analyte(s) are considered confidential. EPA cannot approve these proprietary methods for nationwide use in compliance monitoring because if the entire method is CBI, it is unlikely that the public would have an adequate opportunity to comment on these procedures. Therefore, proprietary methods will not be approved through the rulemaking process whether they are Tier 1, 2, or 3 new methods, or Tier 2 or Tier 3 method modifications.

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Chapter 6

Assessing Method Equivalency

6.1 Introduction

This chapter provides guidance on reviewing method validation study reports to assess whether a modified method has been demonstrated to produce results equivalent to results produced by the reference method. The guidance provided in this chapter is for use by regulatory authorities in assessing method equivalency when reference methods have been modified. Analytical laboratories may find the information in this chapter useful when validating a new or modified method.

According to streamlining procedures, validation study results for modified methods, regardless of tier, need not be submitted to EPA for approval. Rather, the organization responsible for developing the method modification must maintain on file complete records of all validation study documentation. Laboratories using the modification should provide a copy of the validation study report to all regulated entities whose samples are analyzed by the modified method. Regulated entities must retain validation study reports on file and make the files available for review on request by a regulatory authority or auditor.

Results of the method validations studies are documented on the *Checklist for Initial Demonstration of Method Performance*, the *Checklist for Continuing Demonstration of Method Performance*, and the *Certification Statement* (collectively called the "Checklists"). The Checklists are used by auditors and reviewers to evaluate new methods and method modifications against reference methods promulgated at Title 40 of the *Code of Federal Regulations* (CFR) parts 136 and 141. The process of assessing method equivalency involves (1) checking completeness of the method validation study report package, (2) reviewing the Checklists submitted in the validation package to ensure that the quality control (QC) acceptance criteria of the reference method have been met by the modified method, and (3) examining the raw data to clarify any questions or inconsistencies identified on the Checklists.

For Tier 1 method modifications, the completed Checklists, along with the raw data and example calculations, are adequate to document method equivalency, and a full method validation study report is not required. For all other validation tiers, the data reviewer must ensure that the validation study report is complete and includes all supporting data.

The key concepts presented and discussed in this chapter are*: the Checklists, completness assessment, validation study report checksheet,* and *method equivalency assessment.*

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6.2 Checking Completeness of the Method Validation Study Report Package

A method validation study report must be prepared for every study conducted to validate new or modified methods. Section 4.6 of this guide details the required contents of the method validation study report and the supporting data that must accompany the report. The following form can be used to check completeness of the validation package.

Table 6-1: Validation Study Report Checksheet

✓	Items Required
	Background section: Does it...
	Identify the method as a new method or a modification of a reference method?
	Include a method summary?
	If a modification, cite the organization and method number (given in 40 CFR parts 136, 141, and 405 - 503) for the reference method?
	If a modification, describe the reasons for and extent of the modification, the logic behind the technical approach to the modification, and the result of the modification?
	If a new method, describe the rationale for developing the method and explain how the method meets the criteria for a new method specified in the Streamlining Guide?
	Identify the matrices, matrix types, and/or media to which the method is believed to be applicable?
	List the analytes measured by the method or modification including corresponding CAS Registry or EMMI numbers? (Alternatively, is this information provided on the data reporting forms in the Supporting Data appendix to the validation study report? ___ Yes)
	Indicate whether any, some, or all known metabolites, decomposition products, or known commercial formulations containing the analyte are included in the measurement?
	State the purpose of the study?
	Study Design and Objectives section: Does it ...
	Describe the study design? [Validation study plan appended? ___ Yes]
	Identify overall objectives and data quality objectives of the study?
	Identify any study limitations?
	Study Implementation section: Does it ...
	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?

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Table 6-1: Validation Study Report Checksheet

✓	Items Required
	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?
	Data Reporting and Validation section: Does it ...
	Describe the procedures that were used and organizations involved in reporting and validating study data?
	Results section: Are results presented on the *Checklist for Initial Demonstration of Method Performance*, or in a tabular format attached to the Checklist?
	Are results presented on the *Checklist for Continuing Demonstration of Method Performance*, or in a tabular format attached to the Checklist?
	Is a signed *Certification Statement* attached to the Checklists?
	Development of QC Acceptance Criteria section (*for new methods only*):
	Does the section adequately describe the basis for development of QC acceptance criteria for all of the required QC tests?
	Data Analysis/Discussion section: Does it ...
	Provide a statistical analysis and discussion of the study results?
	For modified methods, address any discrepancies between the results and the QC acceptance criteria of the reference method?
	Conclusions section: Does it ...
	Describe the conclusions drawn from the study based on the data analysis discussion?
	Contain a statement(s) regarding achievement of the study objective(s)?
	Appendix A - The Method:
	Is it prepared in EPA format (i.e., in accordance with EPA's Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141)? **Appendix B - Validation Study Plan** appended? (Optional)

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Table 6-1: Validation Study Report Checksheet

✓	Items Required
	Appendix C - Supporting Data:
	Raw Data: Are raw data provided for all samples and QC analyses that will allow an independent reviewer to verify each determination and calculation performed by the laboratory by tracing the instrument output to the final result reported?
	Are the raw data organized so that an analytical chemist can clearly understand how the analyses were performed?
	Are 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 provided?
	Example Calculations: Are example calculations that will allow the data reviewer to determine how the laboratory used the raw data to arrive at the final results provided?

6.3 Assessing Equivalency Using the Checklists

The method validation results are reported on the Checklists. Copies of the Checklists and an example of completed Checklists are provided in Appendix E to this guide. The Checklists provide a side-by-side identification of the performance criteria (reference method QC acceptance criteria) and the results obtained in the validation study. A checkmark in the final column is used to indicate that the performance specifications of the reference method were achieved.

The data reviewer should review each item on the checklist to ensure that the QC acceptance criteria for each QC element were met. If there are any discrepancies, the reviewer should consult the data analysis/discussion section of the validation study report for a discussion of results and, if necessary, examine the raw data.

6.4 Data Review Guidance

This section provides guidance for reviewing data submitted to EPA and state authorities under CWA and SDWA. This guidance provides a tool for those who want to perform detailed inspection of data analyzed by methods under 40 CFR parts 136 and 141, to assess equivalency when method modifications are used or for other purposes. When performing equivalency assessments, any questions or discrepancies in the Checklists should be resolved by examining the raw data. The material presented in this section is technically detailed and is intended for data reviewers familiar with analytical methods.

6.4.1 Standardized Quality Control

In developing methods for the determination of pollutants and contaminants in water and in developing this streamlining initiative, EPA sought scientific and technical advice from many sources, including EPA's Science Advisory Board; scientists at EPA's environmental research laboratories;

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scientists in industry and academia; scientists, managers, and legal staff at EPA Headquarters and Regions; States; contractors; contract laboratories; the regulated industry; consensus standards organizations; and others. The result of discussions held among these groups was the standardized quality control (QC) approach that is an integral part of the streamlined methods approval program. Standardized QC is specified for each reference method and contains the following elements:

- Calibration linearity
- Calibration verification
- Absolute and relative retention time precision (for chromatographic analyses)
- Initial precision and recovery or “start-up” tests
- Ongoing precision and recovery
- Analysis of blanks
- Surrogate or labeled compound recovery
- Matrix spike and matrix spike duplicate precision and recovery (for non-isotope dilution analyses)
- Demonstration of method detection limits
- Analysis of reference sample

When reviewing method validation data, the permit writer, PWS, or other individual or organization has the authority and responsibility to ensure that the test data submitted contain the elements listed above; otherwise, the data can be considered noncompliant.

6.4.2 Details of Data Review

The details of the data review process depend to a great extent upon the specific analytical method. Even for data from the same method, there may be many approaches to data review. However, given the standardized QC requirements of the streamlined methods approval program, a number of basic concepts apply. The following sections provide the details for reviewing analytical data and discuss EPA's rationale for the QC tests. Results from the QC tests for all standardized QC elements must be within the QC acceptance criteria specified in, or associated with, the reference method to validate that results produced by a method modification are equivalent or superior to results produced by the reference method.

6.3.2.1 Calibration linearity

The relationship between the response of an analytical instrument to the concentration or amount of an analyte introduced into the instrument typically is represented by an averaged response or calibration factor, a calibration line, or a calibration curve. An analytical instrument can be said to be calibrated in any instance in which an instrumental response can be related to a single concentration of an analyte. The response factor or calibration factor is the ratio of the response of the instrument to the concentration (or amount) of analyte introduced into the instrument.

Nearly all analytical methods focus on the range over which the response is a linear function of the concentration of the analyte. This range usually extends from the minimum level of quantitation (ML) on the low end to the point at which the calibration becomes non-linear on the high end. For regulatory compliance, it is important that the concentration of regulatory interest (e.g., permit limit; MCL) fall within this range. Calibration can also be modeled by quadratic or higher

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order mathematical functions. The advantage of a calibration line that passes through the origin is that an averaged response factor or calibration factor can be used to represent the slope of this line. Use of a single factor simplifies calculations and the interpretation of the data. Also, it is easier to discern when an inaccurate calibration standard has been prepared if the calibration function is a straight line.

Many analytical methods, particularly recent methods, specify some criterion for determining the linearity of the calibration. When this criterion is met, the calibration function is sufficiently close to a straight line that passes through the origin to permit the laboratory to use an averaged response factor or calibration factor. Linearity is determined by calculating the relative standard deviation (RSD) of the response factor or calibration factor for each analyte and comparing this RSD to the limit specified in the method. If the RSD does not exceed the specification, linearity through the origin is assumed. If the specification is not met, a calibration curve must be used.

For whatever calibration range is used, a reference method should contain a specification for the RSD of the response or calibration factor to establish the breakpoint between linear calibration through the origin and a line not through the origin or a calibration curve. For new methods, the method developer must provide the RSD results by which one can judge linearity, even in instances where the laboratory is using a calibration curve. In instances where the laboratory employs a curve rather than an average response or calibration factor, the data reviewer should review each calibration point to ensure that the response increases as the concentration increases. If it does not, the instrument is not operating properly, or the calibration curve is out of the range of that instrument, and data are not considered valid.

6.3.2.2 Calibration verification

Calibration verification involves the analysis of a single standard at the beginning of each analytical shift or after the analysis of a fixed number of samples (e.g., 10). The concentration of each analyte in this standard is normally at the same level as in one of the calibration standards, typically at 1 - 5 times the ML. The concentration of each analyte in this standard is calculated using the calibration data. The calculated concentration is compared to the concentration of the standard. Calibration is verified when the concentration is within the calibration verification limits specified in the method. If the results are within the specifications, the laboratory is allowed to proceed with analysis without recalibrating and allowed to use the calibration data to quantify sample the concentration or amount of each analyte in samples, blanks, and QC tests.

If calibration cannot be verified, the laboratory may either recalibrate the instrument or prepare a fresh calibration standard and make a second attempt to verify calibration. If calibration cannot be verified with a fresh calibration standard, the instrument must be recalibrated. If calibration is not verified, subsequent data are considered to be invalid until the instrument is recalibrated.

6.3.2.3 Absolute and relative retention time precision

Retention time specification aid in the identification of analytes in chromatographic analyses. In some methods, a minimum retention time is specified to ensure adequate separation of analytes in complex mixtures. If retention time QC criteria cannot be verified, chromatographic identification of analytes is suspect and reanalysis is necessary.

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6.3.2.4 Initial precision and recovery

This test is required prior to the use of the method by a laboratory. It is sometimes termed the "start-up test." Performing the start-up test "after the fact" or after samples have been analyzed is not acceptable. The laboratory must demonstrate that it can meet the IPR QC acceptance criteria in the method. EPA's experience has been that difficulty in passing the start-up test leads to marginal performance by the laboratory in the routine operation of the method.

The start-up test consists of spiking the analytes of interest into a set of four or more aliquots of a reference matrix and analyzing these four aliquots. The reference matrix simulates the medium being tested. A separate IPR test must be performed for each medium. The mean concentration and the standard deviation of the concentration are calculated for each analyte and compared to QC acceptance criteria in the method. If the mean and standard deviation are within the limits specified, the analysis system is in control and the laboratory can use the system for analysis of blanks, field samples, and other QC tests samples. For some methods (e.g., Methods 625 and 1625), a repeat test is allowed because of the large number of analytes being tested simultaneously.

If there are no start-up test data, or if these data fail to meet the QC acceptance criteria in the method, all data produced by that laboratory using that method are not considered valid. It is important to remember that if a change is made to a method, the start-up test must be repeated with the change as an integral part of the method. Such changes may involve alternative extraction, concentration, or cleanup processes; alternative GC columns, GC conditions, or detectors; or other procedures designed to address a particular matrix problem. If the start-up test is not repeated when a procedure is changed, added, or deletec, data produced by the modified method are considered invalid.

6.3.2.5 Ongoing precision and recovery

An ongoing precision and recovery (OPR) standard (also termed a "laboratory control sample" (LCS) or a "laboratory fortified blank" (LFB)) must be analyzed with each sample batch prior to the analysis of a blank, sample, or matrix spike or duplicate. The number of samples in the batch is usually 10 or 20, depending on the method, or the OPR is required at the beginning of an analysis shift, regardless of the number of samples analyzed during that shift. The data reviewer must determine if the OPR standard has been run with each sample batch or at the beginning of the shift and if all criteria have been met. If the standard was not run with a given set of samples, or if the criteria are not met, the results for that set of samples are considered invalid.

6.3.2.6 Analysis of blanks

Blanks must be analyzed either on a periodic basis on with each sample batch, depending on the method. Blanks may contain contamination at levels no higher than specified in the method. Samples associated with a contaminated blank must be reanalyzed.

6.3.2.7 Surrogate or labeled compound recovery

Surrogate or labeled compounds are used to assess the performance of the method on each sample. Recoveries of these compounds from each sample must be within QC acceptance criteria to demonstrate acceptable method performance on the sample. If the recovery is not within the criteria,

the sample is normally diluted and the dilute sample analyzed to demonstrate that a matrix effect precluded reliable analysis of the undiluted sample.

6.3.2.8 Matrix spike and matrix spike duplicate

Non-isotope dilution methods require a spike of the analytes of interest into a separate aliquot of the sample for analysis with the sample. The purpose of the matrix spike (sometimes termed a "laboratory fortified sample matrix" (LFM)) is to determine if the method is applicable to the sample in question. While many of the approved methods were tested using effluents from a wide variety of industries, samples from some sources may not yield acceptable results. It is therefore important to evaluate method performance in the sample matrix of interest. If the recovery for the MS/MSD is not within the QC acceptance criteria, a matrix interference may be the cause. The sample is usually diluted and the diluted sample spiked and analyzed. If the QC acceptance criteria are met with the diluted MS/MSD, a matrix problem exists. Cleanup and other processing of the sample are then required to overcome the matrix interference if analysis of the undiluted sample is required to establish compliance.

6.3.2.9 Demonstration of method detection limits

A laboratory that wishes to use a new or modified wastewater method must demonstrate that the method detection limit (MDL) specified in the reference method can be achieved. Alternatively, if the regulatory wastewater compliance limit is above the MDL, laboratories must demonstrate that the minimum level (ML) determined with the new or modified wastewater method is at or below 1/3 the compliance limit. A laboratory that wishes to use a new or modified drinking water method must demonstrate that the MDL determined with that method meets the detection limits specified at 40 CFR 141.23, 141.24, and 141.89 and/or as published in the table of QC limits in *Methods and Criteria*. For both drinking and waste water determinations, demonstration of a valid detection limit requires use of an MDL study in accordance with the procedure at 40 CFR part 136, Appendix B. If the MDL determined with the new or modified method is not acceptable, the method may not be used because the laboratory has not demonstrated an ability to detect the analyte at the level required. EPA notes that the required detection limits specified in the regulations and/or in the reference method(s) are usually analyte-specific; and for the same analyte the requirement may differ between the wastewater and the drinking water reference method.

6.3.2.10 Reference Sample Analysis

EPA is considering setting acceptance criteria for a reference material based on the measurement error of the method. Ideally, a laboratory should be able to demonstrate the ability to quantitate the analyte in a reference material to within the acceptance range specified for the reference material.

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Chapter 7

Biological Methods

7.1 Introduction

Although the initial streamlining proposal pertains only to chemical analytical methods, EPA intends to expand method flexibility to include biological methods in the future. Biological methods include both the testing of an environmental sample for the presence of microbiological material (e.g., bacteria, protozoa, and viruses) and the use of biological organisms in tests for whole effluent toxicity (WET) of an environmental sample. EPA believes that flexibility in testing for biological material will be similar to the flexibility allowed in the modification to chemical analytical methods. Test procedures should be able to be modified when the modifications produce equivalent or superior results. EPA has protocols for some microbiological methods that are currently used in the alternate test procedure (ATP) program (EPA 1996b, 1996c). EPA is developing a protocol for approval of new and modified (alternate) WET methods that is based on the tiered validation structure provided by streamlining.

Biological methods are considered to be method-defined analytes. As discussed in Chapter 2, incorporating flexibility into method-defined analytes will likely require more rigorous control than modifications for specific chemical substances. EPA believes, however, that certain parts of the procedures can be modified without adversely affecting method performance. At present, this problem has not been sufficiently addressed to allow proposal of specific flexibility requirements in approved biological methods. Until EPA can clarify the extent of acceptable flexibility, requests for changes in biological methods will be reviewed and approved on an individual basis.

OW is working with EPA's Biological Advisory Committee (BAC) to identify appropriate applications of flexibility in WET test methods. As mentioned above, EPA also is developing a protocol for approval of new and modified (alternate) WET methods that includes procedures for external organizations to develop, validate, and submit WET methods or method modifications for EPA approval. This protocol will be distributed for comment after it is completed and has undergone internal EPA review.

EPA anticipates that requests for approval of new or modified (alternate) WET methods will focus on one of the following areas: organism; test duration; test procedures; reactor type (e.g., batch, flow through, or fill and draw); equipment, volume-to-organism ratio, or system monitoring. Factors that will be considered in reviewing submitted methods include: single- and multi-laboratory precision; the life- stage, sources, and quality of test organisms; the nature and control of test conditions; test data collection and reporting requirements; test acceptability criteria; endpoints; methods of data analysis; and test sensitivity.

7.2 New WET Methods

The following has been suggested as a definition for a new WET test method:

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A WET test procedure will be considered a "new" procedure if it employs a "new" species or requires culture conditions, test conditions, endpoints, and/or methods of data analysis that are substantially different from those used for current Agency-approved species/methods.

7.3 Modified WET Methods

The following has been suggested as a definition for a modified (alternate) WET method:

A proposed test procedure will be considered a "modified" procedure if it involves only minor changes in established test conditions for an approved species/method, or if it employs a "new" species to be used as a substitute for a related, Agency-approved species, and if:

(1) The proposed test with the "new" species can be performed with essentially the same test conditions and methods of data analysis used for current Agency-approved species/methods (i.e., with only minor modifications in one or a few conditions), and
(2) The sensitivity of the proposed test species/method using an approved or "new" species is demonstrated to be equal to or greater than the sensitivity of current Agency-approved species/methods, using reference toxicants or effluents, or
(3) The proposed test results in a significant reduction in the cost or ease of performance of the test, without an unacceptable loss in sensitivity.

7.4 Validation Requirements

In keeping with method flexibility guidance, laboratories would be required to demonstrate that a modified (alternate) method produces results equivalent or superior to those produced by the EPA-approved reference method and would be required to demonstrate that new methods produce data that are acceptable for use in NPDES compliance monitoring. It has been suggested that this demonstration would consist of paired side-by-side tests with effluents and a range of reference toxicants (metal, organic, and salt).

It has been suggested that the following would suffice to document validation of a new or modified (alternate) WET method:

- **Summary of Method:** For modified methods, including a discussion of how the modified method differs from the 40 *CFR* part 136 method and the rationale for requesting the modification

- **Toxicity Test Procedure:** The method or modified portion of the method prepared in EPA standard format.

- **Data:** Data from paired side-by-side tests using both effluents and a range of reference toxicants (metal, organic, and salt).

- **References:** Including all sources of technical information used in developing the new method or method modification.

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Appendix A

Acronyms and Symbols

Acronyms

A	ACS	American Chemical Society
	AOAC	AOAC-International; formerly the Association of Official Analytical Chemists
	AOX	adsorbable organic halides
	APHA	American Public Health Association
	ASTM	formerly the American Society for Testing and Materials
	ATP	alternate test procedure
	AWWA	American Water Works Association
B	BAC	Biological Advisory Committee
	BOD	biochemical oxygen demand
C	CAS	Chemical Abstract Services
	CF	calibration factor
	CFR	*Code of Federal Regulations*
	CVAA	Cold Vapor Atomic Absorption
	CWA	Clean Water Act
D	DEEMS	*Department of Energy Environmental Management Electronic Data Deliverable Master Specification*
E	EAD	Engineering and Analysis Division
	ECD	electron capture detector
	ELCD	electrolytic conductivity detector
	EMMC	Environmental Monitoring Management Council
	EPA	Environmental Protection Agency
F	FID	flame ionization detector
	FLAA	flame atomic absorption
	FOIA	Freedom of Information Act
	FR	*Federal Register*
G	GC	gas chromatography
	GC/HRMS	gas chromatography/high resolution mass spectrometry
	GC/LRMS	gas chromatography/low resolution mass spectrometry
	GC/MS	gas chromatography/mass spectrometry
	GFAA	graphite furnace atomic absorption
H	HPLC	high performance liquid chromatography
	HRGC	high resolution gas chromatography
	HRMS	high resolution mass spectrometry
I	ICP/AES	inductively coupled plasma/atomic emission spectroscopy
	ICP/MS	inductively coupled plasma/mass spectrometry

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	IPR	initial precision and recovery
	IR	infra-red spectroscopy
J	JAOAC	*Journal of AOAC - International*
K		
L	LOQ	limit of quantitation
M	MCAWW	*Methods for Chemical Analysis of Water and Waste*
	MCL	maximum contaminant level
	MDL	method detection limit
	ML	minimum level
	MS	matrix spike
	MSD	matrix spike duplicate
	MSDS	material safety data sheet
N	NCASI	National Council of the Paper Industry for Air and Stream Improvement, Inc.
	NELAC	National Environmental Laboratory Accreditation Committee
	NERL-Ci	National Exposure Research Laboratory - Cincinnati
	NIST	National Institute of Standards and Technology
	NPD	nitrogen phosphorous detector
	NPDES	National Pollutant Discharge Elimination System
	NPDWR	National Primary Drinking Water Regulations
	NTTAA	National Technology Transfer and Advancement Act of 1995
O	OECA	Office of Enforcement and Compliance Assurance
	OFR	Office of Federal Register
	OGC	Office of General Counsel
	OGWDW	Office of Ground Water and Drinking Water
	OPR	ongoing precision and recovery
	ORD	Office of Research and Development
	OST	Office of Science and Technology
	OSW	Office of Solid Waste
	OW	Office of Water
P	PAH	polynuclear aromatic hydrocarbon
	PID	photoionization detector
	POTW	publicly owned treatment works
	PWS	public water system
Q	QA	quality assurance
	QC	quality control
R	RF	response factor
	RPD	relative percent difference
	RR	relative response

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	RRT	relative retention time
	RSD	relative standard deviation
	RT	retention time
S	SDWA	Safe Drinking Water Act
	SEM	standard error of the mean
	SRM	Standard Reference Material
T	TDS	total dissolved solids
	TOC	total organic carbon
	TSS	total suspended solids
U V	USGS	U.S. Geological Survey
W X Y Z	WEF	Water Environment Federation
	WET	whole effluent toxicity

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Appendix B

Glossary

Glossary

	40 *CFR* part 136	Title 40, part 136 of the *Code of Federal Regulations*. This part specifies EPA's test procedures for the analysis of pollutants regulated under the Clean Water Act.
	40 *CFR* part 141	Title 40, part 141 of the *Code of Federal Regulations*. This part specifies EPA's National Primary Drinking Water Regulations pursuant to the Safe Drinking Water Act; Subpart C of 40 *CFR* part 141 lists analytical methods required for monitoring under the Act.
	95% confidence interval	A statistical level indicating a 95 % probability that the parameter variable is enclosed within the given data interval.
A	accuracy	The degree of agreement between an observed value and an accepted reference value. Accuracy includes random error (precision) and systematic error (bias) that are caused by sampling and analysis.
	aliquot	A representative portion of a sample. (QAMS)
	analysis of variance	A study of the effect of a set of qualitative variables on a quantitative response variable, based on a decomposition of the variance of the response variable.
	analyte	The substance, a property of which is to be measured by an analysis. (QAMS)
	analyte of concern	An analyte designated by EPA to adversely affect or have the potential to adversely affect human health, the environment, aesthetics, or the senses. Analytes of concern are listed in approved methods.
	analysis	The determination of the nature or proportion of one or more constituents of a sample.
	approved method	A testing procedure (analytical method) promulgated at 40 *CFR* parts 136, 141, 405-500, and other parts of the CFR that support EPA's water programs.
	average percent recovery	The average of the recovery, expressed as percent. See "recovery."
B	bias	A systematic or persistent distortion of a measurement process that deprives the result of representativeness; i.e.,

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		the expected sample measurement is different than the sample's true value. A data quality indicator. (QAMS)
	blank	See "method blank."
C	calibration	The process of establishing the relationship between the concentration or amount of material introduced into an instrument or measurement process and the output signal.
	calibration factor	The quotient of instrument response and concentration of a standard obtained during instrument calibration. Unknown sample concentrations are determined by multiplying the determined calibration factor by the measured instrument response.
	calibration linearity	The degree to which calibration points lie along a straight line.
	calibration verification	Means of establishing that the instrument performance remains within pre-established limits.
	Code of Federal Regulations	A codification of the general and permanent rules published in the *Federal Register* by the Executive departments and agencies of the Federal Government.
	compliance	A state of meeting all requirements.
	confidence interval	The numerical interval constructed around a point estimated of a population parameter, combined with a probability statement (the confidence coefficient) linking it to the population's true parameter value. If the same confidence interval construction technique and assumptions are used to calculate future intervals, they will include the unknown population parameter with the same specified probability. (EMMC)
	contract laboratory	Private, academic, or commercial laboratory under contract to EPA or other organization to perform testing.
	correlation coefficient	A number between -1 and 1 that indicates the degree of linearity between two variables or sets of numbers. The closer to -1 or +1, the stronger the linear relationship between the two (i.e., the better the correlation.) Values close to zero suggest no correlation between the variables. The most common correlation coefficient is the product-

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		moment, a measure of the degree of linear relationship between two variables. (EMMC)
D	data quality objective	Qualitative and/or quantitative statement of the overall level of uncertainty that a decision-maker is willing to accept in results or decisions derived from environmental data. Data quality objectives provide the statistical framework for planning and managing environmental data operations consistent with the data user's needs. (EMMC)
	determinative technique	The physical and/or chemical process by which measurement of the identity and concentration of an analyte is made. For most methods, the determinative technique consists of an instrumental measurement.
	digestion	Solubilization of the analytes in sample by destruction of the sample matrix. Most commonly performed in the determination of metals.
	direct final promulgation	The promulgation of a final rule in the CFR without first being proposed. This procedure is used when the rules are not expected to generate significant negative comments.
	discharge	Generally, any spilling, leaking, pumping, pouring, emitting, emptying or dumping (40 *CFR* 109.2; 110.1; 116.3); also, see "discharge of a pollutant" (40 *CFR* 122.2); the medium that is spilled, leaked, pumped, poured, emitted, emptied, or dumped.
	discharge of pollutant	Any addition of any pollutant or combination of pollutants to (1) waters of the U.S. from any point source or (2) to the waters of the contiguous zone or the ocean from any point source other than a vessel or other floating craft which is being used as a means of transportation (40 *CFR* 122.2; 401.11)
	distillation	The process of heating a mixture to separate the more volatile from the less volatile parts, then cooling and condensing the resulting vapor so as to produce a more nearly pure or refined substance: nonvolatile impurities remain in the residue. (Webster's)
E	effluent	A medium that flows out of a point source, e.g., the discharge from a sewage treatment plant.
	explicit flexibility	Modifications that are explicitly allowed in an approved method.

