

The EPA Administrator, Lisa P. Jackson, signed the following proposed rule on 05/10/2010, and EPA is submitting it for publication in the *Federal Register* (FR). While we have taken steps to ensure the accuracy of this Internet version of the rule, it is not the official version of the rule for purposes of compliance. Please refer to the official version in a forthcoming FR publication, which will appear on the Government Printing Office's FDSys website (<http://fdsys.gpo.gov/fdsys/search/home.action>) and on Regulations.gov (<http://www.regulations.gov>) in Docket No. EPA-HQ-OAR-2004-0800. Once the official version of this document is published in the FR, this version will be removed from the Internet and replaced with a link to the official version.

6560-50-P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[OAR-2004-0080]

RIN 2060-AF00

**Method 301 - Field Validation of Pollutant Measurement Methods
from Various Waste Media**

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action amends EPA's Method 301, Field Validation of Pollutant Measurement Methods from Various Waste Media. We revised the procedures in Method 301 based on our experience in applying the method and to correct errors that were brought to our attention. The revised Method 301 is more flexible, less

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expensive, and easier to use. This action finalizes amendments to Method 301 after considering comments received on the proposed rule published in the Federal Register on December 22, 2004.

DATES: This final rule is effective on [Insert date of publication in the Federal Register].

ADDRESSES: EPA has established a docket for this action under Docket ID No. EPA-HQ-OAR-2004-0080. All documents in the docket are listed in the <http://www.regulations.gov> index. Although listed in the index, some information is not publicly available, e.g., confidential business information (CBI) or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, is not placed on the Internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically at <http://www.regulations.gov> or in hard copy at the Air Docket, EPA/DC, EPA West, Room 3334, 1301 Constitution Avenue, NW, Washington, DC. The Docket Facility and the Public Reading Room are open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number
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for the Public Reading Room is (202) 566-1744, and the telephone number for the Air Docket is (202) 566-1742.

FOR FURTHER INFORMATION CONTACT: Ms. Lula H. Melton, Office of Air Quality Planning and Standards, Air Quality Assessment Division, Measurement Technology Group (E143-02), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; telephone number: (919) 541-2910; fax number: (919) 541-0516; e-mail address: melton.lula@epa.gov.

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I. General Information

- A. Does this action apply to me?

Method 301 affects/applies to you if you want to propose a new or alternative test method to meet an EPA compliance requirement.

- B. Where can I obtain a copy of this action?

In addition to being available in the docket, an electronic copy of this rule will also be available on the Worldwide Web

(www) through the Technology Transfer Network (TTN). Following This document is a prepublication version, signed by EPA Administrator, Lisa P. Jackson on 05/10/2011. We have taken steps to ensure the accuracy of this version, but it is not the official version.

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the Administrator's signature, a copy of the final rule will be placed on the TTN's policy and guidance page for newly proposed or promulgated rules at <http://www.epa.gov/ttn/oarpg>. The TTN provides information and technology exchange in various areas of air pollution control. A redline strikeout document that compares this final rule to the proposed rule has also been added to the docket.

C. Judicial Review

Under section 307(b)(1) of the Clean Air Act (CAA), judicial review of this final rule is available by filing a petition for review in the United States Court of Appeals for the District of Columbia Circuit by [Insert date 60 days after publication in the Federal Register]. Under section 307(d)(7)(B) of the CAA, only an objection to this final rule that was raised with reasonable specificity during the period for public comment can be raised during judicial review. Moreover, under section 307(b)(2) of the CAA, the requirements established by this action may not be challenged separately in civil or criminal proceedings brought by EPA to enforce these requirements.

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II. Background

This action amends EPA's Method 301, Field Validation of Pollutant Measurement Methods from Various Waste Media. Method 301 was originally promulgated in Appendix A of 40 CFR part 63 on June 3, 1991. We proposed amendments to Method 301 on December 22, 2004 (69 FR 76642). This action responds to comments received on that proposal and corrects errors found in the method.

III. Summary of the Final Method

You would use Method 301 whenever you propose to use a test method to meet an EPA compliance requirement other than a method required under a 40 CFR part 63 rule. The method specifies procedures for determining and documenting the precision and bias of measured concentrations from various media (e.g., sludge, exhaust gas, wastewater) at the level of an applicable standard for a source. Bias (or systemic error) is established by comparing your proposed method against a reference value.

A correction factor is employed to eliminate/minimize bias. This correction factor is established from data obtained during your validation test. Methods that have bias correction factors

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outside a specified range are considered unacceptable. Method precision (or random error) at the level of the standard must be demonstrated to be as precise as the validated method for acceptance.

IV. Significant Comments Received on the Proposed Amendments to Method 301

We proposed five major technical changes to Method 301. These technical changes include the following:

- (1) Replacing the Practical Limit of Quantitation (PLQ) with a procedure to determine the Limit of Detection (LOD),
- (2) Revising the bias acceptance criteria and eliminating correction factors,
- (3) Revising precision acceptance criteria when using analyte spiking,
- (4) Allowing analyte spiking even when there is an existing test method, and
- (5) Establishing new procedures for ensuring sample stability.