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	extraction	The process of selectively transferring a substance from one phase to another or from one liquid to another with differing characteristics, then separating the phases or liquids to isolate the substance; e.g., transferring organic analytes from an aqueous liquid to an organic liquid.
	extreme rank sum test	A test to determine if laboratory performance significantly deviates from that of another lab.
F	facility	A plant or group of plants within a single location that is regulated under a single National Pollutant Discharge Elimination System (NPDES) permit and/or SDWA. A single facility may have multiple water supplies, discharges, waste streams, or other environmental media that are subject to compliance monitoring. For example, a single facility within the Pulp, Paper, and Paperboard industrial category may have a direct discharge, an indirect discharge, and an in-process waste stream that are all subject to compliance monitoring.
	Federal Register	A daily publication that provides a uniform system for publishing Presidential and Federal agency documents. Documents published in the *Federal Register* make changes to the CFR to keep the CFR current. (OFR)
	front-end technique	Any technique in the analytical process that precedes the determinative technique, including all procedures, equipment, solvents, etc. that are used in the preparation and cleanup of a sample for analysis. Front-end techniques does not include conditions and/or procedures for the collection, preservation, shipment, and storage of the sample.
G H	Guidelines and Format	The document titled *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 and 141*; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210448.
I	incorporation by reference	A means for allowing the Federal agencies to comply with the requirement to publish regulations in the *Federal Register* by referring to materials already published elsewhere. The material incorporated by reference has the force and effect of law. (OFR)

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industrial category	A category listed in 40 *CFR* parts 405-503.
industrial subcategory	A subcategory defined at 40 *CFR* parts 405-503.
initial precision and recovery	The analysis of a minimum of four spiked replicate reference matrix samples under the same conditions as will be used for analysis of environmental samples. The IPR is used to demonstrate that a laboratory is able to produce reliable results with the method prior to analysis of environmental samples.
interference	A positive or negative effect on a measurement caused by a substance other than the one being investigated. (QAD)
interlaboratory	Occurring in multiple laboratories.
interlaboratory method	A study conducted according to the principles outlined in Guidelines for Collaborative Study Procedures to Validate Characteristics of a Method of Analysis; JAOAC 78 No. 5, 1995; *Statistical Manual of the Association of Official Analytical Chemists*, W.J. Youden and E.H. Steiner, 1975 (published by AOAC-International, 481 N. Frederick St., Gaithersburg, MD 20877-2417; 301-924-7077); *Use of Statistics to Develop and Evaluate Analytical Methods* (published by AOAC-International); ASTM Standard D-2777 (published by ASTM, 100 Barr Harbour Drive, West Conshocken, PA 19428-2959; 610-832-9500); or other well-established and documented principles for interlaboratory method validation studies.
intralaboratory	Occurring within a single laboratory.

J
K
L

labeled compound	An isotopically labeled form of the native compound.
labeled compound recovery	The percentage of the labeled compound recovered. See "recovery."
laboratory	A person that owns or leases a stationary or mobile facility in which a sample is tested for an analyte.
log-normal	A distribution of a random variable X such that the natural logarithm of X is normally distributed.

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M

matrix	The component or substrate that contains the analytes of interest. (NELAC QS)
matrix effect	Variability in the analytical performance of a method that can be attributed to the type of sample analyzed.
matrix spike	A sample prepared by adding a known mass of target analyte to a specified amount of a sample matrix for which an independent estimate of target analyte concentration is available. A matrix spike is used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)
matrix spike duplicate	A replicate of the matrix spike to test precision. The MS/MSD are used in combination to test the precision of an analysis. (QAMS)
matrix type	A sample medium with common characteristics across a given industrial category or subcategory. For example, C-stage effluents from chlorine bleach mills, effluent from the continuous casting subcategory of the iron and steel industrial category, POTW sludge, and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory are each a matrix type. For the purposes of this initiative all drinking waters constitute a single matrix type.
measurement quality objective	Critical level which, if exceeded, is considered to append additional, and possibly unacceptable, measurement uncertainty to the corresponding data.
medium	The physical phase of a sample matrix. Air, water, soil are sample media.
method	A body of procedures and techniques for performing a task (e.g. sampling, characterization, quantitation) systematically presented in the order in which they are to be executed. (QAMS)
method blank	A clean sample (absent of the analytes of interest and interferences) processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedure. (QAMS)

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method-defined analyte	An analyte without a specific, known composition where the analytical result depends totally on the measurement procedure.
method detection limit	The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. For an MDL study, it is essential that all sample processing steps of the analytical method be included.

[The MDL results from estimating a method's sensitivity at the two lowest levels, zero concentration, and the lowest concentration that the method is capable of distinguishing from zero with a 99% probability.]

method modification	A change made to an approved method. The change may be to a front-end technique or to the determinative technique.
method validation	A process by which a laboratory or vendor establishes the performance of a new method or substantiates the performance of a method modification.
Methods and Criteria	The document titled: *Analysis of Pollutants in Municipal Water and Industrial Wastewater: Test Procedures and Quality Control Acceptance Criteria*; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210463, and incorporated by reference into this part.
mid-point response factor	The response factor at the concentration at which calibration is verified.
minimum level	The lowest concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point for an analyte. It is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been employed. (40 *CFR* 132.2)
modified method	An approved method that has been modified to change a front-end technique or the determinative technique, either using method-specified flexibility or expanded flexibility allowed under streamlining

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N

navigable waters — All waters of the United States, including the territorial seas. (40 *CFR* 110.1)

new method — A method that employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141. In addition, it must (1) employ a determinative technique that is more sensitive and/or selective (specific) than the determinative techniques in all methods previously approved for the analyte, (2) contain the standardized QC elements detailed in Chapter 3 of the Streamlining Guide, (3) specify, for all standardized QC elements, QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3 of the Streamlining Guide, and (4) be documented in accordance with the requirements detailed in the *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141* or other standard format.

O

other approved methods — Promulgated methods that are not designated as a reference method, but continue to carry the same regulatory status.

P

percent recovery — 100 times the recovery.

phthalate — An ester of phthalic acid containing the radical $C_6H_4(COO)_2$=; used for buffers, for standard solutions, and in vacuum pumps. Certain phthalate esters are Priority Pollutants.

precision — The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms. (QAMS)

[The precision obtainable from an environmental measurement method may be estimated from replicate analyses of subsamples taken from the same (homogenous) sample. Generally speaking, the more carefully one executes the various steps of a method and controls the variables affecting the method's capability, the more precise will be the results. The use of a nonhomogeneous sample will compound the precision estimate with the sample variability.]

preparation — Processing performed on a sample prior to analysis, e.g. extraction, concentration, cleanup, etc.

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	procedures	A set of systematic instructions for performing an activity. (QAD)
	promulgated method	A method that has been published or incorporated by reference into 40 *CFR* parts 136, 141, 405-500, or other parts that support EPA's water programs.
	promulgation	Publication of a final rule in the FR.
	public water system (PWS)	A system for the provision to the public of piped water for human consumption, if such system has at least fifteen service connections or regularly serves an average of at least twenty-five individuals daily at least 60 days out of the year. Such term includes (1) any collection, treatment, storage, and distribution facilities under control of the operator of such system and used primarily in connection with such system, and (2) any collection or pretreatment storage facilities not under such control which are used primarily in connection with such system. A public water system is either a “community water system” or a “noncommunity water system.”
Q	quality assurance	An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)
	quality control	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical. (QAMS)
	QC acceptance criteria	Performance specifications developed from validation data and used to control the limits within which an analytical method is operated.
R	recovery	The total amount of the analyte found in the sample divided by the amount of the analyte added into the sample as a spike.
	reference method	A method that has been approved at 40 *CFR* part 136 or 141, contains (or is supplemented with) standardized quality control (QC) and QC acceptance criteria that define the required level of performance, and has been designated as a reference method in the tables appearing at 40 *CFR* part

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136 or 141. The reference method serves as a standard against which method modifications can be statistically compared.

regulated entity	Permittees, PWSs, POTWs, and other entities responsible for compliance with provisions of the CWA or SDWA.
relative response	The ratio of the response of an analyte relative to the response of a labeled compound.
relative retention time	The chromatographic elution time relative to an isotopically labeled compound or internal standard.
relative standard deviation	The standard deviation expressed as a percentage of the mean (100σ/X); i.e., the coefficient of variation.
response factor	The inverse of the calibration factor. The slope of the line.
responsible person/party	See “regulated entity.”
retention time	Elution time specific to a given sample.

S

sample matrix	See "matrix."
sample matrix effect validation	A test of the extent to which differences, if any, in method performance could be attributed to variability between samples obtained from different industrial matrices, facilities, or PWSs.
sample medium	See "medium."
screening method	A method that employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141. In addition, it must (1) be demonstrated to produce a false negative probability of no more than one percent, (2) contain the standardized QC elements detailed in Chapter 3 of the Streamlining Guide, (3) specify, for all standardized QC elements, QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3 of the Streamlining Guide, and (4) be documented in accordance with the requirements detailed in the *Guidelines and Format*

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for Methods to be Proposed at 40 CFR Parts 136 or 141 or other standard format.

selectivity — The capability of a method or instrument to respond to an analyte in the presence of interferences.

sensitivity — The capability of a method or instrument to differentiate between different amounts or concentrations of an analyte.

spike — The process of adding a known amount of target analyte to a sample; used to determine the recovery efficiency of the method. (QAMS)

spike amount — A known mass of analyte added to a sample and used to determine the recovery of a method.

stakeholder — A party with a vested interest in a particular program. For EPA's water methods program, such parties include dischargers, permittees, analytical laboratories, vendors, method-developing organizations, and local, regional, state, and federal permitting and regulatory agencies.

standard deviation — The measure of the dispersion of observed values expressed as the positive square root of the sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one less than the number of values in the set.

standard error of the mean — The standard deviation of the sampling distribution of the mean; a measure of sampling error.

standardized quality control — Uniform performance testing procedures that ensure reliable results. The procedures can include calibration linearity, calibration verification, absolute and relative retention time precision, initial precision and recovery, ongoing precision and recovery, analysis of blanks, surrogate or labeled compound recovery, matrix spike and matrix spike duplicate recovery and precision, demonstration of method detection limits, and analysis of a reference sample.

straw man — A draft document proposed for the purpose of generating public interest, comments, and suggestions to possible changes without committing EPA to a course of action.

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streamlining	A process to improve the performance of a program while retaining the mechanisms to retain data quality (e.g., reducing costs, resources, or wastes).
Streamlining Guide	The document titled: Guide to Method Flexibility and Approval of EPA Water Methods; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210455 and incorporated by reference into this part.
Student's *t* distribution	A type of sampling distribution for a random variable. A normal distribution divided by the square root of a chi-square distribution divided by its degrees of freedom.
surrogate	A substance with properties that mimic the analyte of interest that is unlikely to be found in an environmental sample and that is added to the sample for quality control purposes. (QAMS)
surrogate recovery	The recovery for a surrogate. See "recovery."

T

Tier 1	The application of a new or modified method in a single laboratory to one or more matrices. Method validation requirements are limited to single laboratory testing on the matrix type or matrix types of interest.
Tier 2	The application of a new or modified method to samples from a single matrix type in a single industrial category or subcategory. Method validation requires an interlaboratory study on samples collected from a minimum of 3 separate facilities each in a minimum 3 laboratories to confirm method performance or to establish QC acceptance criteria for the method.
Tier 3	The application of a new or modified method to all matrix types. Method validation requires an interlaboratory method validation study or a study of 9 matrix types in 9 laboratories to confirm method performance or to establish QC acceptance criteria for the method.

U V

variance	A measure of the dispersion of a set of values. The sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one

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	less than the number of values in the set. (The square of the sample standard deviation.) (QAMS)
validate	Method validation

The above definitions are referenced to the following organizations:

EMMC	Environmental Monitoring Management Council
NELAC QS	National Environmental Laboratory Accreditation Conference, Quality Systems
OFR	Office of Federal Register
QAD	Quality Assurance Division, National Center for Environmental Research and Quality Assurance, Office of Research and Development, USEPA
QAMS	Quality Assurance Management Staff

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Appendix C

Current Method Flexibility

This chapter provides a summary report of stakeholder inquiries and EPA responses concerning the method flexibility allowed in the current 40 CFR 136 Appendix A analytical methods. These correspondences, generated in 1994 and 1995, were one impetus for undertaking the initiative to streamline the method approval process and method flexibility in the programs regulated by the Office of Water.

The narrow range of the raised issues reflects the limited flexibility that is currently allowed. The responses indicate the incremental approach that has been historically followed to improve test procedures. This appendix is provided to facilitate a comparison between the proposed and existing method flexibility.

ISSUE # 1 - CRITERIA FOR DETERMINING ACCEPTABLE METHOD MODIFICATIONS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
1.5	603	1.4
	608,625	1.5
8.1.2	603,608,625	8.1.2
EPA 821-B-93-001	603,608,625	EPA 821-B-93-001

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

EPA 821-B-93-001 "Guidance On Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", page 10, Flexibility in Analytical Methods: "The analyst is permitted to 'improve separations or lower the costs of analyses' provided that the results obtained are not less precise and accurate than the results obtained using the unmodified method".

Does this impact those areas in the method where the Agency has used words like "suggested", "should", or "recommended"?

Response: Yes.

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Can changes be made to lower the cost of analyses, even if they are not specifically permitted in the method, so long as the accuracy and precision guidelines in the method can be met?

Response - No. Some method changes, such as substituting a flame ionization detector for a mass spectrometer in Method 624, constitute a new method and need to be brought to the permitting authority for a ruling. On the other hand, some areas of method flexibility, such as those discussed in this communication, have been reviewed by the Agency and judged to be reasonable in view of advances in measurement technology.

ISSUE # 2 - CALIBRATION VERIFICATION

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.4	603	7.5
	608	7.4
	625	7.3

7.4 The working calibration curve or RF must be verified on each working day by the measurement of a QC Check Sample.

Our interpretation of "working day" is every 24 hours. Is that acceptable?

Response: No. A working day for most people is 8 hours. Some methods specify 12 hours. Either is acceptable so long as calibration is verified. If calibration is not verified, samples analyzed during the previous "working day" must be inspected for a possible adverse effects. If instrument performance is degraded during the previous "working day," calibration must be verified or the instrument must be recalibrated, and the samples reanalyzed.

ISSUE # 3 - REQUIRED FREQUENCY OF MATRIX SPIKES

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.1.4	603,608,625	8.1.4
EPA 821-B-93-001	603,608,625	EPA 821-B-93-001

8.1.4 The laboratory must, on an on going basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

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8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

This requirement, when applied to a laboratory dedicated to a single discharge or a single set of discharges, is straightforward. Its application to commercial laboratories that analyze a wide range of discharge samples from many different facilities each month can be confusing. It could be interpreted to mean that a commercial lab that analyzes less than 20 samples per month (10 for Methods 603 and 608) from any one sampling site must spike a sample from that site at least once a month (regardless of how many spikes have been performed for other sampling sites). This could effectively mean that every sample analyzed for every discharge client will need to be spiked. This would greatly increase the cost of analysis to the regulated community. Alternatively, it could be interpreted to require that a commercial lab spike 5% (10% for Methods 603 and 608) of its total sample volume unless it analyzes less than 20 discharge samples per month (10 for Methods 603 and 608), in which case it must spike at least one sample per month.

Which interpretation is correct?

Response: Neither. The hierarchy of requirements are:

(1) The laboratory must analyze one spiked wastewater sample per month per method used in that period.

(2) The laboratory must analyze at least one spiked sample from each sample site.

(3) If the laboratory analyzes more than 20 samples from a site, at least 5% of the samples must be spiked.

Two examples to illustrate: if, using Method 604, laboratory A contracts to analyze one sample per week from a site over one year, and analyzes a total of 20 samples per month by Method 604 from this and other sites, three spiked samples from the site must be analyzed during the year. The laboratory may choose which sample to spike among the first twenty, the second twenty, and the last 12-20. If, using Method 604, laboratory B contracts to analyze one sample per quarter for a year, and analyzes a total of 20 samples by Method 604 from this and other sites in the same month that the sample is analyzed, the laboratory must spike one of the four samples. If the laboratories in these two examples analyzed no other samples with Method 604 during the year, laboratory A would spike 12 samples out of 52 and laboratory B would spike 4 of 4.

ISSUE # 4 - ONGOING METHOD ACCURACY DOCUMENTATION REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

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METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.6	603,608,625	8.5

8.6 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of 5 spiked wastewater samples as in section 8.3, calculate the average percent recovery and the standard deviation of the percent recovery... Update the accuracy assessment for each parameter (on) a regular basis (e.g. after each 5 to 10 new accuracy measurements).

Normally we focus our efforts on meeting the ongoing method QC criteria and the initial demonstration of accuracy and precision. We maintain the data necessary to calculate the accuracy assessment if it were ever requested. Is this acceptable?

Response: Yes.

ISSUE # 5 - INTERNAL STANDARD COMPOUNDS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.3	625	7.2

7.3 Internal standard calibration procedure--To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 3.

Are internal standards not in Table 3 (Table 8 for Method 625) acceptable? For instance, would the 524.2 or 8240 internal standards be acceptable for use in Method 624? Minimizing the number of internal standard solutions that the lab must maintain leads to substantial cost savings that are subsequently passed on to the regulated community.

Response: Alternate internal standards are acceptable provided that method performance is not degraded and the reason is justified and documented.

ISSUE # 6 - QUALITATIVE IDENTIFICATION REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

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METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
12.1.3	625	14.1.3

12.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within +/- 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

When setting up the GC/MS method, if the laboratory sets the limits in the software to 20%, there is a significant risk of false negatives due to coeluting compounds interfering with the ions of the target analytes. However, if the limits are broadened to minimize the chance of false negatives, there is no efficient means by which to measure this percentage. We believe that setting the ion ratio in the software large enough to guard against the possibility of false negatives (40%) and then visually inspecting the spectrum relative to the reference spectrum is within the flexibility allowed by the method. Does the Agency agree?

Response: Yes. The software should be set up to force false positives. The analyst must then determine which of the positives is false.

Section 12.1 (14.1 for Method 625) states that one primary and at least two secondary ions are to be used for quantitation. Tables 3 and 4 (Tables 4 and 5 for Method 625) list primary and secondary ions for the various analytes involved, but do not always list two secondary ions. Can the analyst use professional judgement to drop or add characteristic ions to account for interferences and other analytical problems?

Response: The analyst may choose alternate m/z's provided that the reason is justified and documented.

ISSUE # 7 - SURROGATE COMPOUND RECOVERY REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.5	625	8.6

8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solutions as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

All samples must be spiked with surrogate. No criteria are given. Can optional surrogate criteria be developed using statistical techniques or by using the surrogate limits given in EPA method 8260 (8270 for Method 625)?

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Response: Optional surrogate QC criteria can be used.

ISSUE # 8 - REQUIRED CONCENTRATION OF MATRIX SPIKES

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.3.1	603,625	8.3.1

8.3.1 The concentration of the spike in the sample should be determined as follows:

> *8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*

Quite often the commercial laboratory is not aware that a sample is being tested for regulatory compliance or what the regulatory limit might be. In addition, it is often impractical and expensive to determine background levels before spiking and to vary spiking levels. A single spiking protocol at an acceptable concentration level results in greater efficiencies and a lower cost to the regulated community. Is it acceptable to spike at 20 ug/L (50 ug/L for Method 603, 100 ug/L for Method 625)?

Response: Yes, it is acceptable to alter the concentration of the spike so long as the concentration is (a) greater than the background concentration and (b) less than or equal to the regulatory compliance level.

ISSUE # 9 - ACCEPTABLE TRAP MATERIALS AND DIMENSIONS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.2.2	603	5.2.2
11.1	603	10.1

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5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 8.3.2),15 cm of 2,6-dyphenylene oxide polymer (Section 6.3.1). and 8 cm of silica gel (Section 8.3.3). The minimum specifications for the trap are illustrated in Figure 2.

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

Is the use of newer traps, having different dimensions and packing material with improved (decreased) retention of water and better desorption characteristics, considered "other chromatographic conditions" per Section 11.1 (Section 10.1 for Method 603) and thereby acceptable, so long as the requirements of Section 8.2 are met?

Response: Yes. The Agency has agreed that extension of method flexibility to include trap materials and conditions is appropriate.

ISSUE # 10 - ACCEPTABILITY OF CAPILLARY COLUMNS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.2	603	5.4.1
8.1.2	603	8.1.2
11.1	603	10.1

5.3.2 Column--6 ft long x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met. EPA 821-B-93-001 "Guidance On Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", page 10, Flexibility in Analytical Methods: "For example,

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the analyst is allowed to use professional judgement in selecting packed or open tubular columns, operating temperature programs, carrier gas or solvent flow rates, and detectors".

We believe the use of capillary columns is within the flexibility allowed in sections 8.1.2 and 11.1 (10.1 for Method 603). Does the Agency agree?

Response: Yes. The Agency agrees that extension of method flexibility to include capillary columns is appropriate. Of course, a hardware upgrade may be required to handle the sharper peaks produced by capillary columns.

ISSUE # 11 - TRAP CONDITIONING REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.1	603	7.1

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180-C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

If the laboratory can adequately condition a trap in less time than "overnight", is this acceptable? For example, if a sample foams and the trap must be replaced, if the trap is conditioned during the day and analysis of a blank demonstrates that the system is clean, can analyses proceed?

Response: Yes.

ISSUE # 12 - PREPARATION OF CALIBRATION STANDARDS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.3.1	603	7.3.1

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 uL of one or more secondary dilution standards to 50, 250, or 500 mL of reagent water. A 25 uL syringe with a 0.006 in. ID needle should be used for this operation. One of the calibration standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples

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or should define the working range of the GC/MS system. These aqueous standards can be stored up to 24 h. if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after 1 h.

First, are syringes of other internal diameters acceptable?

Response: Yes.

Second, from this paragraph it would seem that the Agency wants to hold the volume of the intermediate standard pipetted constant and vary the size of the volumetrics. In other words, if we have to add 20 uL of intermediate solution and we only have three final volumes to chose from, there are only three possible concentrations we can make from our intermediate solution. Would it be acceptable to vary the amount of intermediate solution added or chose a different final volume when preparing these standards?

Response: Yes. The objective is to calibrate the instrument; the details may be varied.

ISSUE #13 - REQUIRED MASS ACQUISITION RANGE

This issue relates solely to Method 624.

5.3.3 Mass spectrometer--Capable of scanning from 20 to 280 amu every 7 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet. This paragraph defines the necessary scan speed for the mass spec to be from 20 to 280 in seven seconds or less. Does it also require that the scan range 20 to 280 be used for data acquisition? With this scan range, methanol would be the predominate peak in the total ion chromatogram. We believe that scanning from 33 to 280 is acceptable. This would still bracket all the characteristic ions of the analytes of interest presented in the method and exclude methanol. Does the Agency agree?

Response: No. Scanning from m/z 20 is required in order to rigorously identify acrolein and acrylonitrile, should they be present. If there is concern about the display of the total resolved ion chromatogram, the data can be displayed from m/z 45 upward and the m/z's resulting from air (nitrogen, oxygen, argon, CO_2) and methanol will not be visible.

ISSUE # 14 - SURROGATE COMPOUNDS, PREPARATION AND FINAL CONCENTRATIONS

This issue relates solely to Method 624.

6.7 Surrogate standard spiking solution-- Select a minimum of three surrogate compounds from Table 3. Prepare stock standard solutions for each surrogate standard in methanol as described in Section 6.5. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 15 ug/mL in water. Store the solutions at 4-C in Teflon-sealed glass containers with a minimum of

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headspace. The solutions should be checked frequently for stability. The addition of 10 uL of this solution to 5 mL of sample or standard is equivalent to a concentration of 30 ug/L of each surrogate standard.

TABLE 3. SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	*Retention time (min)[a]*	*Primary m/z*	*Secondary m/z's*
Benzene d-6	*17.0*	*84*	
4-Bromofluorobenzene	*28.3*	*95*	*174,176*
1,2-Dichloroethane d-4	*12.1*	*102*	
1,4-Difluorobenzene	*19.6*	*114*	*63,88*
Ethylbenzene d-5	*26.4*	*111*	
Ethylbenzene d-10	*26.4*	*98*	
Fluorobenzene	*18.4*	*96*	*70*
Pentafluorobenzene	*23.5*	*168*	
Bromochloromethane	*9.3*	*128*	*49,130,51*
2-Bromo-1-chloropropane	*19.2*	*77*	*79,156*
1,4-Dichlorobutane	*25.8*	*55*	*90,92*

(a)For chromatographic conditions, see Table 1.

Since Table 3 gives "Suggested Surrogate and Internal Standards", may alternative surrogates be utilized, such as those used in 524.2 or 8240, or is the laboratory bound to those on this list? Minimizing the number of surrogate solutions that the lab must maintain results in substantial cost savings that can subsequently be passed on to the regulated community.

Response: Alternate surrogates may be used.

When preparing standard solutions can the concentrations and/or volumes of the surrogate solutions be changed? Can the final concentration of the surrogates in the samples be changed? This would facilitate the use of commercially prepared solutions thereby decreasing the cost of performing the analysis.

Response: Yes. Surrogate concentrations may be changed.

ISSUE # 15 - SURROGATE COMPOUND RECOVERY REQUIREMENTS

This issue relates solely to Method 624.

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8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

All samples must be spiked with surrogate. No criteria are given. Can optional surrogate criteria be developed using statistical techniques or by using the surrogate limits given in EPA method 8240?

Response: See issue #7.

ISSUE # 16 - ANALYSIS OF ACROLEIN AND ACRYLONITRILE BY METHOD 624

This issue relates solely to Method 624.

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET No. 34215, CAS No. 107-13-1), however, the preferred method for these two compounds in (sic) Method 603.

Table 1C - List Of Approved Test Procedures For Non-Pesticide Organic Compounds, footnote #4: Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present the preferred method for these two compounds is method 603 or method 1624.

We believe that if Method Detection Limits (MDLs) are documented and if accuracy and precision criteria in method 603 for Acrolein and Acrylonitrile can be met using method 624, that Acrolein and Acrylonitrile can legitimately be reported (at or above reporting limits consistent with the documented MDLs) from a method 624 analysis. Does the Agency agree?

Response: Yes, provided that the performance criteria and MDLs in Method 603 can be met using Method 624.

ISSUE # 17 - SAMPLE PRESERVATION REQUIREMENTS

This issue relates solely to Method 624.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. (3) Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1+1 HCl while stirring vigorously. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2.

This preservation protocol could be interpreted to require three different sample analyses (to permit 14 day hold times) to determine the full 624 list (one sample for acrolein and acrylonitrile, one for purgeable halocarbons, and one for purgeable aromatics).

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Can the purgeable halocarbons be analyzed from an acidified sample with a pH <2? Can acrolein and acrylonitrile be analyzed from an acidified sample with a pH <2 or is there some other preservation routine that will allow for fewer analyses?

Response: EPA recommends acidification and refrigeration as the principle preservation procedures for purgeable organic compounds. If the holding time is to be extended to 14 days, a minimum of two samples will be required. The first for acrolein adjusted to pH 4-5 per footnote 9 to Table II of 40 CFR part 136; the other to pH <2 with HCl per footnote 10 of this table. If free chlorine is present, it must be reacted with sodium thiosulfate per Table II.

ISSUE # 18 - REQUIRED CONCENTRATION OF QC CHECK SAMPLE

This issue relates solely to Method 608.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations:

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10 ug/mL; any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.3.1 The concentration of the spike in the sample should be determined as follows:

> *8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory*

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concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

As we understand the method, 1 mL of the QC Check standard from section 8.2.1 is added to 1 L of sample to prepare a matrix spike. The same amount of QC Check standard would be added to 1 L of reagent water to prepare a QC Check Sample. The samples are then concentrated to a final volume of 10 mL. This would result in the following concentrations in the extracts:

PARAMETER	CONC. IN EXTRACT (ug/L)
Aldrin	200
a-BHC	200
b-BHC	200
d-BHC	200
g-BHC	200
Chlordane	5000
4,4-DDD	1000
4,4-DDE	200
4,4-DDT	1000
Dieldrin	200
Endosulfan I	200
Endosulfan II	1000
Endosulfan Sulfate	1000
Endrin	1000
Heptachlor	200
Heptachlor epoxide	200
Toxaphene	5000
PCB-1016	5000
PCB-1221	5000
PCB-1232	5000
PCB-1242	5000
PCB-1248	5000
PCB-1254	5000
PCB-1260	5000

In all cases except Toxaphene these concentrations are above the normal linear range of an ECD detector when set up to achieve method 608 detection limits. The following are the spike concentrations and upper calibration limits we currently use:

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PARAMETER	CONC. IN EXTRACT (ug/L)	UPPER CAL. LIMIT (ug/L)
Aldrin	30	50
a-BHC	30	50
b-BHC	30	50
d-BHC	30	50
g-BHC	30	50
Chlordane	50	1000
4,4-DDD	60	100
4,4-DDE	60	100
4,4-DDT	60	100
Dieldrin	60	100
Endosulfan I	30	50
Endosulfan II	60	100
Endosulfan Sulfate	60	100
Endrin	60	100
Heptachlor	30	50
Heptachlor epoxide	30	50
Toxaphene	3000	5000
PCB-1016	500	1000
PCB-1221	500	1000
PCB-1232	500	1000
PCB-1242	500	1000
PCB-1248	500	1000
PCB-1254	500	1000
PCB-1260	500	1000

Are these spike concentrations acceptable?

Response: Yes, provided all method-specified QC criteria are met.

ISSUE # 19 - ACCEPTABLE SAMPLE EXTRACTION PROCEDURES

This issue relates solely to Method 608.

10.2 If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

Allowances are made for the use of techniques to overcome emulsion problems. We have found that the most effective technique for dealing with emulsions is the use of continuous liquid/liquid

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extractors. This technique is not specifically mentioned here. Since wastewater samples routinely cause emulsion problems, is continuous extraction an acceptable technique to use with this method?

Response: Yes, provided the procedure is an adaptation of Method 608 (neutral sample pH, methylene chloride-based extraction solvent, extended contact time to assure extraction of analytes from solids) and all method-specified QC criteria are met.

ISSUE # 20 - QUANTITATION PEAK REQUIREMENTS

This issue relates solely to Method 608.

13.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

Please clarify what is meant by the phrase "every identifiable peak". The chromatogram of PCB or multicomponent pesticides may contain over 100 peaks of various heights. Since many of the smaller peaks disappear from low concentration standards and samples, we normally use only the largest, most distinctive peaks for quantitation. This tends to keep responses more linear and provides more accurate results at the lower concentration levels. Quantitation using all peaks tends to skew results near the detection limits so that samples appear to be lower in concentration than they actually are. This phenomenon is caused because the smaller peaks, which were used to develop the response factors, are no longer detectable as part of the sample constituent.

Response: Use the largest number of peaks that will provide reliable quantitation of the compound. Five peaks minimum is suggested.

ISSUE #21 - ACCEPTABILITY OF COMBINING ACID AND BASE/NEUTRAL EXTRACTS PRIOR TO ANALYSIS

This issue relates solely to Method 625.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

Section 10.6 starts with the phrase "For each fraction", and goes on to describe the setup of a K-D concentration apparatus. It also states that alternative concentration techniques can be used if the requirements in section 8.2 are met. We have found that the most efficient way to perform this step is by concentrating the BN and A fractions together into one extract. This results in both an improvement in recoveries and lower costs to the regulated community.

The increase in cost when the fractions are kept separate is dramatic because it carries throughout the entire lab. Twice the amount of glassware is needed. Twice the amount of prep labor is needed to

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perform the concentration step. Instrument time is doubled. Twice the number of reports are generated. Data reduction is slowed.

Also, when the extracts are not combined there is a drop in the recoveries of the acid compounds. This is caused because even at a pH greater than 11 the acid compounds are partially extracted into the basic fraction. Once there, they are essentially lost to the analysis unless the fractions are later combined.

In the end, keeping the fractions separate results in no real increase in quality and a dramatic increase in cost. Good resolution can still be maintained when the extracts are combined and the method detection limits are still easily achievable. Is it acceptable to combine the BN and A fractions as long as the requirements in Section 8.2 and the method detection limits can be met?

Response: Yes and No. If the analytes can be reliably identified and quantified in each sample, the extracts may be combined. If, however, the identification and quantitation of any analyte is adversely affected by another analyte, a surrogate, or an interferant, the extracts must be analyzed separately. If there is ambiguity, the extracts must be analyzed separately.

ISSUE # 22 - CHARACTERISTIC ION REQUIREMENTS

This issue relates solely to Method 625.

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification

Section 14.1 states that one primary and at least two secondary ions are to be used for qualitative identification of all compounds. Can the analyst use professional judgement to drop or add characteristic ions to account for interferences and other analytical difficulties?

Response: Yes, provided the identification of the analyte is as reliable as it would be if the specified m/z's were used.

ISSUE # 23 - CHROMATOGRAPHIC RESOLUTION REQUIREMENTS

This issue relates solely to Method 625.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

What ramifications does this have on compliance monitoring where benzo(k)fluoranthene and benzo(b)fluoranthene need to be identified? Should these compounds be reported as

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"Benzofluoranthenes"? Is there any flexibility for analyst interpretation regarding isomer identification?

Response: If the isomers cannot be differentiated, the concentration should be checked against the lowest regulatory concentration limit for the pair. In this instance, EPA recommends that a column that resolves the pair be used.

ISSUE # 24 - QUANTITATION OF 2,3,7,8-TCDD

This issue relates solely to Method 625.

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows...

Does the term "screen" imply that the method is non-quantitative for 2,3,7,8-TCDD? What should be reported when performing this screen, "D" versus "ND"?

Response: Screen means that if 2,3,7,8-TCDD is detected, the sample must be analyzed using an alternate method specifically designed for the determination of 2,3,7,8-TCDD. EPA recommends Method 1613 for this determination.

ISSUE # 25 - ALTERNATIVE CAPILLARY COLUMNS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.1 5.3.2	602	5.3.1 5.3.2
	624	5.3.2

5.3.1 Column 1 - 6 ft long x 0.082 in ID stainless steel or glass, packed with 5% 1,2,3-1200 and 1.75% Bentone-34 on Supelcoport (100/120 mesh) or equivalent...

5.3.2 Column 2 - 8 ft long x 0.1 in ID stainless steel or glass, packed with 5% Tris(2-cyanoethoxy)propane on Chromo W-AW (60/80 mesh) or equivalent...

Recently, new types of chromatographic columns have been developed that clearly demonstrate an enhancement in the state-of the art. Can these chromatographic columns be used in Methods 601, 602 and 624?

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Response: In response to numerous requests, on July 5, 1989, the Environmental Monitoring Systems Laboratory (EMSL-Ci, now called NERL-Ci) recommended approval of the newer chromatographic columns in Methods 601, 602, and 624 provided that the user demonstrates the achievement of performance criteria. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

ISSUE # 26 - COMBINATION OF 601 AND 602 METHODS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.3	602	5.3.3

5.3.3 Detector - Electrolytic conductivity or microcoulometric detector...

Can Methods 601 and 602 be combined with use of a photoionization detector in series with an electrolytic conductivity detector?

Response: In response to numerous requests, on July 5, 1989, the Environmental Monitoring Systems Laboratory (EMSL-Ci, now called NERL-Ci) recommended approval of the combination of Methods 601 and 602 with the use of a photoionization detector in series with an electrolytic conductivity detector provided that the user demonstrates the achievement of performance criteria. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

ISSUE # 27 - ALTERNATIVE SORBENTS TRAPS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.2.2	602	5.2.2.1
	624	5.2.2

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5.2.2 ...The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.3), 7.7 cm of 2,6-diphenylene oxide polymer (Section 6.3.2), 7.7 cm of silica gel (Section 6.3.4), 7.7 cm of coconut charcoal (Section 6.3.1)...

Recently, new material have become available that appear to provide advantages over the sorbent traps specified in the methods. Can these be used in place of the specified sorbents traps?

Response: On November 7, 1994, EMSL-Ci accepted of the use of alternative sorbents provided the data acquired meets all quality control criteria described in Section 8 and provided the purge and desorption procedures specified in the method are not changed. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

Although alternative adsorbents may be used, only some of the purging and desorption procedures can be adjusted. The purging and desorption procedures were designed to achieve 100% purging efficiency and recovery of the many regulated target analytes. The purge time and purge gas flow rate required to efficiently purge the target analytes from the water samples are largely independent of the sorbent trapping material. Decreasing the purging or desorption times or gas flows will have a negative impact on method precision and may increase adverse matrix effects. Therefore, purge time and purge gas flow rate may not be adjusted. Since many of the potential alternate sorbents may be thermally stable at temperatures higher than 180 °C, however, the alternate traps may be desorbed and baked out at higher temperatures than those described in the current method revisions. If higher temperatures are used, the analyst should monitor the data for analyte and trap decomposition.

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Appendix D

Suggested Data Elements

DEEMS VERSION 1.0
DATA ELEMENT DICTIONARY

DATA ELEMENT	DESCRIPTION
Acid_Reaction Format: Limited_List Record: **Sample_and_Method**	Reaction of the sample to acid. Examples: Weak, Strong.
Record: **Handling**	Same as in a Sample_and_Method record.
Aliquot_Amount Format: Numeric Record: **Analysis**	The amount of sample used for this analysis. This usage of the word aliquot is not consistent with its dictionary definition, but is standard for many chemists.
Aliquot_Amount_Units Format: Limited_List Record: **Analysis**	Units for Aliquot_Amount.
Alternate_Lab_Analysis_ID Format: Identifier Record: **Analysis**	Alternate lab identifier for an analysis. This value is for information purposes only to facilitate tracking back into the lab's systems.
Alternate_Lab_Sample_ID Format: Identifier Record: **Sample_and_Method**	Alternate lab identifier for a sample. This value is for information purposes only to facilitate tracking back into the lab's systems. It might be used when the lab has both a lab-wide sample id and a different, department specific for particular methods.
Amount_Added Format: Numeric Record: **Result**	Specifies a known amount of analyte that has been spiked into the aliquot. Used with method QC samples of QC_Category Blank_Spike, Spike, Spike_Duplicate and Blank_Spike_Duplicate.

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DATA ELEMENT	DESCRIPTION
	Spike analytes should have 'Analyte_Type=Spike'.
Record: **Analyte**	Same as in a Result record extended so Amount_Added can now refer to spikes, surrogates, tracers, standard additions, and calibration standards where known amounts of analytes have been added to samples for QC purposes. ‘Analyte_Type=Spike' should be specified for spiked analytes unless some other Analyte_Type is more appropriate or which analytes were spiked is known based on a QC_Type associated with this data.
Amount_Added_Error Format: Numeric Record: **Result**	The one sigma error in the estimate of the Amount_Added.
Record: **Analyte**	Same as in a Result record.
Amount_Added_Error_Units Format: Limited_List Record: **Result**	Units for Amount_Added_Error. If the client specifies that the Amount_Added_Error_Units must be the same as the Amount_Added_Units, the Amount_Added_Error_Units need not be specified.
Record: **Analyte**	Same as in a Result record.
Amount_Added_Units Format: Limited_List Record: Result	Units for Amount_Added. If the client specifies that the Amount_Added_Units must be the same as the Result_Units, the Amount_Added_Units need not be specified.
Record: **Analyte**	Same as in a Result record.

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DATA ELEMENT	DESCRIPTION
Analysis_Batch Format: Identifier Record: **Analysis**	An identifier for a batch of analyses on one instrument associated with the level of detail at which the instrument is checked to be in control. Example: Analyses QC'd by the same continuing calibration or similar_QC.
Analysis_Duration Format: Numeric Record: **Analysis**	The duration of the instrumental analysis. Example: Radiochemical count time.
Record: **Analyte**	The duration of the instrumental analysis for this analyte. Example: ICP integration time.
Analysis_Duration_Units Format: Limited_List Record: **Analysis**	Units for Analysis_Duration.
Record: **Analyte**	Units for Analysis_Duration.
Analysis_Group Format: Identifier Record: **Analysis_Group**	*Required* A lab defined code for an Analysis_Group. If an Analysis_Group is needed to fully identify what was done, the Lab_Analysis_ID's in related Analysis records might be constructed as the Analysis_Group code combined with a suffix. For example, in dual column GC, the GC data system often has a code for the pair of analyses, which can be used as the Analysis_Group identifier. Adding a column number to this identifier gives a suitable Lab_Analysis_ID.
Record: **Analysis**	The Analysis_Group this analysis is part of. The Client_Method_ID or Analysis_Type should imply whether or not an Analysis_Group is needed.

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DATA ELEMENT	DESCRIPTION
Record: **Result**	If there is any ambiguity about which analyses underlie this result, the Analysis_Group that identifies these analyses.
Analysis_Request_ID Format: Identifier Record: **Sample_and_Method**	Client's code for the paperwork that authorizes the analyses of specific samples by listed methods. Sometimes this is identical to the chain of custody identifier.
Analysis_Type Format: Limited_List Record: Analysis	*Conditionally Required* Client's code to define the type of analysis. This code is only needed if more than one analysis is done per Analysis_Group. Examples: 1. For dual column GC, this code identifies the type of column (first or second) used. In current CLP practice, the column identifier (really a manufacturer's code) might be used for this value in lieu of a CLP-specified value. 2. If several measurements are averaged to produce the final result, codes for the first, second, ... analyses done. 3. When doing a method of standard additions, this code identifies the first, second,...analyses done. For example, CLP codes are MSA0, MSA1,... 4. When every sample is spiked to measure the linear response of the method, this code identifies the spiked and unspiked analyses. This technique is used in some radiochemistry methods (some versions of Tritium and (Total Uranium), but it is rare to report the spiked analysis except in the raw data, so no standard codes exist.

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DATA ELEMENT	DESCRIPTION
	5. When the method involves a secondary measurement of some factor necessary to compute the result, this code identifies the secondary analysis. For example, some methods for PU-241 by liquid scintillation require a separate alpha count of the tracer to determine the yield. 6. If client rules are to report only one (best) result after reanalyses or dilutions, this code could classify each analysis in these terms.
Record: **Analysis_Group**	Client's code to define the type of Analysis_Group. This code is only needed if more than one type of Analysis_Group applies to one Sample_and_Method or Instrument_QC record. Example: For CLP Inorganics Method of Standard Additions, Analysis_Groups are needed for normal and Analytical Spike groups as well as the MSA groups.
Analyst Format: Text Record: **Handling**	Name or initials for the analyst doing the work described in this record.
Record: **Analysis**	Same as in a Handling record.
Record: **Cleanup**	Same as in a Handling record.
Analyte_Name Format: Text Record: **Result**	Lab assigned chemical name for the analyte. For GCMS TICs (Tentatively Identified Compounds), this name may come from a mass spectral library.
Record: **Analyte**	Same as in a Result record
Record: **Analyte_Comparison**	Analyte_Name for the analyte to compare to.
Record: **Peak_Comparison**	Analyte_Name for the analyte to compare to.
Analyte_Type Format: Limited_List	Conditionally Required

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DATA ELEMENT	DESCRIPTION
Record: **Result**	In a Result record, required values, ignoring case, are: Spike -- This analyte has been spiked. TIC -- This analyte is non-routine and is tentatively identified. This field is not used for a routine analyte.
Record: **Analyte**	Same as in a Result record with the following required values, ignoring case, in addition to Spike and TIC: Internal_Standard -- Defined as per CLP usage. Surrogate -- Defined as per CLP usage. System_Monitoring_Compound_ -- Defined as per CLP usage. Tracer -- Like an internal standard except it is added at the beginning of sample preparation, rather than just before analysis.
Analytical_Error Format: Numeric Record: **Result**	The estimated one sigma error in the result due to all effects related to analysis by the lab.
Record: **Analyte**	Same as in a Result record extended to anything considered to be the result of any analysis. Within an Analysis_Group record, applies to a mean or other value computed from several analyses.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Analytical_Error_Units Format: Limited_List Record: Result	Units for Analytical_Error. If the client specifies that the Analytical_Error_Units must be the same as the Result_Units, the Analytical_Error_Units need not be specified.

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DATA ELEMENT	DESCRIPTION
Record: Analyte	Same as in a Result record.
Record: Peak	Same as in a Result record.
Analyzed	
Format: Date	
Record: **Analysis**	Analysis date.
Apparatus_ID	
Format: Identifier	
Record: **Analysis**	The lab's code for the apparatus used to process an aliquot. Example: An identifier for a Purge and Trap device.
Record: **Handling**	The lab's code for the apparatus used to process a sample. Example: An identifier for a TCLP device.
Record: **Cleanup**	The lab's code for the apparatus used to cleanup an aliquot. Example: An identifier for a GPC device.
Artifacts	
Format: Text	
Record: **Sample_and_Method**	Method defined concept used to report anomalies in the sample.
Record: **Handling**	Same as in a Sample_and_Method record.
Autosampler	
Format: Limited_List	
Record: Analysis	Whether an autosampler was used.
Background_Correction	
Format: Limited_List	
Record: **Analysis**	Whether or not background correction was done.
Background_Raw_Data	
Format: Limited_List	

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DATA ELEMENT	DESCRIPTION
Record: **Analysis**	Whether raw data was generated when background correction was done. Example, used for CLP Inorganics ICP.
Background_Type Format: Limited_List Record: **Analysis**	The type of background correction done. Example: CLP Inorganics Furnace AA distinguishes Smith-Hieftje, Deuterium Arc, and Zeeman types.
Record: **Analyte**	Same as in an Analyte record, except specific to an analyte.
Record: **Peak**	Same as in an Analyte record, except specific to a peak.
Bias_Error_Ratio Format: Numeric Record: **Result**	For method QC of QC_Category, Blank_Spike, and Blank_Spike_Duplicate, the difference between the result and amount added as a fraction of the square root of sum of squares of the one sigma analytical error and one sigma amount added error.
Record: **Analyte**	Same as in Result records except applied to the results of analyses in an analysis group rather than a QC sample and original pair.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Billing_ID Format: Identifier Record: **Sample_and_Method**	Client's code to submit with the data for billing purposes.
Boiling_Point Format: Numeric Record: **Sample_and_Method**	Boiling point of the sample.