The following section provides our response to significant comments received on the proposed technical changes and some

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inadvertant errors that occurred with the restructuring of and addition of components to the method.

A. Applicability

Two commenters requested clarification that the final rule changes made to Method 301 only apply to methods submitted to EPA after promulgation of the changes and that Method 301 can be used whether or not a validated method exists. We are clarifying in this final rule that amendments to Method 301 do not apply to methods submitted for approval prior to promulgation. Also, Method 301 can be used whether or not a validated method exists. This action clarifies the effective date of the amended Method 301, and Section 1.0 of the final method clarifies that Method 301 can be used whether or not a validated method exists.

B. Reference Material

One commenter provided that, as written, reference material is analogous to analyte. Inadvertantly, in Section 5 of Method 301, "reference materials" was followed by "(analytes)." This paranthetical was modified for clarification purposes as noted below.

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A few commenters expressed concern that the standard against which precision and bias are compared is not required to be compared against a true value, usually a traceable standard. We agree that the reference material should be compared to a traceable standard.

We have amended Section 5 of the final method to state the following:

You must use reference materials (a material or substance whose one or more properties are sufficiently homogenous to the analyte) that are traceable to a national standards body (e.g., National Institute of Standards and Technology (NIST)) at the level of the applicable emission limitation or standard that the subpart in 40 CFR part 63 requires.

C. Validation Testing Over a Broad Range of Concentrations and Extended Period of Time

One commenter requested that validation testing over a broad range of concentrations and/or over an extended period of time be allowed and mentioned that they had developed technology that could test over a broad range of concentrations for an extended time-period. The commenter argued that if the accuracy and precision requirements can be demonstrated with sequential

sampling procedures, EPA should allow it. We agree with the

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commenter. We have approved methods demonstrated with sequential sampling to determine the precision of a proposed alternative method in the past. The final method explicitly states that sequential sampling procedures are allowed.

D. Performance Audit

One commenter stated that they do not agree that the performance audit requirements in Section 6 of the proposed rule should be included in Method 301. The commenter supported their position by stating that the audit material may not correspond to the matrix for which the alternate test method was designed, and it is similar to having to ask EPA permission to use a method that has passed Method 301 validation criteria. In addition, the commenter stated that the 30-day lead time for requesting the performance audit material reduces an affected party's flexibility in meeting performance testing timing requirements.

The function of an audit sample is to allow a tester to demonstrate that their measurement system, using a well-established measurement method, is operating within established quality assurance limits. If the alternative method is being
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compared to a validated test method as part of the Method 301 validation and an audit sample for the validated method exists, then an audit should be used for the validated method. Since the amendments to Method 301 were proposed on December 22, 2004, EPA promulgated a rule on September 13, 2010 (75 FR 55636), that moves all discussion of audits from the individual rules to the General Provisions of Part 63. Therefore, we have removed the proposed Section 6 which discussed performance audits.

E. Sample Stability Procedures

We proposed procedures for sample stability. Method 301 previously lacked specific procedures for ensuring that samples collected under proposed alternative methods were analyzed within an appropriate time. We revised Section 7.4 to include a requirement to calculate the difference in the sampling results at the minimum and maximum storage times, determine the standard deviation of the differences, and test the difference in the results for statistical significance by calculating the t-statistic and determining if the mean of the differences between the initial results and the results after storage is significant at the 95 percent confidence level. We also added Table 1 to

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compare the calculated t-statistic with the critical value of the t-statistic. These procedures are necessary to ensure sample stability and should have been included in Method 301.

Several commenters provided comments on the minimum and maximum storage holding time limits specified in Section 7.0 of Method 301. Commenters recommended that either the minimum and maximum holding times be removed and that holding times should be defined by the data or that they be liberalized (e.g., increase the minimum hold time from 24 hours to 48 to 72 hours). We agree with the commenters and are revising the minimum hold time to be seven days. The method will also require that the samples be analyzed again at the proposed maximum storage time or two weeks after the initial analysis.

F. Bias and Precision

We proposed to change the acceptance criteria for the bias in a proposed alternative method from ± 30 percent to ± 10 percent and concurrently to eliminate the requirement for correcting all data collected with the method. We provided that we believe that 12 pairs of results from a single source are not sufficient to allow us to establish a correction factor that can or should

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be applied to all future uses of the method.

One commenter stated that they did not believe that bias acceptance criteria should be changed unless uncertainties in the reference value are included in determining the significance of differences.

One commenter provided that the proposed reduction of bias from ± 30 percent to ± 10 percent is too stringent. One commenter suggested allowing a bias of ± 15 percent with no correction factors while continuing to allow a bias of ± 30 percent with the use of correction factors for bias values between 15 percent and 30 percent. The commenter provided a summary of EPA Method 301 validations of several methods to support their position.