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DATA ELEMENT	DESCRIPTION
Record: **Handling**	Same as in a Sample_and_Method record.
Boiling_Point_Units	
Format: Limited_List	
Record: **Sample_and_Method**	Units for the Boiling_Point.
Record: **Handling**	Units for the Boiling_Point.
Bottles	
Format: Numeric	
Record: **Sample_and_Method**	Number of sample bottles.
Bottle_ID	
Format: Identifier	
Record: **Sample_and_Method**	Identifier for the bottle containing the sample being analyzed. May repeat in one record if several bottles are treated as one sample.
Record: **Analysis**	Identifier for the bottle containing the aliquot being analyzed. May repeat in one record if several bottles are used to prepare one aliquot.
Calibration_Factor	
Format: Numeric	
Record: **Analyte**	Factor used to convert measured to final results.
Record: **Peak**	Same as in an Analyte record, except applied to a single peak.
Calibration_Factor_Units	
Format: Limited_List	
Record: **Analyte**	Units for Calibration_Factor
Record: **Peak**	Units for Calibration_Factor.
CAS_Number	
Format: Identifier	
Record: **Result**	The Chemical Abstract Service number for the analyte. Only use values assigned by the Chemical Abstracts Service with this field.

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DATA ELEMENT	DESCRIPTION
	Values can be entered with or without hyphen delimiters.
Record: **Analyte**	Same as in a Result record.
Record: Analyte_Comparison	CAS_Number for the analyte to compare to.
Record: Peak_Comparison	CAS_Number for the analyte to compare to.
Checksum Format: Numeric Record: **All**	A value based on all other data in a record that can be used to check EDD integrity. This field can be used in any record. Its value applies to the record it is in. The required algorithm to compute the data for this field is as follows: For all data in a record, starting with the record type line, ending before the next record type line or end of the data stream, and ignoring: 1. The carriage return and linefeed at the end of each line. 2. Any optional leading spaces in ‘record:’ and ‘field=’lines. 3. The entire line with the checksum field. Compute the sum of the ASCII codes of all non-ignored characters. Report this sum as an integer following the ‘checksum=’.
Clarity Format: Limited_List Record: **Sample_and_Method**	Clarity of the sample as received. Examples: Clear, Cloudy, Opaque.
Record: **Handling**	Clarity of the sample after the handling described in this record.

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DATA ELEMENT	DESCRIPTION
Record: **Analysis**	Clarity of the aliquot after preparation.
Record: **Cleanup**	Clarity of the aliquot after the cleanup described in this record.
Cleaned_Up Format: Date Record: **Cleanup**	Date of cleanup of this aliquot.
Cleanup_Batch Format: Identifier Record: **Cleanup**	The lab's identifier for a batch of aliquots cleaned up together. The definition of a cleanup batch depends on the method but might be linked to cleanup specific QC samples such as GPC calibrations. Example: All analyses associated with one GPC calibration would be in one Cleanup_Batch of Cleanup_Type GPC. The Instrument_QC in the batch might have QC_Type GPC_Calibration.
Cleanup_ID Format: Identifier Record: **Cleanup**	The lab's identifier for this cleanup event for this aliquot.
Cleanup_Type Format: Limited_List Record: **Instrument_QC**	*For Portability* For instrument QC with QC_Linkage 'Cleanup_Batch', a code that identifies the type of cleanup this QC pertains to. The field's value must match that specified as the Cleanup_Type for cleanups of associated analyses.
Record: **Cleanup**	A code the specifies the type of cleanup. Valid values might be specified for each Client_Method_ID. Examples: GPC, Florisil, and Sulfur.
Client_Analysis_ID Format: Identifier Record: **Analysis**	An optional client defined identifier for this analysis.

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DATA ELEMENT	DESCRIPTION
	Examples: In the CLP, required analysis identifiers like VBLKxy and INDALxy.
Client_Analyte_ID	
Format: Identifier	*Required*
Record: **Result**	The client's code for the analyte. This code should be the basis on which the client recognizes the analyte.
Record: **Analyte**	Same as in a Result record.
Record: **Analyte_Comparison**	Client_Analyte_ID for the analyte to compare to.
Record: **Peak_Comparison**	Client_Analyte_ID for the analyte to compare to. If not specified, it is assumed to be the same as the analyte for the Peak record this Peak_Comparison record is in.
Client_ID	
Format: Limited_List	*For Portability*
Record: **Sample_and_Method**	An identifier for the person or organization ordering the analysis. Often client defined. This value is necessary to allow one client to read data reported in a format specified by another. To be fully reliable, Client_ID's must be unique across all potential clients. Someday they might be assigned by a central group. Examples: EPA Region, AFCID (Air Force Client ID), Customer.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Client_Method_ID	
Format: Limited_List	*Required*
Record: **Sample_and_Method**	The client's code for the work to be done. The complete code many be a composite of a number of values, such as a CLP method code (OLM02.0), a fraction (Semivolatiles) and a level (Low). Full details about the meaning of fields and relationships in the EDD are defined relative to the

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DATA ELEMENT	DESCRIPTION
	combination of this value and the Matrix_ID. Values for the Client_Method_ID and Matrix_ID should be specified in the client's DEEMS implementation, possibly by referencing the Client's Statement of Work (SOW). The Client_Method_ID is not a generic method number that only identifies the analytical process. It must address issues such as the number and types of QC samples expected, what types of reanalyses and dilutions are expected, and how to report final results when reanalyses and\or dilutions are done. NOTE: The 'Client_ID' is required to make this code unique across client boundaries.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Client_Name Format: Text Record: **Sample_and_Method**	Descriptive name for the person or organization ordering the analysis. May be lab defined. Examples: EPA Region, AFCID (Air Force Client ID), Customer.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Client_Reanalysis_Type Format: Limited_List Record: **Sample_and_Method**	*Conditionally Required* If the client wants results for reanalyses done by this method to be reported separately, the client defined code to identify the reanalysis. The Client_Method_ID, Client_Sample_ID and Client_Reanalysis_Type together should uniquely identify the data associated with this record except possibly for lab generated QC samples. Reanalysis is defined as generally as possible to include notions such as reextraction, dilution, and rework. Example: DL, RE and REDL as used in the CLP.

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DATA ELEMENT	DESCRIPTION
Client_Sample_ID Format: Identifier Record: Sample_and_Method	*Required* Client's identifier for a sample. This should be the basis on which the client identifies the sample. However, not all clients define values for lab generated QC samples. Example: EPA Sample Number
Collected Format: Date Record: **Sample_and_Method**	Date the sample was collected. If collected over a range of dates, this is the start date.
Collected_End Format: Date Record: **Sample_and_Method**	If the sample was collected over a range of dates, the end of the collection period.
Color Format: Limited_List Record: **Sample_and_Method**	Color of the sample as received.
Record: **Handling**	Color of the sample after the handling described by this record.
Record: **Analysis**	Color of the sample after preparation
Record: **Cleanup**	Color of the aliquot after the cleanup described by this record.
Column Format: Text Record: **Analysis**	Name of the column used for analysis
Record: **Cleanup**	Name of the column used for this Cleanup. Example: GPC column identifier.
Column_Internal_Diameter Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analysis**	Internal diameter of the analytical column.
Column_Internal_Diameter_Units Format: Limited_List Record: **Analysis**	Units for Column_Internal_Diameter.
Comment Format: Text Record: **All**	*Repeals OK* A free-form comment that can occur in any record. Its value applies to the data in the record it is in. The exact location of a Comment field in a record is not significant. There can be many Comment fields in one record. The order in which these occur may be significant to their meaning. Comment fields, as opposed to ';comments', are meant to be related to data reported in other fields in the same record. Readers are not required to take any action based on these comments, but they might choose to record them as text comments in their database.
Composite Format: Limited_List Record: **Sample_and_Method**	If the sample is a composite.
Conductance Format: Numeric Record: **Sample_and_Method**	Conductance of the sample.
Conductance_units Format: Limited_List Record: **Sample_and_Method**	Units for Conductance.
Confirmation_Analysis_ID Format: Identifier Record: **Analysis**	Identifier for an analysis that confirms the results of this analysis. Example: Confirmatory GCMS Lab File ID in CLP Pesticides.

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DATA ELEMENT	DESCRIPTION
Record: **Analysis_Group**	Same as in Analysis record except confirming results from this Analysis_Group.
Consolidation Format: Limited_List Record: **Sample_and_Method**	Degree of consolidation of the sample. Weak, Moderate etc.
Correction_Factor Format: Numeric Record: **Analyte_Comparison**	The correction factor for the peak this record is in, based on interanalyte effects from the analyte named in this record.
Correlation_Coefficient Format: Numeric Record: **Analyte**	The correlation coefficient resulting from linear regression of data. Used for an analyte in an Analysis_Group record.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Counting_Error Format: Numeric Record: **Result**	For methods based on counting discrete events, such as are common in radiochemistry, the one sigma error in the net count rate, usually scaled to the same units as the result. A more precise definition of Counting_Error may specified for each method.
Record: **Analyte**	Same as in a Result record extended to anything considered to be the result of any analysis. Within an Analysis_Group record, applies to a mean or other value computed from several analyses.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Counting_Error_Units Format: Limited_List Record: **Result**	Units for Counting_Error.

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DATA ELEMENT	DESCRIPTION
	If the client specifies that the Counting_Error_Units must be the same as the Result_Units, the Counting_Error_Units need not be specified.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Created Format: Date Record: **Sample_and_Method**	The date a QC sample was generated or derived in the lab.
Custody_ID Format: Identifier Record: **Sample_and_Method**	Client's code for the chain of custody document associated with receipt of this sample in the lab.
Date_Format Format: Limited_List Record: **Header**	A value that specifies the format of all date/time values that follow this Header record. Allowed values for this field are listed with the description of allowed date formats for field values. A required Date_Format value may be specified by the client or implementation.
Density Format: Numeric Record: **Sample_and_Method**	The density of the sample.
Record: **Handling**	The density of the sample after the handling described by this record.
Detection_Limit Format: Numeric Record: **Result**	Detection limit for the analyte being measured.
Record: Analyte	Same as in a Result record extended to anything considered to be the result of any analysis. Within an Analysis_Group record, applies to a mean or other value computed from several analyses. For

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DATA ELEMENT	DESCRIPTION
	Instrument_QC, the value might be an instrument detection limit.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Detection_Limit_Type	
Format: Limited_List	
Record: **Result**	One of a list of client defined acronyms that specify the type of detection limit. Examples: CRDL, MDA, MDL, IDL.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Detection_Limit_Units	
Format: **Limited_List**	
Record: **Result**	Units for Detection_Limit.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Detector_Type	
Format: Limited_List	
Record: **Analysis**	The type of detector used in the instrumental analysis. This is not an instrument identifier. Examples: FID, GCMS.
Difference_Error_Ratio	
Format: Numeric	
Record: **Result**	The absolute value of the difference of two values as fraction of the square root of sum of squares of their one sigma analytical errors. Used with method QC of QC_Category Duplicate, Serial_Dilution,Spike_Duplicate and Blank_Spike_Duplicate.

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DATA ELEMENT	DESCRIPTION
Record: **Analyte**	Same as in Result records except applied to the results of analyses in an analysis group rather than a QC sample and original pair.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Dilution Format: Numeric Record: **Analysis**	The overall dilution of the sample aliquot. A value of one should correspond to nominal conditions for the method. Values less than one correspond to concentrations. Exactly which factors are included in the dilution may depend on the method.
Dilutions Format: Numeric Record: **Analysis**	Number of dilutions done to this aliquot.
Drift Format: Numeric Record: **Analysis**	The difference between the actual location of a peak and its predicted position. For alpha spectroscopy, Drift is computed using the tracer peak.
Record: **Analyte**	Same as in an Analysis record except applied to a specific analyte.
Record: **Peak**	Same as in an Analysis record except applied to a specific peak.
Drift_Units Format: Limited_List Record: **Analyte**	Units for Drift.
Record: **Analysis**	Units for Drift.
Record: **Peak**	Units for Drift.
EDD_ID Format: Limited_List Record: **Header**	*Required* Must have the value DOE_EM_EDD. It can be checked by readers to determine that following data are in a DEEMS compatible format. Since this field need

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DATA ELEMENT	DESCRIPTION
	not be the first line in a Header record, readers need to be prepared to read all the Header record lines before making this check.
EDD_Implementation_ID Format: Limited_List Record: **Header**	*Required* A value specified in a DEEMS implementation document as the identifier of the implementation. This value should be checked by readers to determine that following data are in a processible format. For example, an implementation might specify what records and data elements are required in the EDD, including any implementation defined fields. Since this field need not be the first line in a Header record, readers need to be prepared to read all the fields in this record before checking this value.
EDD_Implementation_Version Format: Limited_List Record: **Header**	*Required* A value specified in each revision of a DEEMS implementation document. The value in an EDD indicates the version of the implementation that following data is compatible with. Reader programs may have to adapt their behavior based on this value. In particular, the list of implementation defined fields may change with version number. Implementors should assign version numbers so that later versions have later alphabetical version numbers.
EDD_Version Format: Limited_List Record: **Header**	*Required* Specified in each revision of this document. Specified by the writer of an EDD to indicate the version of the DEEMS that following data is compatible with. Reader programs may have to adapt their behavior based on this value. In particular, the list of DEEMS defined fields may change with version number.
Efficiency Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analysis**	Efficiency of the instrument as a percent. Usually used in radiochemistry to mean the counts detected as a percentage of the decays actually occurring.
Record: **Analyte**	Same as in an Analysis record except applied to a specific analyte.
Record: **Peak**	Same as in an Analysis record except applied to a specific analyte and peak.
Energy	
Format: Numeric	
Record: **Peak**	The energy of an emission.
Record: **Peak_Comparison**	Same as in a Peak record.
Energy_Units	
Format: Limited_List	
Record: **Peak**	Units for Energy.
Record: **Peak_Comparison**	Units for Energy.
Equipment_Batch	
Format: Identifier	
Record: **Sample_and_Method**	An identifier for a batch of samples collected using the same equipment in a defined period of time. Operationally, this batch associates a field equipment blank with a group of samples. This value is currently often not known to the lab. It might be merged with lab data by a validator.
Field_Sample_ID	
Format: Identifier	
Record: **Sample_and_Method**	Identifier assigned to a sample by the sampler, not the client. This value is currently often not known to the lab. It could be useful as link into the sampling records system.
Final_Amount	
Format: Numeric	
Record: **Analysis**	The amount of sample remaining after final preparation for analysis.

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DATA ELEMENT	DESCRIPTION
Record: **Cleanup**	Amount of material coming out of cleanup.
Final_Amount_Units Format: Limited_List Record: **Analysis**	Units for Final_Amount.
Record: **Cleanup**	Units for Final_Amount.
Flow_Rate Format: Numeric Record: **Analysis**	Rate of flow of gas or liquid mobile phase for GC or HPLC.
Flow_Rate_Units Format: Limited_List Record: **Analysis**	Units for Flow_Rate.
Fraction Format: Limited_List Record: **Sample_and_Method**	The fraction of a sample, based on a physical or chemical separation, to which the method is applied.
Frequency Format: Numeric Record: **Peak**	The frequency of an emission or absorption.
Record: **Peak_Comparison**	Same as in a Peak record.
Frequency_Units Format: Limited_List Record: **Peak**	Units for Frequency.
Record: **Peak_Comparison**	Units for Frequency.
Generating_System_ID Format: Identifier Record: **Header**	A lab defined value that identifies the software system used to generate the EDD. This value may be built into commercial software. The reader may use this value to adapt to known quirks of the generating system.

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DATA ELEMENT	DESCRIPTION
Generating_System_Version Format: Text Record: **Header**	A lab defined version number for the software system used to generate the EDD.
Gradient Format: Numeric Record: **Analysis**	Temperature gradient for GC and mobile phase gradient for HPLC.
Gradient_Units Format: Limited_List Record: **Analysis**	Units for Gradient.
Handled Format: Date Record: **Handling**	Date of handling of this sample.
Handling_Batch Format: Identifier Record: **Handling**	The lab's identifier for a batch of samples handled together. The definition of a handling batch depends on the method but might be linked to handling specific QC samples. Example: All samples associated with one TCLP apparatus blank would be in one Handling_Batch of Cleanup_Type TCLP. The method QC sample in the batch might have QC_Type TCLP_Blank.
Handling_Duration Format: Numeric Record: **Handling**	The duration of the handling. Example: TCLP leaching time.
Handling_Duration_Units Format: Limited_List Record: **Handling**	Units for Handling_Duration.
Handling_Factor Format: Numeric Record: **Handling**	A factor that reflects processing done early in sample handling.

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DATA ELEMENT	DESCRIPTION
	For example, used in radiochemistry with a hot lab that does preliminary processing prior to more routine activities.
Handling_Factor_Units Format: Limited_List Record: **Handling**	Units for Handling_Factor.
Handling_ID Format: Identifier Record: **Handling**	The lab's identifier for this handling event for this sample.
Handling_Type Format: Limited_List Record: **Sample_and_Method**	*Conditionally Required* For a method QC sample with QC_Linkage 'Handling_Batch', a code that identifies the type of handling this QC pertains to. The field's value must match that specified as the Handling_Type for handlings of associated samples.
Record: **Handling**	Code that describes preliminary processing done to a sample prior to aliquotting. Examples: Ashed, Decanted, Distilled, Drained, Dried, Filtered, Leached.
Heated_Purge Format: Limited_List Record: **Analysis**	Whether volatiles analysis used a heated purge.
Initial_Amount Format: Numeric Record: **Cleanup**	Amount of material going into cleanup.
Initial_Amount_Units Format: Limited_List Record: **Cleanup**	Units for Initial_Amount.
Injection_Volume Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analysis**	The volume of sample injected into the instrument.
Injection_Volume_Units Format: Limited_List Record: **Analysis**	Units for Injection_Volume.
Instrument_ID Format: Identifier Record: **Analysis**	The lab's code for an instrument.
Instrument_Serial_Number Format: Text Record: **Analysis**	The serial number of the instrument used for analysis. Note, this is not a numeric field.
Interelement_Correction Format: Limited_List Record: Analysis	Whether ICP interelement correction factors were applied.
Lab_Address Format: Text Record: **Sample_and_Method**	*Repeats OK* Address of the lab doing this analysis. May repeat in one record as needed to report a multi-line address.
Lab_Analysis_ID Format: Identifier Record: **Analysis**	*Required* The lab's identifier for an analysis. This value should be unique at least for all analyses in one lab reporting batch in the context of one method. Example: Lab file ID as used with GCMS analyses, planchet as used in radiochemistry.
Record: **Result**	If there is any ambiguity about which analysis underlies this result, the Lab_Analysis_ID of this analysis. Example: In CLP Inorganics, to identify from which of several dilutions the reported result is chosen.

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DATA ELEMENT	DESCRIPTION
Lab_Analyte_ID	
Format: Identifier	*For traceability*
Record: **Result**	The lab's code for the analyte. This code gives traceability into the lab's systems.
Record: **Analyte**	Same as in a Result record.
Record: **Peak_Comparison**	Lab_Analyte_ID for the analyte to compare to. If not specified, it is assumed to be the same as the analyte for the Peak record this Peak_Comparison record is in.
Record: **Analyte_Comparison**	Lab_Analyte_ID for the analyte to compare to.
Lab_Contact	
Format: Text	
Record: **Sample_and_Method**	The person at the lab to contact with questions about this data.
Lab_Contract	
Format: Text	
Record: **Sample_and_Method**	Contract number under which the lab analyzes the samples. Client defined.
Lab_Data_Package_ID	
Format: Identifier	
Record: **Sample_and_Method**	Lab's code for the data package this data is part of. This code applies to a single deliverable. Use Lab_Reporting_Batch for the logical notion of a group of samples reported as a unit. For example, a document number the lab assigns to the physical data package or a file name for an electronic deliverable.
Lab_Data_Package_Name	
Format: Text	
Record: **Sample_and_Method**	Lab's title for the data package this data is part of.
Lab_Data_Package_Version	
Format: Text	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	If the lab resubmits a data package, this field can be used to distinguish the different versions.
Lab_ID	
Format: Limited_List	*Required*
Record: **Sample_and_Method**	Identifier for the lab doing this analysis. Often client defined.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Lab_Manager	
Format: Text	
Record: **Sample_and_Method**	The person at the lab who takes final responsibility for this data.
Lab_Manager_Title	
Format: Text	
Record: **Sample_and_Method**	The corporate title of the Lab_Manager.
Lab_Method_ID	
Format: Identifier	*For Traceability*
Record: **Sample_and_Method**	The lab's code for the method used. Unlike the Client_Method_ID, this ID is only used to identify work done in the context of a lab defined sample, so it need not have a globally defined meaning by itself.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Lab_Method_Name	
Format: Text	
Record: **Sample_and_Method**	The lab's descriptive name for this method.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Lab_Name	
Format: Text	
Record: **Sample_and_Method**	Descriptive name for the lab doing this analysis. Often lab defined.
Record: **Instrument_QC**	Same as in Sample_and_Method records.
Lab_Narrative_ID	
Format: Identifier	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Lab's code for any narrative document associated with this data.
Lab_Qualifier	
Format: Limited_List	*Repeats OK*
Record: **Result**	A result qualifier code assigned by the lab, based on client defined rules and values. This field may repeat as many times as needed to report multiple codes per result.
Record: **Analyte**	Same as in the Result record.
Record: **Peak**	Same as in the Result record.
Record: **Analyte_Comparison**	Same as in the Result record.
Record: **Peak_Comparison**	Same as in the Result record.
Lab_Qualifiers	
Format: Limited_List	
Record: **Result**	A string of single letter result qualifiers assigned by the lab, based on client defined rules and values.
Record: **Analyte**	Same as in the Result record.
Record: **Peak**	Same as in the Result record.
Record: **Analyte_Comparison**	Same as in the Result record.
Record: **Peak_Comparison**	Same as in the Result record.
Lab_Reanalysis_Suffix	
Format: Identifier	*For Traceability*
Record: **Sample_and_Method**	If the client wants results for reanalyses done by this method to be reported separately, the lab defined code to help identify the reanalysis. The Lab_Method_ID, Lab_Sample_ID and Lab_Reanalysis_Suffix together should uniquely identify the data associated with this record.
Lab_Receipt	
Format: Date	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Date the sample was received in the lab.
Lab Reported Format: Date Record: **Sample_and_Method**	Date these data were reported by the lab.
Lab_Reporting_Batch Format: Identifier Record: **Sample_and_Method**	An identifier for a batch of samples reported as a group by the lab. In addition to its use for administrative purposes, this batch can be used to link certain QC samples to regular ones, for example, a CLP storage blank. Example: Sample Delivery Group (SDG) as in the CLP.
Lab_Result_Status Format: Limited_List Record: **Sample_and_Method**	Lab assigned status, such as preliminary or final, for results for this sample and method. A client might define allowed values for this field.
Record: **Result**	Lab assigned status, such as preliminary or final, for this result. A client might define allowed values for this field.
Lab_Sample_ID Format: Identifier Record: **Sample_and_Method**	*For Traceability* Lab's identifier for a sample. This code is the primary link into the lab's record keeping system. It is not necessarily one-to-one with the Client_Sample_ID.
Level Format: Limited_List Record: **Sample_and_Method**	Approximate level of analytes in the sample, usually specified in client defined concentration ranges and determined via a screening procedure. Examples: Low, Medium, High.
Location_ID Format: Identifier	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Identifier for the sampling location at a site. Often client defined. Examples: Operable unit, well, tank, station, facility (building), installation, aggregate area.
Location_Name Format: Text Record: **Sample_and_Method**	Descriptive name for the sampling location at a site. May be lab defined. Examples: Operable unit, well, tank, station, facility (building), installation, aggregate area.
Lot_Number Format: Text Record: **Cleanup**	Manufacturer's batch number for something used in this cleanup. Example: Florisil cartridge lot number.
Mass_Charge_Ratio Format: Numeric Record: **Peak**	The mass/charge relationship recorded in MS detection.
Record: **Peak_Comparison**	Same as in a Peak record.
Matrix_ID Format: Limited_List Record: **Sample_and_Method**	*Required* A code for the sample matrix or media (e.g., soil, water). Should be client defined. This value, combined with the Client_Method_ID, defines to the reader method details that are implementation specific.
Matrix_Name Format: Text Record: **Sample_and_Method**	A description of the sample matrix or media. Often lab defined.
Melting_Point Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	The temperature at which the sample melts.
Melting_Point_Units Format: Limited_List Record: **Sample_and_Method**	Units for Melting_Point.
Method_Batch Format: Identifier Record: **Sample_and_Method**	An identifier for a batch of samples analyzed by one method and treated as a group for QC purposes. A method batch should group samples with similar matrices and potential interferences. This is a broader grouping than a preparation batch. In particular, a reanalysis of a sample stays in the same method batch, while it is likely to be in a different preparation batch. Operationally, this batch associates sample dependent QC such as duplicates and matrix spikes with a group of samples. Example: All samples of one matrix and level, analyzed by a CLP semivolatiles method and reported in one SDG.
Organism_Class Format: Limited_List Record: **Sample_and_Method**	A broad classification of a sample organism. Not necessarily intended to be the taxonomic class, but that is a possible value. Example: Animal, Commercial Animal, Fish, or Plant.
Organism_Length Format: Numeric Record: **Sample_and_Method**	Length of an organism.
Organism_Length_Units Format: Limited_List Record: **Sample_and_Method**	Units for Organism_Length.