We agree that reducing the acceptable bias to ± 10 percent may be too stringent because there may be testing situations that are so difficult that there are no methods readily available that could meet this requirement. We believe that a reasonable solution is to allow methods that have a bias greater than 10 percent if the results from these methods are corrected to account for that bias. However, we believe that we should

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not approve the use of methods with greater than 30 percent bias even if the user was willing to correct the results. We have changed the final method to allow a bias of ± 10 percent with no correction factors and allow a bias of ± 30 percent with the use of correction factors for bias values between 10 percent and 30 percent.

We proposed to change the acceptance criteria for method precision when using analyte spiking from ± 50 percent to ± 20 percent. In addition, we proposed to eliminate the requirement for different numbers of replicate samples depending on the method's relative precision. We also proposed to tighten the acceptance criteria for the precision of candidate alternative test methods.

One commenter stated that the proposed reduction of precision criteria from ± 50 percent to ± 20 percent is too stringent. The commenter suggested allowing a precision of ± 30 percent with no use of replicate runs and the continued allowance of a precision of ± 50 percent with the use of additional sample runs for precision values between 30 percent and 50 percent. The

commenter provided a summary of EPA Method 301 validations of
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several methods to support their position.

Based on our evaluation of the summary provided by the commenter and their suggestion, we have changed the final method. The method will continue to require a precision of ± 20 percent when only the required three runs per test are performed. However, we have added an option to allow test methods with a precision greater than ± 20 percent, but less than ± 50 percent, provided that the user collect nine sample runs per test during any compliance testing where the method is used.

G. Limit of Detection

We proposed to replace the determination of the PLQ with a procedure to determine the LOD. The purpose of establishing a measurement limit is to ensure that a test method is appropriate for its intended use. The LOD is a better parameter for this purpose. We provided that for most environmental measurements, it appears that precision is a function of the concentration of the analyte being measured. Thus, the relative imprecision will not decrease as the quantity measured increases.

In this case, we stated that the PLQ has no meaning. Several
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commenters disagreed that the PLQ is a meaningless concept and that there are instances that substituting the LOD for the PLQ is not always appropriate. Some of these commenters stated that the Office of Water formed a Federal Advisory Committee Act (FACA) Committee to consider alternative approaches to similar procedures they proposed (40 CFR part 136 Appendix B) and that Method 301 should be deferred until after those discussions have concluded and that consistent application be applied across the Agency based on those discussions.

The PLQ is a limit determined by the standard deviation of an estimate of a concentration; if the standard deviation of the estimate exceeds a threshold, then that estimate is unacceptable. The LOD is a limit determined by the estimate of the concentration itself. If this estimate possesses a value that cannot be distinguished from an estimate resulting from a blank sample with a stated level of confidence, then this estimate is unacceptable. The LOD is clearly a threshold that should be used in Method 301 since an estimate that cannot be distinguished from one resulting from a blank sample is unlikely to provide meaningful results.

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The PLQ does not appear to have any relevance for Method 301. There does not appear to be a good reason for a method that produces a standard deviation that exceeds an established threshold to not go through the full rigor of the bias and precision tests prescribed in Method 301. For these reasons, Method 301 retains the use of the LOD in lieu of the PLQ.

One commenter provided that the proposed LOD determination does not appear appropriate for radiochemical methods and suggested that the content of the Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP) be used. We agree with the commenter and have amended Method 301 to allow for the use of the MARLAP for radiochemical methods.

A few commenters requested that the calculation of the LOD be better defined and clarified in Table 4 of the method. One commenter expressed that the description of the procedures used for estimating the standard deviation at zero concentration (S_0) in Table 4 needs to be clarified.

The LOD is defined as the lowest quantity of a substance that can be distinguished from the absence of that substance

(i.e., blank value) with a stated level of confidence. For
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example, suppose blank samples are normally distributed, and S_0 represents the standard deviation of the blank samples (i.e., the standard deviation of pure "noise"). Then a sample value larger than $3S_0$ will have a probability of not being a blank of at least 99 percent if S_0 is estimated with at least 14 degrees of freedom (or at least 7 degrees of freedom if a 1-sided alternative hypothesis is assumed). If S_0 is "known", then the probability will be 99.74 percent, but this is often truncated to 99 percent.

The method for obtaining S_0 has been clarified to proceed as follows:

(1) Pick a concentration level that you think should approximate the LOD and call this level LOD_1 . Prepare seven samples of a standard set at a concentration of LOD_1 . Estimate the standard deviation of these seven samples, and call it S_1 .

(2) Define $LOD_0 = 3S_1$.

(3) If $LOD_1 \leq 2LOD_0$, then define $S_0 = S_1$.