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DATA ELEMENT	DESCRIPTION
Organism_Portion Format: Limited_List Record: **Sample_and_Method**	Portion of an organism used for analysis.
Organism_Sex Format: Limited_List Record: **Sample_and_Method**	Sex of an organism: Male or Female.
Original_Client_Reanalysis_Type Format: Limited_List Record: **Sample_and_Method**	*Conditionally Required* For a method QC sample with QC_Category Duplicate, Serial_Dilution, Spike or Spike_Duplicate there must be an associated regular sample the QC sample is derived from. This sample is called the original. The value of Original_Client_Reanalysis_Type matches that of the Client_Reanalysis_Type for this original sample.
Original_Client_Sample_ID Format: Identifier Record: **Sample_and_Method**	*Conditionally Required* For a method QC sample of QC_Category Duplicate, Serial_Dilution, Spike or Spike_Duplicate there must be an associated regular sample the QC sample is derived from. This sample is called the original. The value of Original_Client_Sample_ID matches that of the Client_Sample_ID for this original sample. For a method QC sample of QC_Category Blank_Spike_Duplicate, the value of Original_Client_Sample_ID matches that of the Client_Sample_ID for the associated Blank_Spike.
Original_Lab_Reanalysis_Suffix Format: Identifier Record: **Sample_and_Method**	*For Traceability* For a method QC sample with QC_Category Duplicate, Serial_Dilution, Spike or Spike_Duplicate there must be an associated regular sample the QC sample is derived from. This sample is called the original. The value of Original_Lab_Reanalysis_Suffix matches that of the Lab_Reanalysis_Suffix for this original sample.
Original_Lab_Sample_ID	

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DATA ELEMENT	DESCRIPTION
Format: Identifier Record: **Sample_and_Method**	For a method QC sample with QC_Category Duplicate, Serial_Dilution, Spike or Spike_Duplicate there must be an associated regular sample the QC sample is derived from. This sample is called the original. The value of Original_Lab_Sample_ID matches that of the Lab_Sample_ID for this original sample. For a method QC sample with QC_Category Blank_Spike_Duplicate, the value of Original_Lab_Sample_ID matches that of the Lab_Sample_ID for the associated Blank_Spike.
Peak_ID	
Format: Identifier Record: **Result**	*Conditionally Required* If there is any ambiguity about which peak underlies this result, the Peak_ID of that peak.
Record: **Analyte**	If there is any ambiguity about which peak underlies this analyte's result, the Peak_ID of that peak.
Record: **Peak**	A lab specified value, possibly based on client specified rules, that identifies a peak associated with an analyte. Peak_ID is conceptually similar to Client_Analyte_ID, except it identifies a peak rather than an analyte. Its value should be unique among all peaks for one analyte, but not necessarily have physical meaning. Examples: nominal mass for GCMS peaks, integer wavelength for ICP peaks, sequence number (1,2,...) for multicomponent GC peaks.
Record: **Peak_Comparison**	Peak identifier for the peak to compare to. It is combined with the Lab_Analyte_ID in the same Peak_Comparison record to fully specify the peak to compare to.
Percent_Breakdown	
Format: Numeric Record: **Analyte**	The percent breakdown (DDT/Endrin) reported for CLP pesticides.

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DATA ELEMENT	DESCRIPTION
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Percent_Difference	
Format: Numeric	
Record: **Result**	The difference between two measured values as percentage of one of them. The denominator value is usually the more certain one, although details can be method specific. Used with method QC of QC_Category Serial Dilution.
Record: **Analyte**	Same as in Result records except applied to the results of analyses in an analysis group rather than a QC sample and original pair.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Record: **Peak_Comparison**	Same as in a Result record except used to compare values in two Peak_Comparison records.
Percent_Match	
Format: Numeric	
Record: **Analyte**	Percent match of an analyte as compared with a library mass spectrum.
Percent_Moisture	
Format: Numeric	
Record: **Sample_and_Method**	Percent of sample composed of water.
Record: **Handling**	Percent of sample composed of water after the handling described by this record.
Percent_Phase	
Format: Numeric	
Record: **Sample_and_Method**	Percent of sample in analyzed phase. This field may generalize ones like Percent_Solids.
Record: **Handling**	Percent of sample in analyzed phase after the handling described by this record.

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DATA ELEMENT	DESCRIPTION
Percent_Preparation_Error	
Format: Numeric	
Record: **Analysis**	Same as in a Result record, except applies to all results from this analysis.
Record: **Result**	The uncertainty introduced into the final result by all lab activities other than instrumental analysis. Expressed as a percentage of the result value at one sigma.
Record: **Analyte**	Same as in a Result record.
Percent_Ratio	
Format: Numeric	
Record: **Peak_Comparison**	The response of the peak this Peak_Comparison record is in as a percentage of the response of the peak identified by the Peak_ID and Lab_Analyte_ID in this record. Used with mass spectral peaks in System Monitoring Compounds.
Percent_Recovery	
Format: Numeric	
Record: **Result**	For method QC of QC_Category Blank_Spike and Blank_Spike_Duplicate, the result as a percentage of the amount added. For method QC of QC_Category Spike and Spike_Duplicate, the spiked result minus the original result as a percentage of the amount added.
Record: **Analyte**	Same as in Result records except applied to the results from an analysis or analyses in an analysis group rather than a QC sample and original pair.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Percent_Relative_Abundance	
Format: Numeric	
Record: **Peak**	The response of this peak as a percentage of the largest peak response for this analyte.

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DATA ELEMENT	DESCRIPTION
Percent_Relative_Standard_Deviation	
Format: Numeric	
Record: **Analyte**	The standard deviation as a percentage of the mean. Used for an analyte in an Analysis_Group record.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Record: **Peak_Comparison**	Same as in an Analyte record except applied to Peak_Comparison values.
Percent_Solids	
Format: Numeric	
Record: **Sample_and_Method**	Percent of the sample composed of solid material.
Record: **Handling**	Percent of the sample composed of solid material after the handling described by this record.
Percent_Valley	
Format: Numeric	
Record: **Analyte**	The valley between this analyte and another one, as a percentage of the height of the shorter one. The second analyte is assumed to be known based on the method.
Record: **Peak_Comparison**	The valley between the peak this Peak_Comparison record is in and the peak identified by the Peak_ID and Lab_Analyte_ID in this record as a percentage of the height of the shorter one.
pH	
Format: Numeric	
Record: **Sample_and_Method**	The negative of the logarithm of the hydrogen ion potential.
Record: **Handling**	Same as in a Sample_and_Method record.
Phase_Analyzed	
Format: Limited_List	
Record: **Sample_and_Method**	That portion of a multiphase sample actually analyzed.

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DATA ELEMENT	DESCRIPTION
Preparation_Batch Format: Identifier Record: **Analysis**	An identifier for a batch of aliquots that are prepared together. For methods with no processing prior to analysis, the preparation batch can be simply a group of aliquots selected for analysis at roughly the same time. Preparation batches are used to link analyses of regular samples with lab generated method QC samples of QC_Category Blank, Blank_Spike and Blank_Spike_Duplicate, such as method blanks, lab control samples and duplicate lab control samples.
Preparation_Type Format: Limited_List Record: **Analysis**	A client defined code for the basic type of preparation done. Example: Extraction technique for semivolatiles. Could be a 3000 series SW-846 method code.
Prepared Format: Date Record: **Analysis**	Preparation date. Preparation is used generally to include method specific techniques such as extraction, digestion and separation.
Preservative Format: Text Record: **Sample_and_Method**	Preservative added to the sample.
Preserved_By Format: Text Record: **Sample_and_Method**	Organization that added preservative to the sample.
Priority_ID Format: Limited_List Record: **Sample_and_Method**	Client's code that identifies the priority assigned to this data. The priority may affect the desired turn around time and the cost of analysis.

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DATA ELEMENT	DESCRIPTION
	Examples: Rush or quick turn around work.
Procedure_ID Format: Identifier Record: **Analysis**	Identifier for the lab's procedure (SOP) for this analysis.
Record: **Handling**	Identifier for the lab's procedure (SOP) for this handling.
Record: **Cleanup**	Identifier for the lab's procedure (SOP) for this cleanup.
Procedure_Name Format: Text	
Record: **Analysis**	Description of the lab's procedure (SOP) for this analysis.
Record: **Handling**	Description of the lab's procedure (SOP) for this handling.
Record: **Cleanup**	Description of the lab's procedure (SOP) for this cleanup.
Project_ID Format: Identifier Record: **Sample_and_Method**	Identifier for the project this sample is a part of. Often client defined. Typically, a project consists of samples from one site collected over some defined period of time. Examples: Case no, Episode, Sampling round.
Project_Name Format: Text Record: **Sample_and_Method**	Descriptive name for the project this sample is a part of. May be lab defined. Examples: Case no, Episode, Sampling round.

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DATA ELEMENT	DESCRIPTION
QC_Category Format: Limited_List Record: **Sample_and_Method**	*For Portability* DEEMS defined code that specifies basic properties of a method QC sample. In a Sample_and_Method record, allowed values, with case ignored, are: Blank -- A QC sample with 'nothing' in it. Examples: Field, equipment, method (reagent), sulfur, and storage blanks. Blank_Spike -- A QC sample with a known amount added to a blank. Examples: lab control sample, QC check samples and interference check samples. Duplicate -- A reanalysis of a regular sample done for QC purposes. Examples: duplicates and splits. Blank_Spike Duplicate -- A reanalysis of a Blank_Spike. Serial_Dilution -- A dilution and reanalysis of a regular sample done for QC purposes. Spike -- A reanalysis of a regular sample with a known amount added and done for QC purposes. Examples: matrix spikes, post digestion spikes and analytical spikes. Spike_Duplicate -- A second reanalysis of a regular sample with a known amount added and done for QC purposes. There must be another sample with QC_Category "Spike" with the same original sample.
QC_Linkage Format: Limited_List Record: **Sample_and_Method**	*For Portability of QC* For a method QC sample, specifies which batch is the basis for the association between the QC sample and regular ones. Allowed values, ignoring case, include the following fields that define batches:

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DATA ELEMENT	DESCRIPTION
	Sampling_Batch Equipment_Batch Shipping_Batch Lab_Reporting_Batch Method_Batch Handling_Batch Preparation_Batch Analysis_Batch If QC_Linkage is 'Handling_Batch', there should be a Handling_Type field in the Sample_and_Method record whose value clarifies which type of handling batch is intended. Example: In a Sample_and_Method record, if the QC_Type is Lab_Duplicate, the QC_Category is Duplicate and the QC_Linkage is Method_Batch, a reader knows that this data for is a client defined type of QC called a Lab_Duplicate, that it is processed with rules typical for Duplicates and that it is to be associated with other Sample_and_Method records with the same value for the Method_Batch field. QC_Linkage is most useful if the batch it names is a required field in appropriate records, based on implementation rules. The correct linkage for a field QC sample may not be known to the lab, so must be merged with lab data at a later time.
Record: **Instrument_QC**	Same as in a Sample_and_Method Record except allowed values for instrument QC, ignoring case, are Cleanup_Batch, Preparation_Batch, Analysis_Batch and Run_Batch. If QC_Linkage is 'Cleanup_Batch', there should be a Cleanup_Type field in the Instrument_QC record whose value clarifies which type of cleanup batch is intended.
QC_Type	

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DATA ELEMENT	DESCRIPTION
Format: Limited_List	
Record: **Sample_and_Method**	For a method QC sample, the client's code for the type of QC. In the context of the Client_Method_ID and Matrix_ID, this code determines all special processing rules for the QC sample. The presence of this field in the Sample_and_Method record with a value allowed by the implementation defines the sample as a method QC sample. A lab may not know that certain samples are field QC. In this case the lab reports them as regular samples and their type is changed later, possibly by the validator.
Record: **Instrument_QC**	For instrument QC, a client defined code that specifies what type of instrument QC data follows. In the context of the Client_Method_ID, the value must imply enough detail for the reader to understand the method specific details of the following Analysis_Group, Analysis, Cleanup, Analyte, Peak, Peak_Comparison and Analyte_Comparison records.
Quantitation_Limit	
Format: Numeric	
Record: **Result**	Quantitation limit for the analyte being measured.
Record: **Analyte**	Same as in a Result record extended to anything considered to be the result of any analysis. Within an Analysis_Group record, applies to a mean or other value computed from several analyses.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Quantitation_Limit_Type	
Format: Limited_List	
Record: **Result**	One of a list of client defined acronyms that specify the type of quantitation limit. Examples: CRQL, PQL, SQL.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.

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DATA ELEMENT	DESCRIPTION
Quantitation_Limit_Units	
Format: Limited_List	
Record: **Result**	Units for Quantitation_Limit. If the client specifies that the Quantitation_Limit_Units must be the same as the Result_Units, the Quantitation_Limit_Units need not be specified.
Record: **Analyte**	Same as in a Result record
Record: **Peak**	Same as in a Result record.
Quench	
Format: Numeric	
Record: **Analysis**	Result of quench calculation for scintillation counters.
Refractive_Index	
Format: Numeric	
Record: **Sample_and_Method**	Refractive index of sample.
Relative_Percent_Difference	
Format: Numeric	
Record: **Result**	The absolute value of the difference of two values as a percentage of their average. Used with method QC of QC_Category Duplicate, Spike_Duplicate and Blank_Spike_Duplicate.
Record: **Analyte**	Same as in Result records except applied to the results of analyses in an analysis group rather than a QC sample and original pair.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Record: **Peak_Comparison**	Same as in a Result record except used to compare values in two Peak_Comparison records.
Relative_Response_Factor	
Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analyte**	The relative response factor for this analyte, based on the assumption that the method specifies the analyte to compare to and which peaks to use.
Record: **Peak_Comparison**	The relative response factor of the peak this Peak_Comparison record is in compared to the peak identified by the Peak_ID and Lab_Analyte_ID in this record. A relative response factor is the ratio of two response factors, one for each peak. A response factor is the ratio of a response to an amount added.
Requestor_ID Format: Identifier Record: **Sample_and_Method**	An identifier for the organization that requested that this sample be analyzed. May not be the same as the client, which specifies the SOW to follow.
Requestor_Name Format: Text Record: **Sample_and_Method**	A name for the organization that requested that this sample be analyzed.
Required_Detection_Limit Format: Numeric Record: **Result**	A contractually specified upper limit for the detection limit for the analyte being measured. Depending on client and method specific rules, required detection limits might be scaled by factors such as dilution and percent moisture prior to reporting.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Required_Detection_Limit_Units Format: Limited_List Record: **Result**	Units for Required_Detection_Limit. If the client specifies that the Required_Detection_Limit_Units must be the same as

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DATA ELEMENT	DESCRIPTION
	the Result_Units, the Detection_Limit_Units need not be specified.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Residue Format: Numeric Record: **Analysis**	Solid material remaining after preparation of an aliquot.
Residue_Units Format: Limited_List Record: **Analysis**	Units for Residue.
Resolution Format: Numeric Record: **Analysis**	A possibly sample and method dependent estimate of the resolution of the instrument used in the analysis. For example, in isotopic alpha spectroscopy, the width of the tracer peak.
Record: **Analyte**	A possibly sample and method dependent estimate of the resolution of the instrument that applies to the analysis and analyte.
Record: **Peak**	Resolution for this peak. Details of how resolution is computed depend on the method.
Resolution_Units Format: Limited_List Record: **Analysis**	Units for Resolution.
Record: **Analyte**	Units for Resolution.
Record: **Peak**	Units for Resolution.
Response Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analyte**	Response from a detector. Can be any type of response from ICP, AA, GC, MS, etc. Often, these are unitless numbers relating to a signal from the detector. Examples: Area, height, count rate.
Record: **Peak**	Same as in an Analyte record, except for a single peak. Example: individual Aroclor peak concentrations used for CLP reporting.
Response_Units	
Format: Limited_List	
Record: **Analyte**	Units for Response.
Record: **Peak**	Units for Response.
Result	
Format: Numeric	
Record: **Result**	Reportable result for the analyte. Example: Concentration.
Record: **Analyte**	Same as in a Result record extended to anything considered to be the result of any analysis. Within an Analysis_Group record, applies to a mean or other value computed from several analyses.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Result_Limit_Lower	
Format: Numeric	
Record: **Result**	Lower limit for a result based on external knowledge about the sample. Units are the same as for Results.
Record: **Analyte**	Same as in the Result record.
Result_Limit_Upper	
Format: Numeric	
Record: **Result**	Upper limit for a result based on external knowledge about the sample. Units are the same as for Results.

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DATA ELEMENT	DESCRIPTION
Record: **Analyte**	Same as in the Result record.
Result_Units	
Format: Limited_List	
Record: **Result**	Units for Result.
Record: **Analyte**	Same as in a Result record.
Record: **Peak**	Same as in a Result record.
Retention_Time	
Format: Numeric	
Record: **Result**	The time between injection and detection for mobile phase separation techniques such as GC and HPLC. (Time format hh:mm:ss is not allowed.) In a result record, this is the retention time from the analysis underlying this result.
Record: **Analyte**	Same as in a result record. Used when there is a well defined retention time for the analyte, not just for a peak measurement for the analyte. For example, this applies to GCMS analyses.
Record: **Peak**	Same as in a Result record except for a single peak. Used with techniques like GC where there can be multiple peaks with different retention times for one analyte.
Retention_Time_High	
Format: Numeric	
Record: **Analyte**	High limit for a retention time window. Units are specified with Retention_Time_Units.
Record: **Peak**	Same as in an Analyte record, except for a single peak.
Retention_Time_Low	
Format: Numeric	
Record: **Analyte**	Low limit for a retention time window. Units are specified with Retention_Time_Units.
Record: **Peak**	Same as in an Analyte record, except for a single peak.

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DATA ELEMENT	DESCRIPTION
Retention_Time_Units	
Format: Limited_List	
Record: **Result**	Units for Retention_Time.
Record: **Analyte**	Units for Retention_Time.
Record: **Peak**	Units for Retention_Time.
Run_Batch	
Format: Identifier	
Record: **Analysis**	An identifier for a batch of analyses that make up a run, a sequence of analyses during which the instrument is continuously in control. Example: A batch of samples analyzed on one instrument under the control of one initial calibration or similar Instrument_QC.
Sample_Amount	
Format: Numeric	
Record: **Sample_and_Method**	Weight or volume of sample as received by the lab.
Record: **Handling**	Weight or volume of sample after the handling described by this record.
Sample_Amount_Units	
Format: Limited_List	
Record: **Sample_and_Method**	Units for Sample_Amount.
Record: **Handling**	Units for the Sample_Amount.
Sampling_Batch	
Format: Identifier	
Record: **Sample_and_Method**	An identifier for a batch of samples collected together. Operationally, this batch associates a field blank with a group of samples. This value is currently often not known to the lab. It might be merged with lab data by a validator.
Screen_Value	
Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Result from a screening analysis of the sample, as in an alpha particle screen.
Screen_Value_Units Format: Limited_List Record: **Sample_and_Method**	Units for Screen_Value.
Services_ID Format: Identifier Record: **Sample_and_Method**	Client's code for optional services performed for this data. This includes nonstandard work, such as modified detection limits, or changed QC requirements. Examples: Special Analytical Services (SAS) number or Analytical Service Level.
Shipping_Batch Format: Identifier Record: **Sample_and_Method**	An identifier for a batch of samples shipped together, such as in the same crate, cooler or ice chest. Operationally, this batch associates a trip blank with a group of samples. This value, as defined by the shippers, is currently often not known to the lab. It might be merged with lab data by a validator.
Site_ID Format: Identifier Record: **Sample_and_Method**	Identifier for the broadly defined site where the sample was collected. Often client defined.
Site_Name Format: Text Record: **Sample_and_Method**	Descriptive name for the broadly defined site where the sample was collected. May be lab defined.
Standard_Deviation Format: Numeric	

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DATA ELEMENT	DESCRIPTION
Record: **Analyte**	The standard deviation of several measurements of one analyte. Used for an analyte in an Analysis_Group record.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Record: **Peak_Comparison**	Same as in an Analyte record when reporting peak comparisons.
Standard_Deviation_Units	
Format: Limited_List	
Record: **Analyte**	Units for Standard_Deviation. If the client specifies that the Standard_Deviation_Units must be the same as the Result_Units, the Standard_Deviation_Units need not be specified.
Record: **Peak**	Same as in an Analyte record when results are measured per peak.
Record: **Peak_Comparison**	Same as in an Analyte record except applied to Peak_Comparison values.
Standard_ID	
Format: Identifier	
Record: **Analysis**	Lab's identification for a standard, such as a spiking material, used in this analysis.
Standard_Source	
Format: Text	
Record: **Analysis**	Source for a standard used in this analysis.
Suspended_Solids	
Format: Numeric	
Record: **Sample_and_Method**	Solids remaining on the filter paper after filtration of a water or other liquid sample.
Record: **Handling**	Same as in a Sample_and_Method record.
Suspended_Solids_Units	
Format: Limited_List	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Units for Suspended_Solids.
Record: **Handling**	Units for Suspended_Solids.
Temperature Format: Numeric Record: **Sample_and_Method**	Temperature of the sample as received.
Temperature_units Format: Limited_List Record: **Sample_and_Method**	Units for temperature.
Texture Format: Limited_List Record: **Sample_and_Method**	Descriptive information about a solid sample. Example: Fine, medium and coarse; or: boulder, pebble and sand; or: round and angular; or uniform and irregular.
Record: **Handling**	Descriptive information about a solid sample after the handling described by this record.
Turbidity Format: Numeric Record: **Sample_and_Method**	Turbidity of the sample.
Turbidity_Units Format: Limited_List Record: **Sample_and_Method**	Units for Turbidity.
Validated Format: Date Record: **Sample_and_Method**	Date validation completed.
Validation_Qualifier Format: Limited_List Record: **Result**	*Repeats OK* A result qualifier code assigned by the validator, based on client defined rules and values. This field is only used with results for regular samples. This field may

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DATA ELEMENT	DESCRIPTION
	repeat as many times as needed per result to report multiple codes.
Validation_Qualifiers Format: Limited_List Record: **Result**	A string of single letter result qualifiers assigned by the validator, based on client defined rules and values. This field is only used with results for regular samples.
Validator_Address Format: Text Record: **Sample_and_Method**	*Repeats OK* Address of the validator doing the validation. May repeat in one record as needed to report a multi-line address.
Validator_Contact Format: Text Record: **Sample_and_Method**	The person at the validator to contact with questions about this data.
Validator_Contract Format: Text Record: **Sample_and_Method**	Contract number under which the validator validates the samples. Client defined.
Validator_Data_Package_ID Format: Identifier Record: **Sample_and _Method**	Validator's code for the data package this data is part of.
Validator_Data_Package_Name Format: Text Record: **Sample_and_Method**	Validator's title for the data package this data is part of.
Validator_Data_Package_Version Format: Text Record: **Sample_and_Method**	If the validator resubmits a data package, this field can be used to distinguish the different versions.
Validator_ID Format: Limited_List	

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DATA ELEMENT	DESCRIPTION
Record: **Sample_and_Method**	Identification for the validator doing the validation. Often client defined. This and other 'validator_' fields are not typically known to the lab. They are included for use by validators who might receive a lab EDD, validate it and pass on an updated EDD to the client.
Validator_Manager Format: Text Record: **Sample_and_Method**	The person at the validator who takes final responsibility for this data.
Validator_Manager_Title Format: Text Record: **Sample_and_Method**	The corporate title of the Validator_Manager.
Validator_Method_ID Format: Identifier Record: Sample_and_Method	The validator's code for the work it does.
Validator_Method_Name Format: Text Record: **Sample_and_Method**	The validator's descriptive name for the work it does when validating data analyzed by this method.
Validator_Name Format: Text Record: **Sample_and_Method**	Descriptive name for the validator doing the validation. Often validator defined.
Validator_Narrative_ID Format: Identifier Record: **Sample_and_Method**	Validator's code for any narrative document associated with this data.
Validator_Receipt Format: Date Record: **Sample_and_Method**	Date sample data received by the validator.
Validator_Reported	

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DATA ELEMENT	DESCRIPTION
Format: Date	
Record: **Sample_and_Method**	Date this work reported by the validator.
Wavelength	
Format: Numeric	
Record: **Peak**	The wavelength used for an analytical measurement; e.g., UV/vis, GFAA and ICP.
Record: **Peak_Comparison**	Same as in a Peak record.
Wavelength_Units	
Format: Limited_List	
Record: **Peak**	Units for Wavelength.
Record: **Peak_Comparison**	Units for Wavelength.
Yield	
Format: Numeric	
Record: **Analysis**	A measure of the success of the preparation part of the method as a percent. For radiochemistry, the number of atoms of interest making it through sample preparation as a percentage of the number in the aliquot.

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Appendix E

Equivalency Checklists

The *Checklist for Initial Demonstration of Method Performance*, *Checklist for Continuing Demonstration of Method Performance*, and *Certification Statement* (collectively called "Checklists") and instructions for their completion are provided in this appendix. The Checklists, as 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 methods approval program; these categories will be indicated by "NA" (not applicable). The EMMC instructions have been annotated to clarify each checklist item's applicability to the streamlined methods approval program. Annotated sections are highlighted within text boxes as shown in Figure E-1.

Streamlining:

Annotated instructions.

Figure E-50. Example Annotated Box

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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 & 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)				

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Initial Demonstration of Method Performance *(1)*				
Category	**Performance Criteria *(2)* Based on**		**Results Obtained**	**Perf. Spec. Achieved (✓)**
	Measurement Quality Method	**Reference Objective**		
8. Sample(s) used in initial demonstration have recommended preservative, where applicable.				
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				

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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)				
27. Bias (analyte by analyte)				
28. Detection Limit (w/ units; analyte by analyte)				
29. Confirmation of Detection Limit, if applicable				
30. Quantitation Limit (w/ units: analyte by analyte)				
31. Qualitative Confirmation				
32. Frequency of performance of the Initial Demonstration				
33. Other criterion (specify)				
34. Other criterion (specify)				

[1] Provide a detailed narrative description of the initial demonstration.

[2] 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.

[3] 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):

_____ _____ _____

Name **Signature** **Date**

_____ _____ _____

Name **Signature** **Date**

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_____	_____	_____
Name	**Signature**	**Date**

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

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Checklist for Continuing 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 & 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.)

Continuing Demonstration of Method Performance				
Category	**Required Frequency**	**Specific Perf. Criteria**	**Results Obtained**	**Perf. Spec. Achieved (✓)**
1. Method blank result (taken through all steps in the procedure)				
2. Concentrations of calibration standards used to verify working range (with units), where applicable				
3. Calibration verification				
4. Laboratory Control Sample				
5. External QC sample (where available)				
6. Performance evaluation (PE) studies, if applicable Latest study sponsor and title: Latest study number:				
7. List analytes for which results were "not acceptable" in PE study	----	----	----	----
8. Surrogates used, if applicable				
9. Concentration of surrogates, if applicable				
10. Recovery of surrogates (acceptance range for multi-analyte methods), if applicable				
11. Matrix				
12. Matrix spike compounds				

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Continuing Demonstration of Method Performance				
Category	**Required Frequency**	**Specific Perf. Criteria**	**Results Obtained**	**Perf. Spec. Achieved (✓)**
13. Concentration of matrix spike compounds				
14. Recoveries of matrix spike compounds				
14a. Recoveries of matrix spike duplicate compounds				
15. Qualitative identification criteria used				
16. Precision (analyte by analyte)				
17. Other category (specify)				
18. Other category (specify)				

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

_____ _____ _____
Name **Signature** **Date**

_____ _____ _____
Name **Signature** **Date**

_____ _____ _____
Name **Signature** **Date**

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

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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[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.

_____ _____

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.

[1] True: Consistent with supporting data.

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

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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.

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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.

Streamlining:

EMMC's definition of media is equivalent to Streamlining's 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.

Streamlining:

Under the streamlining, the term "new method" 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).

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* **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).

Streamlining:

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.

Streamlining:

Enter the matrix 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).

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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 :***

Streamlining:

Categories which do not apply to streamlining method validation will be marked with "NA".

#1. <u>Written Method</u> (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.

Streamlining:

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 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

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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.

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#11. <u>Qualitative identification criteria used</u>.

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. <u>Performance Evaluation Studies performed for analytes of interest, where available (last study sponsor and title:; last study number:)</u>.

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. <u>Analysis of external reference material</u>.

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.

Streamlining:

Analysis of a reference sample is one of streamlining's standardized QC elements. The most common reference sample is a Reference Material from the National Institute of Standards and Technology. EPA will provide further guidance on its streamlining reference sample program when EPA initiates its pilot study of the streamlined methods approval process.

#14. <u>Source of reference material</u>.

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. <u>Surrogates used if applicable</u>.

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.

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#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 attached 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 intermediatory 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”.

Streamlining:

Enter the same matrix as specified in the header.

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

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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 onto 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.

Streamlining:

Under streamlining, initial spikes, also known as initial precision and recovery (IPR) standards, will be performed in reagent water. Using reagent water will allow the comparison of IPR spike recoveries determined with the modified method against IPR criteria specified in the reference method because reference 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,

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difference from true, etc.), the numeric value with associated units for each analyte obtained for each analyte spiked in the initial demonstration procedure.

Streamlining:

Bias is not required under streamlining. 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).

Streamlining:

For method modifications, enter the detection limits specified in the reference method. For new methods, enter the calculated detection limits.

#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.

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#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.

Streamlining:

Under streamlining 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. For new methods, two sets of MS/MSD samples must be analyzed to provide sufficient data for QC acceptance criteria development.

#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.

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Continuing Demonstration of Capability Checklist:

The process by which a laboratory documents that their previously established performance of an analytical procedure continues to meet performance specifications as delineated in this checklist.

#1. Method Blank.

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.

#2. Concentrations of calibration standards used to verify working range, where applicable (include units).

The range of the concentrations of materials used to confirm the established 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). Enter the concentrations of the calibration standards.

#3. Calibration Verification.

A means of confirming that the previously determined calibration relationship still holds. This process typically involves the analyses of two standards with concentrations which bracket the concentrations measured in the sample/s. Enter the procedure to be used to verify the calibration and the results obtained for each analyte.

#4. Calibration check standard.

A single analytical standard introduced into the instrument as a means of establishing that the previously determined calibration relationship still holds. Enter the concentrations and result for each analyte.

#5. External QC sample (where applicable).

Enter the results of analyses for reference material (e.g., Quality Control samples/ampules) from a source different from that used to prepare calibration standards (where applicable). Enter the concentration, as well as, the source of this material. This performance category is

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of particular importance if Performance Evaluation studies are not available for the analytes of interest.

#6. <u>Performance Evaluation studies performed for analytes of interest, where available (Last study sponsor and title:; Last study number:).</u>

Several EPA Programs conduct periodic performance evaluation (PE) studies. Other organizations, outside of the Agency, also 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***.

 # 7. <u>List of analytes for which results were "not acceptable" in PE study</u>.

#8. <u>Surrogate Compounds used. if applicable</u>.

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. They are compounds not expected to be present in environmental samples. Surrogates are often used in analyses for organic analytes. Enter the names of the surrogate compounds in this performance category.

#9. <u>Concentration of surrogates (if applicable)</u>.

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

#10. <u>Recoveries of Surrogates appropriate to the proposed use (if applicable)</u>.

Enter the summary of the surrogate recovery limits and attached a detailed listing (each surrogate compound), if more space is needed.

#11. <u>Matrix (reagent water, drinking water, soil, waste solid, air, etc.).</u>

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".

#12. <u>Matrix Spike Compounds</u>.

In preparing a matrix spike a known amount of analyte is added to an aliquot of a real-world sample matrix. This aliquot is analyzed to help evaluate the effects of the sample matrix on the analytical procedure. Matrix spike results are typically used to calculate recovery of analytes as a measure of bias for that matrix. Enter the analytes spiked.

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#13. Matrix Spike Concentrations (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.

#14. Recovery of Matrix Spike (w/units).

The ratio of the standard deviation of a series of at least three measurements to the mean of the measurements. This value is often expressed as a percentage of the mean.

Note: Some programs/projects have utilized matrix spike duplicates (a separate duplicate of the matrix spike) to help verify the matrix spike result and to provide precision data for analytes which are not frequently found in real-world samples, i.e., duplication of non-detects provides little information concerning the precision of the method.

#15. **Qualitative identification criteria used**.

Enter all relevant criteria used for identification, including such items as retention times, 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.

#16. 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.

#17. Clean-up Procedures.

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

#18. Confirmation.

Qualitative identification criteria used. Enter all relevant criteria used for identification, including such items as: retention time; use of second chromatographic column; use of second (different) analytical technique; spectral wavelengths, ion abundance rations. If the instrumental techniques for the Performance-based method are similar to 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.

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#19-20. Other.

Enter other necessary program/project specific method performance categories.

Signatures:

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

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This 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 at 40 CFR 141.24 (59 FR 62468), and proposed for use in wastewater (56 FR 62468) and 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.

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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*** **Page __of __**
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)***			*EPA Method 1613 Rev. B*	✔
3. Copy of the reference method, if applicable, maintained at facility				✔
4. Differences between the modified and reference method (if applicable) attached				*N/A*
5. Concentrations of calibration standards	*Attach 1*		*Attach 1*	✔
6. %RSD or correlation coefficient of calibration regression	*Attach 2*		*Attach 2*	✔
7. Performance range tested (with units)	*Attach 3*		*Attach 3*	✔
8. Sample(s) used in initial demonstration have recommended preservative, where applicable.				*N/A*

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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	*Attach 4*		*Attach 4*	✔
11. Qualitative identification criteria used	*Attach 5*		*Attach 5*	✔
12. Performance Evaluation studies performed for analytes of interest, where available: Latest study sponsor and title: Latest study number:			*John Doe, PE Study, 1234*	✔
13. Analysis of external reference material				*N/A*
14. Source of reference material				*N/A*
15. Surrogates used, if applicable	*Attach 6 & 8*		*Attach 6 & 8*	✔
16. Concentrations of surrogates, if applicable	*Attach 6 & 8*		*Attach 6 & 8*	✔
17. Recoveries of surrogates appropriate to the proposed use, if applicable	*Attach 6 & 8*		*Attach 6 & 8*	✔
18. Sample preparation	*Extraction*		*Extraction*	✔
19. Clean-up procedures				*N/A*
20. Method Blank Result	*Attach 8*		*Attach 8*	✔
21. Matrix (reagent water, drinking water, waste solid, etc.)			*Paper Mill Effluent*	✔
22. Spiking system, appropriate to method and application	*volumetric pipet*		*volumetric pipet*	✔
23. Spike concentrations (w/ units corresponding to final sample concentration)	*Attach 6*		*Attach 6*	✔

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Initial Demonstration of Method Performance *(1)*				
Category	**Performance Criteria *(2)* Based on**		**Results Obtained**	**Perf. Spec. Achieved (✓)**
	Measurement Quality Method	**Reference Objective**		
24. Source of spiking material			*Acme Standards lot #105 cat #41*	✔
25. Number of replicate spikes	*at least four*		*four*	✔
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*

[1] Provide a detailed narrative description of the initial demonstration.

[2] 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.

[3] 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**

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_____	_____	_____
Name	**Signature**	**Date**

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

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Certification Statement

Date: *February 2, 1994* **Page _1 of _1**
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 _____ *2/2/94*
Facility Manager's Name and Title Signature Date

John Doe, Chemist _____ *2/2/94*
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.

(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.

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Attachment 1
Concentration(s) of Calibration Solution(s)

Compound	Specification in Reference Method					Result Obtained
	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)	(Concentrations Used)
2,3,7,8-TCDD	0.5	2	10	40	200	Same
2,3,7,8-TCDF	0.5	2	10	40	200	Same
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	Same
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	Same
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	Same
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	Same
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	Same
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	Same
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	Same
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	Same
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	Same
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	Same
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	Same
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	Same
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	Same
OCDD	5.0	20	100	400	2000	Same
OCDF	5.0	20	100	400	2000	Same
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	Same
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	Same
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	Same
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	Same
$^{13}C_{12}$-OCDD	200	200	200	200	200	Same
Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200	Same
Internal Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	Same
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	Same

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Attachment 2
Percent Relative Standard Deviation (%RSD)

Compound	Specification in Reference Method (%)	Result Obtained (%)
2,3,7,8-TCDD	< 20	4.5
2,3,7,8-TCDF	< 20	7.3
1,2,3,7,8-PeCDD	< 20	3.6
1,2,3,7,8-PeCDF	< 20	2.7
2,3,4,7,8-PeCDF	< 20	2.8
1,2,3,4,7,8-HxCDD	< 20	5.5
1,2,3,6,7,8-HxCDD	< 20	2.0
1,2,3,7,8,9-HxCDD	< 20	2.8
1,2,3,4,7,8-HxCDF	< 20	1.6
1,2,3,6,7,8-HxCDF	< 20	3.0
1,2,3,7,8,9-HxCDF	< 20	4.4
2,3,4,6,7,8-HxCDF	< 20	5.4
1,2,3,4,6,7,8-HpCDD	< 20	5.6
1,2,3,4,6,7,8-HpCDF	< 20	4.1
1,2,3,4,7,8,9-HpCDF	< 20	3.4
OCDD	< 20	2.5
OCDF	< 20	1.9
$^{13}C_{12}$-2,3,7,8-TCDD	< 35	2.0
$^{13}C_{12}$-2,3,7,8-TCDF	< 35	3.0
$^{13}C_{12}$-1,2,3,7,8-PeCDD	< 35	5.1
$^{13}C_{12}$-1,2,3,7,8-PeCDF	< 35	6.8
$^{13}C_{12}$-2,3,4,7,8-PeCDF	< 35	6.1
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	< 35	8.1
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	< 35	1.7
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	< 35	7.8
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	< 35	3.3
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	< 35	8.9
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	< 35	4.8
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	< 35	5.0
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	< 35	4.9
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	< 35	8.3
$^{13}C_{12}$-OCDD	< 35	9.3
Cleanup Standard		
$^{37}Cl_4$-2,3,7,8-TCDD	< 35	15

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Attachment 3
Performance Range

Compound	Specification in Reference Method (pg/L)	Result Obtained (pg/L)
2,3,7,8-TCDD	10 - 4000	10 - 4000
2,3,7,8-TCDF	10 - 4000	10 - 4000
1,2,3,7,8-PeCDD	50 - 20,000	50 - 20,000
1,2,3,7,8-PeCDF	50 - 20,000	50 - 20,000
2,3,4,7,8-PeCDF	50 - 20,000	50 - 20,000
1,2,3,4,7,8-HxCDD	50 - 20,000	50 - 20,000
1,2,3,6,7,8-HxCDD	50 - 20,000	50 - 20,000
1,2,3,7,8,9-HxCDD	50 - 20,000	50 - 20,000
1,2,3,4,7,8-HxCDF	50 - 20,000	50 - 20,000
1,2,3,6,7,8-HxCDF	50 - 20,000	50 - 20,000
1,2,3,7,8,9-HxCDF	50 - 20,000	50 - 20,000
2,3,4,6,7,8-HxCDF	50 - 20,000	50 - 20,000
1,2,3,4,6,7,8-HpCDD	50 - 20,000	50 - 20,000
1,2,3,4,6,7,8-HpCDF	50 - 20,000	50 - 20,000
1,2,3,4,7,8,9-HpCDF	50 - 20,000	50 - 20,000
OCDD	100 - 40,000	100 - 40,000
OCDF	100 - 40,000	100 - 40,000

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Attachment 4
Specificity in Presence of Interferences

Compound	Specification in Reference Method (%)	Result Obtained (%)
1,2,3,4-TCDD	The height of the valley between the most closely eluted isomers and the 2,3,-7,8- isomers is less than 25 percent.	0
1,2,7,8-TCDD		0
1,4,7,8-TCDD		0
1,2,3,7-TCDD		0
1,2,3,8-TCDD		0
2,3,7,8-TCDD		0

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Attachment 5
Qualitative Identification Criteria

Criteria	Specification in Reference Method (%)	Specification Achieved (Y/N)
Mass-to-charge ratios (m/z's)	The signals for the two exact m/z's being monitored must be present and must maximize within ± 2 seconds of one another.	Y
Signal-to-noise ratios	The signal-to-noise ratio of each of the two exact m/z's must be greater than or equal to 2.5 for sample extracts and greater than or equal to 10 for calibration standards.	Y
Ion abundance ratios	The ratio of the integrated ion currents for the two exact m/z's being monitored must be within the limits of the table below.	Y

Theoretical Ion Abundance Ratios and QC Limits

Number of Chlorine Atoms	m/z's Forming Ratio	Theoretical Ratio	QC Limits (1)	
			Lower	Upper
4 (2)	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 (3)	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.05	0.88	1.20
7 (4)	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

(1) QC limits represent ± 15% windows around the theoretical ion abundance ratios.

(2) Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).

(3) Used for $^{13}C_{12}$-HxCDF only.

(4) Used for $^{13}C_{12}$-HpCDF only.

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Attachment 6

IPR Spike Levels, Surrogates Used, and Surrogate Recovery Limits

Compound	Spike Level (1) (ng/mL)	Concentration Found IPR-1 (ng/mL)	IPR-2 (ng/mL)	IPR-3 (ng/mL)	IPR-4 (ng/mL)
2,3,7,8-TCDD	10	9.5	9.9	9.9	10.0
2,3,7,8-TCDF	10	9.5	10.0	9.7	10.0
1,2,3,7,8-PeCDD	50	46.7	48.4	49.0	48.3
1,2,3,7,8-PeCDF	50	46.4	48.7	49.2	49.0
2,3,4,7,8-PeCDF	50	47.7	48.7	49.5	50.5
1,2,3,4,7,8-HxCDD	50	45.6	47.2	48.0	49.8
1,2,3,6,7,8-HxCDD	50	48.3	51.9	52.2	50.3
1,2,3,7,8,9-HxCDD	50	52.4	53.7	57.3	54.3
1,2,3,4,7,8-HxCDF	50	49.6	50.0	49.7	49.9
1,2,3,6,7,8-HxCDF	50	49.4	52.6	52.7	54.1
1,2,3,7,8,9-HxCDF	50	46.0	48.0	48.8	48.1
2,3,4,6,7,8-HxCDF	50	47.5	50.4	50.1	48.4
1,2,3,4,6,7,8-HpCDD	50	49.5	54.5	55.2	51.9
1,2,3,4,6,7,8-HpCDF	50	46.3	49.4	50.4	49.9
1,2,3,4,7,8,9-HpCDF	50	48.1	51.0	52.3	49.6
OCDD	100	98.4	115.9	106.4	107.0
OCDF	100	84.9	89.2	97.2	92.8
$^{13}C_{12}$-2,3,7,8-TCDD	100	77.6	80.2	83.6	82.7
$^{13}C_{12}$-2,3,7,8-TCDF	100	78.1	79.9	81.3	79.2
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	69.7	66.2	70.0	69.7
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	68.7	69.5	71.8	70.6
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	67.0	66.9	67.8	65.1
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	108.4	106.3	108.9	108.3
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	77.3	80.1	78.8	85.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	54.8	57.8	80.8	70.7
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	49.6	53.9	71.9	62.6
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	77.4	82.2	82.3	89.1
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	96.1	98.4	103.7	112.9
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	81.2	78.4	80.4	89.1
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	52.2	50.9	71.7	64.5
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	85.9	85.1	88.9	97.2
$^{13}C_{12}$-OCDD	200	133.1	120.3	132.6	146.2
$^{37}Cl_4$-2,3,7,8-TCDD	10	8.4	8.0	8.0	7.7

Note: The shaded compounds are the surrogates (labeled compounds) required by the reference method. The labeled compound recovery limits are 25 - 150%.

ALL NATIVE AND LABELED COMPOUNDS REQUIRED BY THE METHOD WERE SPIKED AT THE APPROPRIATE LEVEL.

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Attachment 7
IPR Precision and Recovery Limits

Compound	Specification in Reference Method (1) s (ng/mL)	Specification in Reference Method (1) X (ng/mL)	Specification in Reference Method (1) s (ng/mL)	Specification in Reference Method (1) X (ng/mL)
2,3,7,8-TCDD	1.1	8.0 - 12.5	0.2	9.8
2,3,7,8-TCDF	0.5	8.2 - 12.8	0.2	9.8
1,2,3,7,8-PeCDD	1.5	44.2 - 53.1	1.0	48.1
1,2,3,7,8-PeCDF	1.5	44.1 - 55.2	1.3	48.3
2,3,4,7,8-PeCDF	3.4	45.7 - 58.7	1.2	49.1
1,2,3,4,7,8-HxCDD	5.3	40.6 - 64.6	1.7	47.6
1,2,3,6,7,8-HxCDD	3.7	47.5 - 50.6	1.8	50.7
1,2,3,7,8,9-HxCDD	5.6	35.6 - 73.9	2.1	54.4
1,2,3,4,7,8-HxCDF	3.7	41.7 - 54.5	0.2	49.8
1,2,3,6,7,8-HxCDF	1.9	47.0 - 54.2	1.9	52.2
1,2,3,7,8,9-HxCDF	3.6	46.6 - 54.0	1.2	47.7
2,3,4,6,7,8-HxCDF	2.2	44.8 - 52.8	1.4	49.1
1,2,3,4,6,7,8-HpCDD	3.3	39.6 - 58.0	2.6	52.8
1,2,3,4,6,7,8-HpCDF	2.6	43.9 - 55.4	1.8	49.0
1,2,3,4,7,8,9-HpCDF	2.9	49.5 - 52.1	1.8	50.2
OCDD	11.3	73.8 - 149.1	7.2	106.9
OCDF	5.8	74.0 - 128.7	5.2	91.0
$^{13}C_{12}$-2,3,7,8-TCDD	16.0	25.0 - 150.0	2.7	81.0
$^{13}C_{12}$-2,3,7,8-TCDF	18.4	25.0 - 150.0	1.3	79.6
$^{13}C_{12}$-1,2,3,7,8-PeCDD	21.2	25.0 - 150.0	1.8	68.9
$^{13}C_{12}$-1,2,3,7,8-PeCDF	15.9	25.0 - 150.0	1.3	70.2
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20.1	25.0 - 150.0	1.1	66.7
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	18.7	25.0 - 150.0	1.1	108.0
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	24.1	25.0 - 150.0	3.3	80.3
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	14.5	25.0 - 150.0	12.0	66.0
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	11.5	25.0 - 150.0	9.9	59.5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	14.8	25.0 - 150.0	4.8	82.8
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	10.4	25.0 - 150.0	7.5	102.8
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	20.4	25.0 - 150.0	4.7	82.3
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	18.8	25.0 - 150.0	10.0	59.8
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	22.9	25.0 - 150.0	5.5	89.3
$^{13}C_{12}$-OCDD	43.9	50.0 - 300.0	10.6	133.0
$^{37}Cl_4$-2,3,7,8-TCDD	-	2.5 - 15.0	-	8.0

(1) s = standard deviation of the concentration, X = average concentration.

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Attachment 8
Method Blank

Compound	Specification in Reference Method (1)	Result Obtained
	pg/L	pg/L
2,3,7,8-TCDD	< 10	< 10
2,3,7,8-TCDF	< 10	< 10
1,2,3,7,8-PeCDD	< 50	< 50
1,2,3,7,8-PeCDF	< 50	< 50
2,3,4,7,8-PeCDF	< 50	< 50
1,2,3,4,7,8-HxCDD	< 50	< 50
1,2,3,6,7,8-HxCDD	< 50	< 50
1,2,3,7,8,9-HxCDD	< 50	< 50
1,2,3,4,7,8-HxCDF	< 50	< 50
1,2,3,6,7,8-HxCDF	< 50	< 50
1,2,3,7,8,9-HxCDF	< 50	< 50
2,3,4,6,7,8-HxCDF	< 50	< 50
1,2,3,4,6,7,8-HpCDD	< 50	< 50
1,2,3,4,6,7,8-HpCDF	< 50	< 50
1,2,3,4,7,8,9-HpCDF	< 50	< 50
OCDD	< 100	< 100
OCDF	< 100	< 100
	% Recovery	% Recovery
$^{13}C_{12}$-2,3,7,8-TCDD	25 - 150	76
$^{13}C_{12}$-2,3,7,8-TCDF	25 - 150	72
$^{13}C_{12}$-1,2,3,7,8-PeCDD	25 - 150	65
$^{13}C_{12}$-1,2,3,7,8-PeCDF	25 - 150	67
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25 - 150	61
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25 - 150	92
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25 - 150	86
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25 - 150	68
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	25 - 150	58
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25 - 150	104
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	25 - 150	75
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25 - 150	82
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25 - 150	69
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25 - 150	93
$^{13}C_{12}$-OCDD	25 - 150	73
Cleanup Standard		
$^{37}Cl_4$-2,3,7,8-TCDD	25 - 150	94

(1) For native analytes, the concentration found must be below the Minimum Level for that analyte.
For labeled compounds, the percent recovery must be within the limit of 25 - 150%.