(4) If $LOD_1 > 2LOD_0$, then proceed as follows:

a. Prepare two additional standards at concentrations

lower than LOD_1 , and call these LOD_2 and LOD_3 . Prepare

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seven samples of each of these two standards and estimate their standard deviations and call them S_2 and S_3 , respectively.

b. Plot S_1 , S_2 , and S_3 as a function of concentration, draw a best-fit straight line through them, and extrapolate to zero concentration.

c. Define S_0 as the extrapolation of the standard deviation at zero concentration.

H. Critical Values of t for the Two-Tailed 95 Percent Confidence Limit

Two commenters provided that the values of t for the two-tailed 95 percent confidence limit are wrong since they reflected an 80 percent confidence limit and there are some apparent typesetting errors. We corrected these values to reflect the 95 percent confidence limit and eliminated the typesetting errors in the final method.

I. Paired Sampling Procedure

Two commenters pointed out several errors and expressed concerns with the methods to ascertain and test precision in Section 12.

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Upon evaluation, we have decided to revise Section 12.2 in Method 301. We are deleting the comparison of the precision of the alternative method to that of the validated method. This decision was made because the paired sampling method described in it does not allow for the estimation of the within-sample standard deviation for either the alternative or validated methods.

J. Standard Deviation

One commenter expressed that the precision is a function of concentration; in other words, as the concentration level increases, so does the standard deviation of the estimate of that concentration. This could render the relative standard deviation (Eq. 301-8 in Section 10.4) meaningless.

A second commenter also expressed that the standard deviation is a function of concentration. This commenter noted that pollutant concentrations from an emission source are variable, resulting in a range of possible concentration values being measured. The commenter suggested that the appropriate procedure to compare two methods under these circumstances is to

compare the regression lines of the two methods across a range

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of concentrations.

We agree that this could be a potentially serious concern if there is little control over the concentrations being measured. However, if there is an appropriate level of control, then the procedures given in Method 301 are sufficient. In most situations, we believe that an appropriate level of control exists. For example, consider the case where an alternative method is compared against a validated method using quadruple samples. We believe that an appropriate level of control exists if the following four conditions are met: (1) there is positive correlation between the estimates within both alternative and validated pairs in the quadruple samples, and the respective correlation coefficients are reasonably constant as a function of concentration; (2) there is positive correlation between the alternative and validated estimates in the quadruple samples, and the correlation coefficient is reasonably constant as a function of concentration; (3) the within-quadruple sample concentrations are reasonably similar; and (4) if the between-quadruple sample concentrations vary greatly, then the

functional relationship between the standard deviation and

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concentration is reasonably similar for both the alternative and validated methods. We believe that these four conditions hold, for most cases, and an appropriate level of control exists. If one or more of these conditions is violated, then the user may request that they be allowed to compare the regression lines resulting from the alternative and validated estimates as a function of concentration as an alternative to the requirements in Method 301.

V. Statutory and Executive Order Reviews

A. Executive Order 12866 - Regulatory Planning and Review and Executive Order 13563 - Improving Regulation and Regulatory Review

This action is not a "significant regulatory action" under the terms of Executive Order 12866 (58 FR 51735, October 4, 1993) and is therefore not subject to review under Executive Orders 12866 and 13563 (76 FR 3821, January 21, 2011).

B. Paperwork Reduction Act

This action does not impose an information collection burden under the provisions of the Paperwork Reduction Act, 44 U.S.C.

3501 et seq. Burden is defined at 5 CFR 1320.3(b). We are not
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promulgating any new paperwork requirements (e.g., monitoring, reporting, recordkeeping) as part of this final action. This final rule amends Method 301 which may be used to validate test data or a new test method.

C. Regulatory Flexibility Analysis

The Regulatory Flexibility Act (RFA) generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this action on small entities, a small entity is defined as: (1) a small business as defined by the Small Business Administration's (SBA) regulations at 13 CFR 121.201; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population of less than 50,000; and (3) a small organization that is any not-for-

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profit enterprise that is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this final rule on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. This final rule will not impose any requirements on small entities. Small entities may chose to use this regulatory option of validating their own new or alternative compliance test method, but they are not required to choose this option. Any small entity choosing to use Method 301 to validate a new or alternative test method would likely do so because this option is less burdensome than the original method in the regulations.

D. Unfunded Mandates Reform Act

This action contains no federal mandates under the provisions of Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), 2 U.S.C. 1531-1538 for State, local, or tribal governments or the private sector. This action imposes no enforceable duty on any State, local or tribal governments or the private sector. Therefore, this action is not subject to the requirements of sections 202 or 205 of the UMRA. This action is also not

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subject to the requirements of section 203 of UMRA because it contains no regulatory requirements that might significantly or uniquely affect small governments. Any small entity that chooses to use Method 301 would likely do so because this option is less burdensome.

E. Executive Order 13132 - Federalism

This action does not have federalism implications. It will not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. This final rule simply amends Method 301 which may be used to validate test data or a new test method.

F. Executive Order 13175 - Consultation and Coordination with Indian Tribal Governments

This action does not have tribal implications, as specified in Executive Order 13175 (65 FR 67429, November 9, 2000). This final rule amends Method 301 which can be used to validate a new or alternative compliance test method. It does not add any new requirements and does not affect pollutant emissions or air

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quality. Thus, Executive Order 13175 does not apply to this action.

Although EO 13175 does not apply to this final rule, EPA specifically solicited comment on the proposed rule from tribal officials. No comments were received.

G. Executive Order 13045 - Protection of Children from Environmental Health Risks and Safety Risks

EPA interprets EO 13045 (62 F.R. 19885, April 23, 1997) as applying only to those regulatory actions that concern health or safety risks, such that the analysis required under section 5-501 of the EO has the potential to influence the regulation. This action is not subject to EO 13045 because it does not establish an environmental standard intended to mitigate health or safety risks.

H. Executive Order 13211 - Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use

This action is not subject to Executive Order 13211, (66 FR 28355 (May 22, 2001)) because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act

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Section 12(d) of the National Technology Transfer and Advancement Act of 1995 (NTTAA), Public Law 104-113, 12(d) (15 U.S.C. 272 note) directs EPA to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (for example, materials specifications, test methods, sampling procedures, and business practices) that are developed or adopted by voluntary consensus standards bodies. The NTTAA directs EPA to provide Congress, through OMB, explanations when the Agency decides not to use available and applicable voluntary consensus standards.

This action involves technical standards. While EPA has identified ASTM D4855-97 as being potentially applicable, we have decided not to use it in this rulemaking. The use of this voluntary consensus standard would have been impractical as the ASTM standard is less prescriptive than Method 301 for many procedures. For example, the ASTM standard does not require the use of a t-test explicitly to test the precision of an

alternative method, but instead states that a t-test or F-test

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should be used as appropriate. The primary difference between the ASTM standard and EPA Method 301 is that the ASTM standard addresses the testing of "materials" rather than environmental samples. Therefore, we believe the ASTM is impractical as an alternative to Method 301.

J. Executive Order 12898 - Federal Actions to Address Environmental Justice in Minority Populations and Low-income Populations

Executive Order (EO) 12898 (59 FR 7629 (Feb. 16, 1994)) establishes federal executive policy on environmental justice. Its main provision directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

EPA has determined that this final rule will not have disproportionately high and adverse human health or

environmental effects on minority or low-income populations

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because it does not affect the level of protection provided to human health or the environment. This action amends a method for validating new or alternative compliance test methods. It does not change any existing rules that limit air pollution emission limits.

K. Congressional Review Act

The Congressional Review Act, 5 U.S.C. 801 et seq., as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect, the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of the Congress and to the Comptroller General of the United States. EPA will submit a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives, and the Comptroller General of the United States prior to publication of the rule in the Federal Register. A major rule cannot take effect until 60 days after it is published in the Federal Register. This action is not a "major rule" as defined by 5 U.S.C. 804(2). This rule will be effective [Insert date of publication in the Federal Register]. This document is a prepublication version, signed by EPA Administrator, Lisa P. Jackson on 05/10/2011. We have taken steps to ensure the accuracy of this version, but it is not the official version.

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**Method 301 - Field Validation of Pollutant Measurement Methods
from Various Waste Media**

List of Subjects in 40 CFR Part 63

Environmental protection, Alternative test method, Air
pollution control, Field validation, Hazardous air pollutants,
Method 301.

Dated:

Lisa P. Jackson,
Administrator.

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For the reasons stated in the preamble, title 40, chapter I of the Code of the Federal Regulations is amended as follows:

PART 63--[AMENDED]

1. The authority citation for Part 63 continues to read as follows:

Authority: 42 U.S.C. 7401, et seq.

2. Appendix A is amended by revising Method 301 to read as follows:

Appendix A to Part 63 - Test Methods

* * * * *

**Method 301--Field Validation of Pollutant Measurement Methods
From Various Waste Media**

Sec.

Using Method 301

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18.0 Where can I find additional information?

Using Method 301

1.0 What is the purpose of Method 301?

The purpose of Method 301 is to provide a set of procedures that you, the owner or operator of an affected source subject to requirements under 40 CFR part 63 can use to validate an alternative test method to a test method required in 40 CFR part 63 or to validate a stand-alone alternative test method based on established precision and bias criteria. If you use Method 301 to validate your proposed alternative method, you must use the procedures described in this method. This method describes the minimum procedures that you must use to validate an alternative test method to meet 40 CFR part 63 compliance requirements. If you choose to propose a validation method other than Method 301, you must submit and obtain the Administrator's approval for the alternative validation method.

2.0 When must I use Method 301?

If you want to use an alternative test method to meet requirements in a subpart of 40 CFR part 63, you can use Method 301 to validate the alternative test method. You must request

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approval to use this alternative test method according to the procedures in Sections 16 and 63.7(f). You must receive the Administrator's written approval to use the alternative test method before you use the alternative test method to meet requirements under 40 CFR part 63. In some cases, the Administrator may decide to waive the requirement to use Method 301 for alternative test methods. Section 17 describes the requirements for obtaining a waiver.