Note: **All labeled compounds were spiked at the same level as for the IPR requirements.**

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Attachment 9
Minimum Levels

Compound	Specification in Reference Method (pg/L) (1)		Result Obtained
	Minimum Level (pg/L)	Signal-to-noise ratio	
2,3,7,8-TCDD	10	> 10	> 10
2,3,7,8-TCDF	10	> 10	> 10
1,2,3,7,8-PeCDD	50	> 10	> 10
1,2,3,7,8-PeCDF	50	> 10	> 10
2,3,4,7,8-PeCDF	50	> 10	> 10
1,2,3,4,7,8-HxCDD	50	> 10	> 10
1,2,3,6,7,8-HxCDD	50	> 10	> 10
1,2,3,7,8,9-HxCDD	50	> 10	> 10
1,2,3,4,7,8-HxCDF	50	> 10	> 10
1,2,3,6,7,8-HxCDF	50	> 10	> 10
1,2,3,7,8,9-HxCDF	50	> 10	> 10
2,3,4,6,7,8-HxCDF	50	> 10	> 10
1,2,3,4,6,7,8-HpCDD	50	> 10	> 10
1,2,3,4,6,7,8-HpCDF	50	> 10	> 10
1,2,3,4,7,8,9-HpCDF	50	> 10	> 10
OCDD	100	> 10	> 10
OCDF	100	> 10	> 10

(1) The peaks representing the native analytes in the CS1 calibration standard must have a signal-to-noise ratio greater than or equal to 10.

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Appendix F

Inorganic Criteria

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

		Data								Specs									
									IPR			OPR		MS/MSD					
		Reference		Prec-				Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
1.	Acidity (CaCO3)	305.1	---	1.00	Multi	MCAWW	2	---	---	---	---	3.6	---	---	---	---	3.6		10 mg/L	Range
2.	Alkalinity "	310.1	---	2.00	Multi	"	2	---	---	---	---	7.2	---	---	---	---	7.2		10 mg/L	310.2
	"	310.2	99.50	0.50	Single	"	2	---	100 mg/L	97.0	102.0	1.8	97.0	102.0	97.0	102.0	1.8		10 mg/L	Range
3.	Aluminum - Flame	202.1	99.13	31.60	Multi	Apx D	5	25 %	100 ug/L	35.0	163.0	64.0	29.0	169.0	29.0	169.0	64.0		300 ug/L	3.18 x DL
	" - Furnace	202.2	103.69	42.74	Multi	Apx D	5	25 %	100 ug/L	18.0	190.0	86.0	9.0	198.0	9.0	198.0	86.0		20 ug/L	Range
	" - ICP	200.7	96.33	24.19	Multi	Apx C	5	25 %	100 ug/L	47.0	145.0	49.0	43.0	150.0	43.0	150.0	49.0	20 ug/L	50 ug/L	3.18 x MDL
	" - DCP	---																		
	" - Color	---																		
4.	Ammonia - distill																			
	" - Nessler	350.2	100.46	14.27	Multi	MCAWW	3	10 %	2.0 mg/L	71.0	129.0	29.0	69.0	132.0	69.0	132.0	29.0		50 ug/L	Range
	" - Titr	350.2	100.46	14.27	Multi	MCAWW	3	10 %	2.0 mg/L	71.0	129.0	29.0	69.0	132.0	69.0	132.0	29.0		1.0 mg/L	Range
	" - ISE	350.3	91.00	2.31	Single	MCAWW	3	10 %	130 ug/L	82.0	100.0	8.4	81.0	101.0	81.0	101.0	8.4		30 ug/L	Range
	" - Phenate	350.1	103.00	1.16	Single	MCAWW	1	---	0.5 mg/L	98.0	108.0	4.2	98.0	108.0	98.0	108.0	4.2		10 ug/L	Range
	" - Auto elec	---																		
5.	Antimony - Flame	204.1	96.50	1.13	Single	MCAWW	1	---	10 mg/L	92.0	101.0	4.1	91.0	102.0	91.0	102.0	4.1		1.0 mg/L	Range
	Antimony - Furnace	204.2	71.20	38.17	Multi	Apx D	5	25 %	100 ug/L	d	148.0	77.0	d	156.0	d	156.0	77.0		20 ug/L	Range
	Antimony - ICP	200.7	76.00	15.44	Multi	Apx C	3	10 %	500 ug/L	45.0	107.0	31.0	42.0	110.0	42.0	110.0	31.0	8 ug/L	20 ug/L	3.18 x MDL
6.	Arsenic	206.5	Digestion - no specs																	
	" - Hydride	206.3	98.38	8.19	Single	3114 B	3	10 %	200 ug/L	68.0	128.0	30.0	65.0	132.0	65.0	132.0	30.0		2.0 ug/L	Range
	" - Furnace	206.2	98.63	15.98	Multi	Apx D	3	10 %	100 ug/L	66.0	131.0	32.0	63.0	134.0	63.0	134.0	32.0		5.0 ug/L	Range
	" - ICP	200.7	92.17	14.79	Multi	Apx C	3	10 %	100 ug/L	62.0	122.0	30.0	59.0	125.0	59.0	125.0	30.0	8 ug/L	20 ug/L	3.18 x MDL
	" - Color (SDDC)	206.4	100.00	13.80	Multi	MCAWW	3	10 %	40 ug/L	72.0	128.0	28.0	69.0	131.0	69.0	131.0	28.0		10 ug/L	Method
7.	Barium - Flame	208.1	103.50	8.63	Single	MCAWW	3	10 %	1 mg/L	72.0	135.0	32.0	69.0	138.0	69.0	138.0	32.0		1.0 mg/L	Range
	" - Furnace	208.2	142.14	31.10	Multi	Apx D	5	25 %	100 ug/L	79.0	205.0	63.0	73.0	211.0	73.0	211.0	63.0		10 ug/L	Range
	" - ICP	200.7	77.30	20.97	Multi	Apx C	3	10 %	100 ug/L	35.0	120.0	42.0	31.0	124.0	31.0	124.0	42.0	1 ug/L	2 ug/L	3.18 x MDL
	" - DCP	---																		

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
8.	Beryllium - Flame	210.1	98.33	4.27	Single	MCAWW	3	10 %	50 ug/L	82.0	114.0	16.0	81.0	116.0	81.0	116.0	16.0		50 ug/L	Range
	" - Furnace	210.2	106.66	21.76	Multi	Apx D	5	25 %	100 ug/L	63.0	151.0	44.0	58.0	155.0	58.0	155.0	44.0		1.0 mg/L	Range
	" - ICP	200.7	96.34	2.31	Multi	Apx C	3	10 %	100 ug/L	91.0	101.0	4.7	91.0	102.0	91.0	102.0	4.7	0.3 ug/L	1.0 ug/L	3.18 x MDL
	" - DCP	---																		
	" - Color	---																		
9.	BOD	405.1		24.10	Multi	MCAWW	---	---	100 mg/L			49.0					49.0		N/A	
10.	Boron - Color	212.3	100.00	22.80	Multi	MCAWW	5	25 %	240 ug/L	54.0	146.0	46.0	49.0	151.0	49.0	151.0	46.0		100 ug/L	Range
	" - ICP	200.7	97.07	25.60	Multi	Apx C	5	25 %	100 ug/L	45.0	149.0	52.0	40.0	154.0	40.0	154.0	52.0	3 ug/L	10 ug/L	3.18 x MDL
	" - DCP	---																		
11.	Bromide	320.1	93.75	7.17	Single	MCAWW	3	10 %	5 mg/L	67.0	120.0	26.0	65.0	123.0	65.0	123.0	26.0		2 mg/L	Range
12.	Cadmium - Flame	213.1	94.87	15.88	Multi	Apx D	3	10 %	100 ug/L	63.0	127.0	32.0	59.0	130.0	59.0	130.0	32.0		50 ug/L	Range
	Cadmium - Furnace	213.2	98.43	23.05	Multi	Apx D	5	25 %	100 ug/L	52.0	145.0	47.0	47.0	150.0	47.0	150.0	47.0		0.5 ug/L	Range
	Cadmium - ICP	200.7	98.56	7.59	Multi	Apx C	3	10 %	100 ug/L	83.0	114.0	16.0	81.0	116.0	81.0	116.0	16.0	1 ug/L	2 ug/L	3.18 x MDL
	Cadmium - DCP	---																		
	Cadmium - Volt	---																		
	Cadmium - Color	---																		
13.	Calcium - Flame	215.1	99.00	3.33	Single	MCAWW	3	10 %	10 ug/L	87.0	111.0	12.0	85.0	113.0	85.0	113.0	12.0		200 ug/L	Range
	Calcium - ICP	200.7	89.22	22.38	Multi	Apx C	5	25 %	100 ug/L	44.0	134.0	45.0	39.0	139.0	39.0	139.0	45.0	10 ug/L	20 ug/L	3.18 x MDL
	Calcium - DCP	---																		
	Calcium - Titr	215.2	98.10	9.20	Single	MCAWW	3	10 %	100 ug/L	64.0	132.0	34.0	61.0	135.0	61.0	135.0	34.0		2 mg/L	3.18 x LDL
14.	CBOD5	---																		
15.	COD - Titr	410.1	95.30	17.76	Multi	MCAWW	3	10 %	250 mg/L	59.0	131.0	36.0	56.0	135.0	56.0	135.0	36.0		50 mg/L	Method
	COD - Titr	410.2	100.30	4.15	Multi	MCAWW	3	10 %	10 mg/L	92.0	109.0	8.3	91.0	110.0	91.0	110.0	8.3		5 mg/L	Range
	COD - Titr	410.3	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0			
	COD - Spectro	410.4	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0			

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
16.	Chloride - Titr/Ag	---																		
	Chloride - Titr/Hg	325.3	97.10	3.30	Multi	MCAWW	3	10 %	250 mg/L	90.0	104.0	6.6	89.0	105.0	89.0	105.0	6.6		---	
	Chloride - Color	---																		
	Chloride - Auto	325.1	100.50	3.00	Single	MCAWW	3	10 %	10 mg/L	89.0	112.0	11.0	88.0	113.0	88.0	113.0	11.0		1 mg/L	Range
	Chloride - Auto	325.2	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 mg/L	Range
17.	Chlorine - Ampere	330.1	91.20	12.50	Multi	MCAWW	3	10 %	250 mg/L	66.0	117.0	25.0	63.0	119.0	63.0	119.0	25.0		---	
	Chlorine - Iodo	330.3	81.50	32.40	Multi	MCAWW	5	25 %	1.0 mg/L	16.0	147.0	65.0	10.0	153.0	10.0	153.0	65.0		0.1 mg/L	Method
	Chlorine - Back titr	330.2	98.80	4.30	Single	MCAWW	3	10 %	1.0 mg/L	83.0	115.0	16.0	81.0	116.0	81.0	116.0	16.0		---	
	Chlorine - DPD-FAS	330.4	91.90	19.20	Multi	MCAWW	3	10 %	1.0 mg/L	53.0	131.0	39.0	49.0	135.0	49.0	135.0	39.0		0.1 mg/L	Method
	Chlorine - Spectro	330.5	84.40	27.60	Multi	MCAWW	5	25 %	1.0 mg/L	29.0	140.0	56.0	23.0	146.0	23.0	146.0	56.0		0.2 mg/L	Method
	Chlorine - Electrode	---																		
18.	Chromium VI - AA	218.4	98.49	6.96	Multi	MCAWW	3	10 %	100 ug/L	84.0	113.0	14.0	83.0	114.0	83.0	114.0	14.0		10 ug/L	Range
	Chromium VI - Color	---																		
19.	Chromium - Flame	218.1	101.54	17.36	Multi	Apx D	3	10 %	100 ug/L	66.0	137.0	35.0	63.0	140.0	63.0	140.0	35.0		250 ug/L	Method
	Chromium - Chelate	218.3	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 ug/L	Method
	Chromium - Furnace	218.2	91.43	17.69	Multi	Apx D	3	10 %	100 ug/L	56.0	127.0	36.0	52.0	131.0	52.0	131.0	36.0		5 ug/L	Range
	Chromium - ICP	200.7	98.54	9.39	Multi	Apx C	3	10 %	100 ug/L	79.0	118.0	19.0	77.0	120.0	77.0	120.0	19.0	4 ug/L	10 ug/L	3.18 x MDL
	Chromium - DCP	---																		
	Chromium - Color	---																		
20.	Cobalt - Flame	219.1	98.00	1.00	Single	MCAWW	3	10 %	1.0 mg/L	94.0	102.0	3.6	94.0	102.0	94.0	102.0	3.6		500 ug/L	Range
	Cobalt - Furnace	219.2	89.38	22.27	Multi	Apx D	5	25 %	100 ug/L	44.0	134.0	45.0	40.0	139.0	40.0	139.0	45.0		5 ug/L	Range
	Cobalt - ICP	200.7	87.59	8.16	Multi	Apx C	3	10 %	100 ug/L	71.0	104.0	17.0	69.0	106.0	69.0	106.0	17.0	2 ug/L	5 ug/L	3.18 x MDL
	Cobalt - DCP	---																		

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
21.	Color - ADMI	110.1	100.00	10.00	No data	Default	1	---	100 C.U.	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		25 C.U.	Range
	Color - Pt/Co	110.2	100.00	10.00	No data	Default	3	---	100 C.U.	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		---	No data
	Color - Spectro	110.3	100.00	10.00	No data	Default	3	---	100 C.U.	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0			
22.	Copper - Flame	220.1	99.79	17.00	Multi	MCAWW	3	10 %	100 ug/L	65.0	134.0	34.0	62.0	138.0	62.0	138.0	34.0		100 ug/L	Method
	Copper - Furnace	220.2	92.54	27.29	Multi	Apx D	5	25 %	100 ug/L	37.0	148.0	55.0	32.0	153.0	32.0	153.0	55.0		5 ug/L	Range
	Copper - ICP	200.7	95.82	7.07	Multi	Apx C	3	10 %	100 ug/L	81.0	110.0	15.0	80.0	112.0	80.0	112.0	15.0	3 ug/L	10 ug/L	3.18 x MDL
	Copper - DCP	---																		
	Copper - Color/Neo	---																		
	Copper - Color/Bicin	---																		
23.	Cyanide - Distill	---																		
	Cyanide - Titr	---																		
	Cyanide - Spectro	335.2	85.00	11.07	Single	MCAWW	3	10 %	250 ug/L	45.0	125.0	40.0	40.0	130.0	40.0	130.0	40.0		60 ug/L	Data
	Cyanide - Auto	335.3	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		5 ug/L	Range
24.	CATC - Titr	335.1	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0			
	CATC - Spectro	335.1	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0			
25.	Fluoride - Distill	---																		
	Fluoride - Elec/man	340.2	98.82	3.53	Multi	MCAWW	3	10 %	1.0 mg/L	91.0	106.0	7.1	91.0	107.0	91.0	107.0	7.1		100 ug/L	Range
	Fluoride - Elec/auto	---																		
	Fluoride - SPADNS	340.1	97.59	10.72	Multi	MCAWW	3	10 %	1.0 mg/L	76.0	120.0	22.0	74.0	122.0	74.0	122.0	22.0		100 ug/L	Range
	Fluoride - Auto	340.3	89.00	12.00	Single	MCAWW	3	10 %	150 ug/L	45.0	133.0	44.0	41.0	137.0	41.0	137.0	44.0		50 ug/L	Range
26.	Gold - Flame	231.1	100.00	10.00	No data	Default	3	10 %	1.0 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		500 ug/L	Range
	Gold - Furnace	231.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		5 ug/L	Range

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Gold - DCP	---																		
27.	Hardness - Color/auto	130.1	89.00	7.89	Single	MCAWW	3	10 %	50 mg/L	60.0	118.0	29.0	57.0	121.0	57.0	121.0	29.0		10 mg/L	Range
	Hardness - Titr/EDTA	130.2	99.13	9.26	Multi	MCAWW	3	10 %	30 mg/L	80.0	118.0	19.0	78.0	120.0	78.0	120.0	19.0		50 mg/L	Data
28.	pH - Electrode	150.1	N/A	1.30	Multi	MCAWW	2	---	N/A			2.6					2.6		N/A	
	pH - Auto	---																		
29.	Iridium - Flame	235.1	100.00	10.00	No data	Default	3	10 %	100 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		20 mg/L	Range
	Iridium - Furnace	235.2	100.00	10.00	No data	Default	3	10 %	200 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		100 ug/L	Range
30.	Iron - Flame	236.1	97.69	17.00	Multi	Apx D	3	10 %	100 ug/L	63.0	132.0	34.0	60.0	136.0	60.0	136.0	34.0		300 ug/L	Range
	Iron - Furnace	236.2	144.71	36.03	Multi	Apx D	5	25 %	100 ug/L	72.0	217.0	73.0	65.0	224.0	65.0	224.0	73.0		5 ug/L	Range
	Iron - ICP	200.7	95.29	18.33	Multi	Apx C	3	10 %	100 ug/L	58.0	132.0	37.0	54.0	136.0	54.0	136.0	37.0	30 ug/L	100 ug/L	3.18 x MDL
	Iron - DCP	---																		
	Iron - Color	---																		
31.	TKN - Digest	351.3	101.03	25.76	Multi	MCAWW	5	25 %	2 mg/L	49.0	153.0	52.0	44.0	158.0	44.0	158.0	52.0		50 ug/L	Range
	TKN - Titr	351.3	101.03	25.76	Multi	MCAWW	5	25 %	2 mg/L	49.0	153.0	52.0	44.0	158.0	44.0	158.0	52.0		50 ug/L	Range
	TKN - Nessler	351.3	101.03	25.76	Multi	MCAWW	5	25 %	2 mg/L	49.0	153.0	52.0	44.0	158.0	44.0	158.0	52.0		50 ug/L	Range
	TKN - Electrode	351.3	101.03	25.76	Multi	MCAWW	5	25 %	2 mg/L	49.0	153.0	52.0	44.0	158.0	44.0	158.0	52.0		50 ug/L	Range
	TKN - Phenate	351.1	71.70	27.98	Multi	MCAWW	5	25 %	2 mg/L	15.0	128.0	56.0	10.0	134.0	10.0	134.0	56.0		50 ug/L	Range
	TKN - Block/color	351.2	99.00	8.82	Single	MCAWW	3	10 %	2 mg/L	67.0	131.0	32.0	63.0	135.0	63.0	135.0	32.0		100 ug/L	Range
	TKN - Potentio	351.4	100.00	10.00	No data	Default	3	10 %	10 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		30 ug/L	Range
32.	Lead - Flame	239.1	109.90	36.70	Multi	Apx D	5	25 %	100 ug/L	36.0	184.0	74.0	29.0	191.0	29.0	191.0	74.0		40 ug/L	Data
	Lead - Furnace	239.2	93.80	22.75	Multi	Apx D	5	25 %	100 ug/L	48.0	140.0	46.0	43.0	144.0	43.0	144.0	46.0		5 ug/L	Range
	Lead - ICP	200.7	94.79	12.58	Multi	Apx C	3	10 %	100 ug/L	69.0	120.0	26.0	67.0	123.0	67.0	123.0	26.0	10 ug/L	20 ug/L	3.18 x MDL
	Lead - DCP	---																		
	Lead - Volt	---																		

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Lead - Color	---																		
33.	Magnesium - Flame	242.1	97.90	29.81	Multi	MCAWW	5	25 %	100 ug/L	38.0	158.0	60.0	32.0	164.0	32.0	164.0	60.0		20 ug/L	Range
	Magnesium - ICP	200.7	97.71	17.67	Multi	Apx C	3	10 %	100 ug/L	62.0	134.0	36.0	58.0	137.0	58.0	137.0	36.0	20 ug/L	50 ug/L	3.18 x MDL
	Magnesium - DCP	---																		
	Magnesium - Grav	---																		
34.	Manganese - Flame	243.1	95.43	13.15	Multi	Apx D	3	25 %	100 ug/L	69.0	122.0	27.0	66.0	125.0	66.0	125.0	27.0		100 ug/L	Range
	Manganese - Furnace	243.2	106.20	21.05	Multi	Apx D	5	25 %	100 ug/L	64.0	149.0	43.0	59.0	153.0	59.0	153.0	43.0		1 ug/L	Range
	Manganese - ICP	200.7	94.30	4.12	Multi	Apx C	3	10 %	100 ug/L	86.0	103.0	8.3	85.0	104.0	85.0	104.0	8.3	1 ug/L	2 ug/L	3.18 x MDL
	Manganese - DCP	---																		
	Manganese - Persulf	---																		
	Manganese - Perioda	---																		
35.	Mercury - CV/Man	245.1	92.90	29.40	Multi	MCAWW	5	25 %	4 ug/L	34.0	152.0	59.0	28.0	158.0	28.0	158.0	59.0		0.2 ug/L	DL
	Mercury - CV/Auto	245.2	102.00	2.00	Single	MCAWW	3	10 %	10 ug/L	94.0	110.0	7.2	94.0	110.0	94.0	110.0	7.2		0.2 ug/L	DL
36.	Molybdenum - Flame	246.1	97.00	2.33	Single	MCAWW	3	10 %	300 ug/L	88.0	106.0	8.4	87.0	107.0	87.0	107.0	8.4		300 ug/L	Data
	Molybdenum - Furnace	246.2	100.00	10.00	No data	Default	3	10 %	10 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		3 ug/L	Range
	Molybdenum - ICP	200.7	96.92	7.78	Multi	Apx C	3	10 %	100 ug/L	81.0	113.0	16.0	79.0	115.0	79.0	115.0	16.0	4 ug/L	10 ug/L	3.18 x MDL
	Molybdenum - DCP	---																		
37.	Nickel - Flame	249.1	96.67	2.00	Single	MCAWW	3	10 %	1 ug/L	89.0	104.0	7.2	88.0	105.0	88.0	105.0	7.2		0.2 ug/L	Data
	Nickel - Furnace	249.2	90.37	26.65	Multi	Apx D	5	25 %	100 ug/L	37.0	144.0	54.0	31.0	149.0	31.0	149.0	54.0		5 ug/L	Range
	Nickel - ICP	200.7	95.48	10.44	Multi	Apx C	3	10 %	100 ug/L	74.0	117.0	21.0	72.0	119.0	72.0	119.0	21.0	5 ug/L	20 ug/L	3.18 x MDL
	Nickel - DCP	---																		
	Nickel - Color	---																		
38.	Nitrate	352.1	104.12	22.69	Multi	MCAWW	5	25 %	1 mg/L	58.0	150.0	46.0	54.0	155.0	54.0	155.0	46.0		0.1 mg/L	Range
39.	NO2-NO3 - Cd/Man	353.3	100.00	12.50	Single	MCAWW	3	10 %	40 ug/L	55.0	145.0	45.0	50.0	150.0	50.0	150.0	45.0		10 ug/L	Range
	NO2-NO3 - Cd/Auto	353.2	105.75	4.14	Single	MCAWW	3	10 %	290 ug/L	90.0	121.0	15.0	89.0	123.0	89.0	123.0	15.0		50 ug/L	Range

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

		Data											Specs							
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	NO2-NO3 - Cd/Hydra	353.1	99.00	5.13	Single	MCAWW	3	10 %	400 ug/L	80.0	118.0	19.0	78.0	120.0	78.0	120.0	19.0		10 ug/L	Range
40.	Nitrite - Spec/Man	354.1	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		10 ug/L	Range
	Nitrite - Spec/Auto	---																		
41.	Oil & Grease	413.1	93.00	6.43	Single	MCAWW	1	10 %	15 mg/L	69.0	117.0	24.0	67.0	119.0	67.0	119.0	24.0		5 mg/L	Range
42.	TOC	415.1	101.01	7.78	Multi	MCAWW	3	10 %	100 mg/L	85.0	117.0	16.0	83.0	119.0	83.0	119.0	16.0		1 mg/L	Method
43.	Organic nitrogen	---																		
44.	O-phosphate - Auto	365.1	87.20	22.00	Multi	MCAWW	5	25 %	300 ug/L	43.0	132.0	45.0	38.0	136.0	38.0	136.0	45.0		10 ug/L	Range
	O-phosphate - Man 1	365.2	97.25	5.37	Multi	MCAWW	3	10 %	300 ug/L	86.0	108.0	11.0	85.0	110.0	85.0	110.0	11.0		10 ug/L	Range
	O-phosphate - Man 2	365.3	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		10 ug/L	Range
45.	Osmium - Flame	252.1	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 mg/L	Method
	Osmium - Furnace	252.2	100.00	10.00	No data	Default	3	10 %	10 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		50 ug/L	Range
46.	DO - Winkler	360.2	100.00	1.00	Single	MCAWW	3	10 %	1 mg/L	96.0	104.0	3.6	96.0	104.0	96.0	104.0	3.6		50 ug/L	Range
	DO - Electrode	360.1	100.00	1.00	Single	MCAWW	3	10 %	1 mg/L	96.0	104.0	3.6	96.0	104.0	96.0	104.0	3.6		50 ug/L	Range
47.	Palladium - Flame	253.1	100.00	10.00	No data	Default	3	10 %	1 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		500 ug/L	Range
	Palladium - Furnace	253.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		20 ug/L	Range
	Palladium - DCP	---																		
48.	Phenol - Color/Man	420.1	100.00	10.31	Multi	MCAWW	3	10 %	300 ug/L	79.0	121.0	21.0	77.0	123.0	77.0	123.0	21.0		5 ug/L	Method
	Phenol - Color/Auto	420.2	98.00	1.12	Single	MCAWW	3	10 %	1 mg/L	93.0	103.0	4.1	93.0	103.0	93.0	103.0	4.1		2 ug/L	Range
49.	Phosphorus - GC	---																		
50.	Phosphorus - Asc/Man	365.2	103.09	30.00	Multi	MCAWW	5	25 %	300 ug/L	43.0	164.0	60.0	37.0	170.0	37.0	170.0	60.0		10 ug/L	Range