3.0 What does Method 301 include?

3.1 Procedures. This method includes minimum procedures to determine and document systematic error (bias) and random error (precision) of measured concentrations from exhaust gases, wastewater, sludge, and other media. It contains procedures for ensuring sample stability if such procedures are not included in the test method. This method also includes optional procedures for ruggedness and detection limits.

3.2 Definitions.

Affected source means affected source as defined in 40 CFR 63.2 and in the relevant subpart under 40 CFR part 63.

Alternative test method means the sampling and analytical
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methodology selected for field validation using the method described in this appendix.

Paired sampling system means a sampling system capable of obtaining two replicate samples that were collected as closely as possible in sampling time and sampling location.

Quadruplet sampling system means a sampling system capable of obtaining four replicate samples that were collected as closely as possible in sampling time and sampling location.

Surrogate compound means a compound that serves as a model for the types of compounds being analyzed (i.e., similar chemical structure, properties, behavior). The model can be distinguished by the method from the compounds being analyzed.

4.0 How do I perform Method 301?

First, you introduce a known concentration of an analyte or compare the alternative test method against a validated test method to determine the alternative test method's bias. Then, you collect multiple, collocated simultaneous samples to determine the alternative test method's precision.

Alternatively, though it is not required, we allow validation

testing over a broad range of concentrations over an extended

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time period to determine precision of a proposed alternative method. Sections 5.0 through 17.0 describe the procedures in detail.

Reference Materials

5.0 What reference materials must I use?

You must use reference materials (a material or substance whose one or more properties are sufficiently homogenous to the analyte) that are traceable to a national standards body (e.g., National Institute of Standards and Technology (NIST)) at the level of the applicable emission limitation or standard that the subpart in 40 CFR part 63 requires. If you want to expand the applicable range of the method, you must conduct additional runs with higher and lower analyte concentrations. You must obtain information about your analyte according to the procedures in Sections 5.1 through 5.4.

5.1 Exhaust Gas Tests Concentration. You must get a known concentration of each analyte from an independent source such as a speciality gas manufacturer, specialty chemical company, or chemical laboratory. You must also get the manufacturer's certification for the analyte concentration and stability.

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5.2 Tests for Other Waste Media. You must get the pure liquid components of each analyte from an independent manufacturer. The manufacturer must certify the purity and shelf life of the pure liquid components. You must dilute the pure liquid components in the same type medium as the waste from the affected source.

5.3 Surrogate Analytes. If you demonstrate to the Administrator's satisfaction that a surrogate compound behaves as the analyte does, then you may use surrogate compounds for highly toxic or reactive compounds. A surrogate may be an isotope or one that contains a unique element (for example, chlorine) that is not present in the source or a derivation of the toxic or reactive compound if the derivative formation is part of the method's procedure. You may use laboratory experiments or literature data to show behavioral acceptability.

5.4 Isotopically Labeled Materials. Isotope mixtures may contain the isotope and the natural analyte. The isotope labeled analyte concentration must be more than five times the natural concentration of the analyte.

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Sampling Procedures

6.0 What sampling procedures must I use?

You may determine bias and precision by comparing against a validated test method, using isotopic sampling, or using analyte spiking (or the equivalent). Isotopic sampling can only be used for procedures requiring mass spectrometry or radiological procedures. You must collect samples according to the requirements in Table 1. You must perform the sampling according to the procedures in Sections 6.1 through 6.4.

6.1 Isotopic Spiking. Spike all 12 samples with the analyte at the concentration in the applicable emission limitation or standard in the subpart of 40 CFR part 63. If there is no applicable emission limitation or standard, spike at the expected level of the samples. Follow the appropriate spiking procedures in Sections 6.3.1 through 6.3.2 for the applicable waste medium.

6.2 Analyte Spiking. In each quadruplet set, spike half of the samples (two out of the four) with the analyte according to the applicable procedure in Section 6.3.

6.3 Spiking Procedure.

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6.3.1 Gaseous Analyte with Sorbent or Impinger Sampling Trains. Sample the analyte (in the laboratory or in the field) at a concentration that is close to the concentration in the applicable emission limitation or standard in the subpart of 40 CFR Part 63 (or the expected sample concentration where there is no standard) for the time required by the method, and then sample the gas stream for an equal amount of time. The time for sampling both the analyte and gas stream should be equal; however, the time should be adjusted to avoid sorbent breakthrough. The stack gas and the gaseous analyte may be sampled at the same time. The analyte must be introduced as close to the tip of the sampling train as possible.

6.3.2 Gaseous Analyte with Sample Container (Bag or Canister). Spike the sample containers after completion of each test run with an amount equal to the concentration in the applicable emission limitation or standard in the subpart of 40 CFR part 63 (or the expected sample concentration where there is no standard). The final concentration of the analyte would be approximately equal to the analyte concentration in the stack plus the applicable emission standard (corrected for spike

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volume). The volume amount of analyte must be less than 10 percent of the sample volume.