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Phosphorus - Asc/Man	365.3	99.00	22.00	Multi	MCAWW	5	25 %	300 ug/L	55.0	143.0	44.0	50.0	148.0	50.0	148.0	44.0		10 ug/L	Range
	Phosphorus - Asc/Auto	365.1	87.20	22.00	Multi	MCAWW	5	25 %	300 ug/L	43.0	132.0	45.0	38.0	136.0	38.0	136.0	45.0		10 ug/L	Range
	Phosphorus - Block	365.4	98.00	3.00	Single	MCAWW	3	10 %	2 mg/L	87.0	109.0	11.0	86.0	110.0	86.0	110.0	11.0		10 ug/L	Range
51.	Platinum - Flame	255.1	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		5 mg/L	Range
	Platinum - Furnace	255.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		100 ug/L	Range
	Platinum - DCP	---																		
52.	Potassium - Flame	258.1	103.00	12.50	Single	MCAWW	3	10 %	2 mg/L	58.0	148.0	45.0	53.0	153.0	53.0	153.0	45.0		100 ug/L	Range
	Potassium - ICP	200.7	83.05	17.12	Multi	Apx C	3	10 %	1 mg/L	48.0	118.0	35.0	45.0	121.0	45.0	121.0	35.0	300 ug/L	1 mg/L	3.18 x MDL
	Potassium - FPD	---																		
	Potassium - Color	---																		
53.	Total Solids	160.3	100.00	10.00	No data	Default	1	---	100 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		10 mg/L	Range
54.	TDS	160.1	100.00	10.00	No data	Default	1	---	100 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		10 mg/L	Range
55.	TSS	160.2	100.00	10.00	No data	Default	1	---	100 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		4 mg/L	Range
56.	Settleable Solids	160.5	100.00	10.00	No data	Default	1	---	100 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		0.2 mL/L/h	Method
57.	Volatile Residue	160.4	100.00	6.47	Multi	MCAWW	3	10 %	300 ug/L	87.0	113.0	13.0	85.0	115.0	85.0	115.0	13.0		10 mg/L	Range
58.	Rhodium - Flame	265.1	100.00	10.00	No data	Default	3	10 %	1 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 mg/L	Range
	Rhodium - Furnace	265.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		20 ug/L	Range
59.	Ruthenium - Flame	267.1	100.00	10.00	No data	Default	3	10 %	1 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 mg/L	Range
	Ruthenium - Furnace	267.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		100 ug/L	Range
60.	Selenium - Furnace	270.2	96.12	16.72	Multi	Apx D	3	10 %	100 ug/L	62.0	130.0	34.0	59.0	133.0	59.0	133.0	34.0		5 ug/L	Range
	Selenium - ICP	200.7	91.13	26.35	Multi	Apx C	5	25 %	1 mg/L	38.0	144.0	53.0	33.0	150.0	33.0	150.0	53.0	20 ug/L	50 ug/L	3.18 x MDL

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Selenium - Hydride	---																		
61.	Silica - Color/Man	370.1	85.70	7.80	Multi	MCAWW	3	10 %	5 mg/L	70.0	102.0	16.0	68.0	103.0	68.0	103.0	16.0		2 mg/L	Range
	Silica - Color/Auto	---																		
	Silica - ICP	200.7	53.86	45.38	Multi	Apx C	5	25 %	1 mg/L	d	145.0	91.0	d	154.0	d	154.0	91.0	20 ug/L	50 ug/L	3.18 x MDL
62.	Silver - Flame	272.1	89.40	17.60	Multi	MCAWW	3	10 %	50 ug/L	54.0	125.0	36.0	50.0	129.0	50.0	129.0	36.0		100 ug/L	Range
	Silver - Furnace	272.2	94.88	18.20	Multi	Apx D	3	10 %	100 ug/L	58.0	132.0	37.0	54.0	135.0	54.0	135.0	37.0		1 ug/L	Range
	Silver - ICP	200.7	49.73	47.50	Multi	Apx C	5	25 %	100 ug/L	d	145.0	95.0	d	155.0	d	155.0	95.0	2 ug/L	5 ug/L	3.18 x MDL
	Silver - DCP	---																		
63.	Sodium - Flame	273.1	100.00	1.54	Multi	MCAWW	3	10 %	5 mg/L	96.0	104.0	3.1	96.0	104.0	96.0	104.0	3.1		30 ug/L	Range
	Sodium - ICP	200.7	99.77	24.27	Multi	Apx C	5	25 %	1 mg/L	51.0	149.0	49.0	46.0	154.0	46.0	154.0	49.0	30 ug/L	100 ug/L	3.18 x MDL
	Sodium - DCP	---																		
	Sodium - FPD	---																		
64.	Specific conductance	120.1	97.98	7.55	Multi	MCAWW	3	10 %	5 mg/L	82.0	114.0	16.0	81.0	115.0	81.0	115.0	16.0		No data	
65.	Sulfate - Color/Auto	375.1	99.00	1.80	Single	MCAWW	3	10 %	100 mg/L	92.0	106.0	6.5	91.0	107.0	91.0	107.0	6.5		10 mg/L	Range
	Sulfate - Grav	375.3	102.00	1.45	Single	MCAWW	3	10 %	100 mg/L	96.0	108.0	5.3	96.0	108.0	96.0	108.0	5.3		10 ug/L	Range
	Sulfate - Turbid	375.4	96.99	7.15	Multi	MCAWW	3	10 %	100 mg/L	82.0	112.0	15.0	81.0	113.0	81.0	113.0	15.0		1 mg/L	DL
66.	Sulfide - Turbid	376.1	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 mg/L	DL
	Sulfide - Color	376.2	100.00	10.00	No data	MCAWW	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		No data	
67.	Sulfite - Turbid	377.1	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		3 mg/L	DL
68.	Surfactants	425.1	101.36	9.13	Multi	MCAWW	3	10 %	3 mg/L	83.0	120.0	19.0	81.0	122.0	81.0	122.0	19.0		25 ug/L	Range
69.	Temperature	170.1	---	---															N/A	
70.	Thallium - Flame	279.1	100.00	3.00	Single	MCAWW	3	10 %	600 ug/L	89.0	111.0	11.0	88.0	112.0	88.0	112.0	11.0		600 ug/L	Data
	Thallium - Furnace	279.2	87.10	11.79	Multi	Apx D	5	25 %	100 ug/L	63.0	111.0	24.0	61.0	114.0	61.0	114.0	24.0		5 ug/L	Range
	Thallium - ICP	200.7	82.90	28.34	Multi	Apx C	5	25 %	1 mg/L	26.0	140.0	57.0	20.0	146.0	20.0	146.0	57.0	20 ug/L	50 ug/L	3.18 x MDL

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

		Data								Specs										
										IPR			OPR		MS/MSD					
		Reference		Prec-					Spike	Recovery		Prec-	Recovery		Recovery				ML	ML
No.	Analyte	Method	Recovery	ision	Labs	Source	CAL points	CAL lin	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
71.	Tin - Flame	282.1	96.00	6.25	Single	MCAWW	3	10 %	4 mg/L	73.0	119.0	23.0	71.0	121.0	71.0	121.0	23.0		10 mg/L	Range
	Tin - Furnace	282.2	100.00	10.00	No data	Default	3	10 %	10 mg/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		20 ug/L	Range
	Tin - ICP	200.7	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0	7 ug/L	20 ug/L	3.18 x MDL
72.	Titanium - Flame	283.1	97.00	3.50	Single	MCAWW	3	10 %	2 mg/L	84.0	110.0	13.0	83.0	111.0	83.0	111.0	13.0		2 mg/L	Data
	Titanium - Furnace	283.2	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		50 ug/L	Range
	Titanium - ICP	200.7	100.00	10.00	No data	Default	3	10 %	100 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		1 ug/L	Range
73.	Turbidity	180.1	100.00	2.31	Single	MCAWW	3	10 %	25 NTU	91.0	109.0	8.4	90.0	110.0	90.0	110.0	8.4		0.05 NTU	Est
74.	Vanadium - Flame	286.1	100.00	5.00	Single	MCAWW	3	10 %	2 mg/L	82.0	118.0	18.0	80.0	120.0	80.0	120.0	18.0		2 mg/L	Range
	Vanadium - Furnace	286.2	85.11	32.80	Multi	Apx D	5	25 %	100 ug/L	19.0	151.0	66.0	12.0	158.0	12.0	158.0	66.0		10 ug/L	Range
	Vanadium - ICP	200.7	94.15	7.88	Multi	Apx C	3	10 %	100 ug/L	78.0	110.0	16.0	76.0	112.0	76.0	112.0	16.0	3 ug/L	10 ug/L	3.18 x MDL
	Vanadium - DCP	---																		
	Vanadium - Color	---																		
75.	Zinc - Flame	289.1	99.93	18.60	Multi	Apx D	3	10 %	100 mg/L	62.0	138.0	38.0	59.0	141.0	59.0	141.0	38.0		50 ug/L	Range
	Zinc - Furnace	289.2	168.59	67.06	Multi	Apx D	7	25 %	100 ug/L	34.0	303.0	135.0	21.0	317.0	21.0	317.0	140.0		0.2 ug/L	Range
	Zinc - ICP	200.7	93.26	12.89	Multi	Apx C	5	25 %	100 ug/L	67.0	120.0	26.0	64.0	122.0	64.0	122.0	26.0	2 ug/L	5 ug/L	3.18 x MDL
	Zinc - DCP	---																		
	Zinc - Color/Dithiz	---																		
	Zinc - Color/Zincon	---																		

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Standardized QC and QC Acceptance Criteria for Methods in 40 CFR 141.23(k)(1)

		Data					Specs														
											IPR			OPR		MS/MSD					
		Reference		Prec-			CAL		MCL	Spike	Recovery		Prec-	Recover y		Recover y			ML	ML	
No.	Analyte	Method	Recover y	ision	Labs	Source	Point s	Lin	(ug/L)	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
1.	Alkalinity - Titr/Man	---																			
	Alkalinity - Titr/Auto	---																			
2.	Antimony - Furnace	---							6.0												
	Antimony - Hydride	---							6.0												
	Antimony - ICP/MS	200.8	98.8	8.067	Multi	Tbl 12	3	10 %	6.0	6 ug/L	82.0	115.0	17.0	81.0	117.0	81.0	117.0	17.0	0.4 ug/L	1 ug/L	3.18 x MDL
	Antimony - STGFAA	200.9	95.4	2.8	Single	Tbl IE	3	10 %	6.0	20 ug/L	85.0	106.0	11.0	84.0	107.0	84.0	107.0	11.0	0.8 ug/L	2 ug/L	3.18 x MDL
3.	Arsenic - Furnace	---							50												
	Arsenic - Hydride	---							50												
	Arsenic - ICP	200.7	98.27	13.59	Multi	Apx C	3	10 %	50	200 ug/L	71.0	126.0	28.0	68.0	129.0	68.0	129.0	28.0	53 ug/L	200 ug/L	3.18 x MDL
	Arsenic - ICP/MS	200.8	100.44	6.9	Multi	Tbl 12	3	10 %	50	50 ug/L	86.0	115.0	14.0	85.0	116.0	85.0	116.0	14.0	1.4 ug/L	5 ug/L	3.18 x MDL
	Arsenic - STGFAA	200.9	88.4	10	Single	Tbl IE	3	10 %	50	10 ug/L	52.0	125.0	36.0	48.0	129.0	48.0	129.0	36.0	0.5 ug/L	2 ug/L	3.18 x MDL
4.	Asbestos - TEM	100.1							7 MFL												
	Asbestos - TEM	100.2							7 MFL												
5.	Barium - Flame	---							2000												
	Barium - Furnace	---							2000												
	Barium - ICP	200.7	76.88	18.47	Multi	Apx C	3	10 %	2000	1 mg/L	39.0	114.0	37.0	36.0	118.0	36.0	118.0	37.0	2 ug/L	5 ug/L	3.18 x MDL
	Barium - ICP/MS	200.8	96.31	4.55	Multi	Tbl 12	3	10 %	2000	1 mg/L	87.0	106.0	9.1	86.0	107.0	86.0	107.0	9.1	0.8 ug/L	2.0 ug/L	3.18 x MDL
6.	Beryllium - Flame	---							4.0												
	Beryllium - ICP	200.7	97.54	25.11	Multi	Apx C	3	10 %	4.0	4 ug/L	47.0	148.0	51.0	42.0	153.0	42.0	153.0	51.0	0.3 ug/L	1 ug/L	3.18 x MDL
	Beryllium - ICP/MS	200.8	110.50	12.70	Multi	Tbl 12	3	10 %	4.0	4 ug/L	85.0	136.0	26.0	82.0	139.0	82.0	139.0	26.0	0.3 ug/L	1 ug/L	3.18 x MDL
	Beryllium - STGFAA	200.9	106	9.4	Single	Tbl IE	3	10 %	4.0	2.5 ug/L	72.0	140.0	34.0	68.0	144.0	68.0	144.0	34.0	0.02 ug/L	0.05 ug/L	3.18 x MDL
7.	Cadmium - Furnace	---							5.0												
	Cadmium - ICP	200.7	95.14	45.97	Multi	Apx C	3	10 %	5.0	5 ug/L	3.0	188.0	92.0	d	197.0	d	197.0	92.0	4 ug/L	10 ug/L	3.18 x MDL
	Cadmium - ICP/MS	200.8	100.5	16.1	Multi	Tbl 12	3	10 %	5.0	5 ug/L	68.0	133.0	33.0	65.0	136.0	65.0	136.0	33.0	0.5 ug/L	2 ug/L	3.18 x MDL
	Cadmium - STGFAA	200.9	105.2	6.3	Single	Tbl IE	3	10 %	5.0	0.5 ug/L	82.0	128.0	23.0	80.0	131.0	80.0	131.0	23.0	0.05 ug/L	0.2 ug/L	3.18 x MDL
8.	Calcium - Flame	---							---												
	Calcium - ICP	200.7	89.22	22.38	Multi	Apx C	3	10 %	---	100 ug/L	44.0	134.0	45.0	39.0	139.0	39.0	139.0	45.0	10 ug/L	20 ug/L	3.18 x MDL
	Calcium - Titr	---							---												

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Standardized QC and QC Acceptance Criteria for Methods in 40 CFR 141.23(k)(1)

		Data					Specs				IPR			OPR		MS/MSD					
No.	Analyte	Reference Method	Recovery	Precision	Labs	Source	CAL Points	Lin	MCL (ug/L)	Spike conc	Recovery Low	Recovery High	Precision	Recovery Low	Recovery High	Recovery Low	Recovery High	RPD	ML MDL	ML Value	Calc
9.	Chromium - Furnace	---							100												
	Chromium - ICP	200.7	98.54	9.39	Multi	Apx C	3	10 %	100	100 ug/L	79.0	118.0	19.0	77.0	120.0	77.0	120.0	19.0	7 ug/L	20 ug/L	3.18 x MDL
	Chromium - ICP/MS	200.8	100.45	3.69	Multi	Tbl 12	3	10 %	100	100 ug/L	93.0	108.0	7.4	92.0	109.0	92.0	109.0	7.4	0.9 ug/L	2 ug/L	3.18 x MDL
	Chromium - STGFAA	200.9	105.7	3.1	Single	Tbl IE	3	10 %	100	2.5 ug/L	94.0	117.0	12.0	93.0	119.0	93.0	119.0	12.0	0.1 ug/L	0.2 ug/L	3.18 x MDL
10.	Conductivity	---																			
11.	Copper - Flame	---							1000												
	Copper - Furnace	---							1000												
	Copper - ICP	200.7	92.94	4.71	Multi	Apx C	3	10 %	1000	1 mg/L	83.0	103.0	9.5	82.0	104.0	82.0	104.0	9.5	6 ug/L	20 ug/L	3.18 x MDL
	Copper - ICP/MS	200.8	97.56	6.39	Multi	Tbl 12	3	10 %	1000	1 mg/L	84.0	111.0	13.0	83.0	112.0	83.0	112.0	13.0	0.09 ug/L	0.2 ug/L	3.18 x MDL
	Copper - STGFAA	200.9	111.5	10	Single	Tbl IE	3	10 %	1000	10 ug/L	75.0	148.0	36.0	71.0	152.0	71.0	152.0	36.0	0.7 ug/L	2 ug/L	3.18 x MDL
12.	Cyanide - CATC	---							200												
	Cyanide - Spectro/Man	---							200												
	Cyanide - Spectro/Auto	335.4	100	10	No data	Default	3	10 %	200	200 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0		5 ug/L	Range
	Cyanide - ISE	---							200												
13.	Fluoride - Elec/man	---							2000												
	Fluoride - Elec/auto	---							2000												
	Fluoride - SPADNS	---							2000												
	Fluoride - Auto/Aliz	---							2000												
	Fluoride - IC	300.0	87.7	5	Single	MCAWW	3	10 %	2000	2 mg/L	69.0	106.0	18.0	67.0	108.0	67.0	108.0	18.0	5 ug/L	20 ug/L	3.18 x MDL
14.	pH - Electrode	150.1	---	---					6.5-8.5												
	pH - Auto	150.2	---	---					6.5-8.5												
15.	Lead - Furnace	---							---												
	Lead - ICP/MS	200.8	100.20	12.10	Multi	Tbl 12	3	10 %	---	10 ug/L	76.0	125.0	25.0	73.0	127.0	73.0	127.0	25.0	0.6 ug/L	2 ug/L	3.18 x MDL
	Lead - STGFAA	200.9	101.80	4.00	Single	Tbl IE	3	10 %	---	10 ug/L	87.0	117.0	15.0	85.0	118.0	85.0	118.0	15.0	0.7 ug/L	2 ug/L	3.18 x MDL
16.	Mercury - CV/Man	245.1	100.34	43.82	Multi	MCAWW	3	10 %	2.0	2 ug/L	12.0	188.0	88.0	3.0	197.0	3.0	197.0	88.0		0.2 ug/L	Range
	Mercury - CV/Auto	245.2	102	4.5	Single	MCAWW	3	10 %	2.0	2 ug/L	85.0	119.0	17.0	84.0	120.0	84.0	120.0	17.0		0.2 ug/L	Range

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Standardized QC and QC Acceptance Criteria for Methods in 40 CFR 141.23(k)(1)

		Data					Specs														
											IPR			OPR		MS/MSD					
		Reference		Prec-			CAL		MCL	Spike	Recovery		Prec-	Recover y		Recover y			ML	ML	
No.	Analyte	Method	Recover y	ision	Labs	Source	Point s	Lin	(ug/L)	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Mercury - ICP/MS	200.8	100	10	No data	Default	3	10 %	2.0	2 ug/L	64.0	136.0	36.0	60.0	140.0	60.0	140.0	36.0	No data		
17.	Nickel - Flame	---							100												
	Nickel - Furnace	---							100												
	Nickel - ICP	200.7	95.48	10.44	Multi	Apx C	3	10 %	100	100 ug/L	74.0	117.0	21.0	72.0	119.0	72.0	119.0	21.0	15 ug/L	50 ug/L	3.18 x MDL
	Nickel - ICP/MS	200.8	95.11	5.16	Multi	Tbl 12	3	10 %	100	100 ug/L	84.0	106.0	11.0	83.0	107.0	83.0	107.0	11.0	0.5 ug/L	2 ug/L	3.18 x MDL
	Nickel - STGFAA	200.9	103.8	4.3	Single	Tbl IE	3	10 %	100	20 ug/L	88.0	120.0	16.0	86.0	121.0	86.0	121.0	16.0	0.6 ug/L	2 ug/L	3.18 x MDL
18.	Nitrate - IC	300.0	100.7	5	Single	MCAW W	3	10 %	10000	10 mg/L	82.0	119.0	18.0	80.0	121.0	80.0	121.0	18.0	13 ug/L	50 ug/L	3.18 x MDL
	Nitrate - Cd/Auto	353.2	97.31	7.10	Multi	MCAW W	3	10 %	10000	2.5 mg/L	83.0	112.0	15.0	81.0	113.0	81.0	113.0	15.0		50 ug/L	Range
	Nitrate - ISE	---							10000												
19.	Nitrite - IC	300.0	97.7	5	Single	MCAW W	3	10 %	1000	0.1 ug/L	79.0	116.0	18.0	77.0	118.0	77.0	118.0	18.0	4 ug/L	10 ug/L	3.18 x MDL
	Nitrite - Cd/Auto	353.2	97.31	7.10	Multi	MCAW W	3	10 %	1000	2.5 mg/L	83.0	112.0	15.0	81.0	113.0	81.0	113.0	15.0		50 ug/L	Range
	Nitrite - Spec/Auto	---							1000												
	Nitrite - Spec/Auto	---							1000												
20.	O-phosphate - IC	300.0	100.4	3.8	Single	MCAW W	3	10 %	---	500 ug/L	86.0	115.0	14.0	85.0	116.0	85.0	116.0	14.0	61 ug/L	200 ug/L	3.18 x MDL
	O-phosphate - Asc/Auto	365.1	87.2	22	Multi	MCAW W	3	10 %	---	300 ug/L	43.0	132.0	45.0	38.0	136.0	38.0	136.0	44.0		10 ug/L	Range
	O-phosphate - Asc/Sing	---							---												
	O-phosphate - Phos/Mo	---							---												
	O-phosphate - Auto/seg	---							---												
	O-phosphate - Auto/Dis	---							---												
21.	Selenium - Furnace	---							50												
	Selenium - Hydride	---							50												
	Selenium - ICP/MS	200.8	102.48	9.8	Multi	Tbl 12	3	10 %	50	50 ug/L	82.0	123.0	20.0	80.0	125.0	80.0	125.0	20.0	7.9 ug/L	20 ug/L	3.18 x MDL

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Standardized QC and QC Acceptance Criteria for Methods in 40 CFR 141.23(k)(1)

		Data					Specs														
											IPR			OPR		MS/MSD					
		Reference		Prec-			CAL		MCL	Spike	Recovery		Prec-	Recovery		Recovery			ML	ML	
No.	Analyte	Method	Recovery	ision	Labs	Source	Points	Lin	(ug/L)	conc	Low	High	ision	Low	High	Low	High	RPD	MDL	Value	Calc
	Selenium - STGFAA	200.9	88.9	10	Single	Tbl IE	3	10 %	50	25 ug/L	52.0	125.0	36.0	48.0	129.0	48.0	129.0	36.0	0.6 ug/L	2 ug/L	3.18 x MDL
22.	Silica - ICP	200.7	53.86	45.38	Multi	Apx C	5	25 %	---	1 mg/L	d	145.0	91.0	d	154.0	d	154.0	91.0	58 ug/L	200 ug/L	3.18 x MDL
	Silica - Color	---							---												
	Silica - Color/Mo Blue	---							---												
	Silica - Molybdosil	---							---												
	Silica - Heteropoly	---							---												
	Silica - Auto/Mo react	---							---												
23.	Sodium - Flame	---							---												
	Sodium - ICP	200.7	99.77	24.27	Multi	Apx C	5	25 %	---	1 mg/L	51.0	149.0	49.0	46.0	154.0	46.0	154.0	49.0	29 ug/L	100 ug/L	3.18 x MDL
24.	Temperature	---																			
25.	Thallium - ICP/MS	200.8	101.5	14.5	Multi	Tbl 12	3	10 %	2.0	2 ug/L	72.0	131.0	29.0	69.0	134.0	69.0	134.0	29.0	0.3 ug/L	1 ug/L	3.18 x MDL
	Thallium - STGFAA	200.9	95.4	2.8	Single	Tbl IE	3	10 %	2.0	20 ug/L	85.0	106.0	11.0	84.0	107.0	84.0	107.0	11.0	0.7 ug/L	2 ug/L	3.18 x MDL

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Appendix G

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