6.3.3 Liquid and Solid Analyte with Sorbent or Impinger Trains. Spike the trains with an amount equal to the concentration in the applicable emission limitation or standard in the subpart of 40 CFR part 63 (or the expected sample concentration where there is no standard) before sampling the stack gas. If possible, do the spiking in the field. If it is not possible to do the spiking in the field, you can do it in the laboratory.

6.3.4 Liquid and Solid Analyte with Sample Container (Bag or Canister). Spike the containers at the completion of each test run with an amount equal to the concentration in the applicable emission limitation or standard in the subpart of 40 CFR part 63 (or the expected sample concentration where there is no standard).

6.4 Probe Placement and Arrangement for Stationary Source Stack or Duct Sampling. To sample a stationary source as defined in 40 CFR 63.2, you must place the probe according to the procedures in this subsection. You must place the probes in

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the same horizontal plane.

6.4.1 Paired Sampling Probes. For paired sampling probes, the probe tip should be 2.5 cm from the outside edge of the other sample probe, with a pitot tube on the outside of each probe. The Administrator may approve a validation request where other paired arrangements for the pitot tube (where required) are used.

6.4.2 Quadruplet Sampling Probes. For quadruplet sampling probes, the tips should be in a 6.0 cm x 6.0 cm square area measured from the center line of the opening of the probe tip with a single pitot tube (where required) in the center or two pitot tubes (where required) with their location on either side of the probe tip configuration. You must propose an alternative arrangement whenever the cross-sectional area of the probe tip configuration is approximately five percent or more of the stack or duct cross-sectional area.

7.0 How do I ensure sample stability?

7.1 Developing Storage and Analysis Procedures. If the alternative test method includes well-established procedures

supported by experimental data for sample storage and the time

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within which the collected samples must be analyzed, you must store the samples according to the procedures in the alternative test method. You are not required to conduct the procedures in Section 7.2 or 7.3. If the alternative test method does not include such procedures, you must propose procedures for storing and analyzing samples to ensure sample stability. At a minimum, your proposed procedures must meet the requirements in Section 7.2 or 7.3. The minimum storage time should be as soon as possible, but no longer than 72 hours after collection of the sample. The maximum storage time should be no longer than two weeks.

7.2 Storage and Sampling Procedures for Stack Test Emissions. You must store and analyze samples of stack test emissions according to Table 3. If you are using analyte spiking procedures, you must include equal numbers of spiked and unspiked samples.

7.3 Storage and Sampling Procedures for Testing Other Waste Media (e.g., Soil/Sediment, Solid Waste, Water/Liquid).

You must analyze half of the replicate samples at the proposed minimum storage time and the other half at the proposed maximum

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storage time or within two weeks of the initial analysis to identify the effect of storage times on analyte samples. The minimum storage time should be as soon as possible, but no longer than seven days after collection of the sample.

7.4 Sample Stability. After you have conducted sampling and analysis according to Section 7.2 or 7.3, compare the results at the minimum and maximum storage times. Calculate the difference in the results using Equation 301-1.

$$d_i = R_{\text{mini}} - R_{\text{maxi}} \quad \text{Eq. 301-1}$$

Where:

d_i = difference between the results of the i th sample.

R_{mini} = results from the i th sample at the minimum storage time.

R_{maxi} = results from the i th sample at the maximum storage time.

7.4.1 Standard Deviation. Determine the standard deviation (SD_d) of the differences (d_i 's) of the paired samples using Equation 301-2.

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$$SD_d = \sqrt{\frac{\sum_i^n (d_i - d_m)^2}{n-1}} \quad \text{Eq. 301-2}$$

Where:

d_i = The difference between the results of the i th sample, $R_{\text{mini}} - R_{\text{maxi}}$.

d_m = The mean of the paired sample differences.

n = total number of paired samples.

7.4.2 t Test. Test the difference in the results for statistical significance by calculating the t-statistic and determining if the mean of the differences between the initial results and the results after storage is significant at the 95 percent confidence level and $n - 1$ degrees of freedom.

Calculate the value of the t-statistic using Equation 301-3.

$$t = \frac{|d_m|}{\frac{SD_d}{\sqrt{n}}} \quad \text{Eq. 301-3}$$

Where:

n = the total number of paired samples.

Compare the calculated t-statistic with the critical value of the t-statistic from Table 2. If the calculated t-value is less

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than the critical value, the difference is not statistically significant; thus, the sampling and analysis procedure ensures stability, and you may submit a request for validation of the proposed alternative test method. If the calculated t-value is greater than the critical value, the difference is statistically significant, and you must repeat the procedures in Section 7.2 or 7.3 with new samples using shorter proposed maximum storage times.

Bias and Precision

8.0 What are the requirements for bias?

You must establish bias by comparing the results of the sampling using the alternative test method against a reference value. The bias must be no more than ± 10 percent without the use of correction factors, and no more than ± 30 percent with the use of correction factors for bias values between 10 and 30 percent for the alternative test method to be acceptable.

9.0 What are the requirements for precision?

At a minimum, you must use paired sampling systems to establish precision. If you are using analyte spiking,

including isotopic samples, the precision expressed as the

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relative standard deviation (RSD) of the alternative test method at the level of the applicable emission limitation or standard in the subpart of 40 CFR part 63 must be less than or equal to 20 percent. For samples with a precision greater than 20 percent but less than 50 percent, a minimum of nine sample runs will be required. If you are comparing to a validated test method, the alternative test method must be at least as precise as the validated method at the level of the applicable emission limitation or standard in the subpart of 40 CFR part 63 as determined by an F test (Section 11.2.2).

10.0 What calculations must I perform for isotopic spiking?

You must analyze the bias, precision, relative standard deviation, and data acceptance for isotopic spiking tests according to the provisions in Sections 10.1 through 10.3.

10.1 Numerical Bias. Calculate the numerical value of the bias using the results from the analysis of the isotopically spiked field samples and the calculated value of the isotopically labeled spike according to Equation 301-4.

$$B = S_m - CS$$

Eq. 301-4

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Where:

B = Bias at the spike level.

S_m = Mean of the measured values of the isotopically spiked samples.

CS = Calculated value of the isotopically labeled spike.

10.2 Standard Deviation. Calculate the standard deviation of the S_i values according to Equation 301-5.

$$SD = \sqrt{\frac{\sum_i^n (S_i - S_m)^2}{(n-1)}} \quad \text{Eq. 301-5}$$

Where:

S_i = Measured value of the isotopically labeled analyte in the i-th field sample,

n = Number of isotopically spiked samples, 12.

10.3 t Test. Test the bias for statistical significance by calculating the t-statistic using Equation 301-6. Use the standard deviation determined in Section 10.2 and the numerical bias determined in Section 10.1.

$$t = \frac{|B|}{\frac{SD}{\sqrt{n}}} \quad \text{Eq. 301-6}$$

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Compare the calculated t-value with the critical value of the two-sided t-distribution at the 95 percent confidence level and n-1 degrees of freedom. When spiking is conducted according to the procedures specified in Sections 6.2 and 6.4 as required, this critical value is 2.201 for the 11 degrees of freedom. If the calculated t-value is less than the critical value, the bias is not statistically significant, and the bias of the candidate test method is acceptable. If the calculated t-value is greater than the critical value, the bias is statistically significant, and you must evaluate the relative magnitude of the bias using Equation 301-7.

$$B_R = \left| \frac{B}{CS} \right| \times 100\% \quad \text{Eq. 301-7}$$

Where:

B_R = Relative bias.

If the relative bias is less than or equal to ten percent, the bias of the candidate test method is acceptable and no correction factors are required. If the relative bias is greater than 10 percent but less than 30 percent, and if you correct all future data collected with the method for the

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magnitude of the bias, the bias of the candidate test method is acceptable. If either of the preceding two cases applies, you may continue to evaluate the method by calculating its precision. If not, the candidate method will not meet the requirements of Method 301.

10.4 Relative Standard Deviation. Calculate the RSD according to Equation 301-8.

$$RSD = \left(\frac{SD}{S_m} \right) \times 100 \qquad \text{Eq. 301-8}$$

Where:

S_m = the measured mean of the isotopically labeled spiked samples.

The data and alternative test method are unacceptable if the RSD is greater than 20 percent.

11.0 What calculations must I perform for comparison with a validated method if I am using quadruplet replicate sampling systems?

If you are using quadruplet replicate sampling systems to compare an alternative test method to a validated method, then you must analyze the data according to the provisions in this

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section. If the data from the alternative test method fail either the bias or precision test, the data and the alternative test method are unacceptable. If the Administrator determines that the affected source has highly variable emission rates, the Administrator may require additional precision checks.

11.1 Bias Analysis. Test the bias for statistical significance at the 95 percent confidence level by calculating the t-statistic.

11.1.1 Bias. Determine the bias, which is defined as the mean of the differences between the alternative test method and the validated method (d_m). Calculate d_i according to Equation 301-9.

$$d_i = \frac{(V_{1i} + V_{2i})}{2} - \frac{(P_{1i} + P_{2i})}{2} \quad \text{Eq. 301-9}$$

Where:

V_{1i} = First measured value with the validated method in the i-th sample.

V_{2i} = Second measured value with the validated method in the i-th sample.

P_{1i} = First measured value with the alternative test method

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in the i -th sample.

P_{2i} = Second measured value with the alternative test method
in the i -th sample.

11.1.2 Standard Deviation of the Differences. Calculate the standard deviation of the differences, SD_d , using Equation 301-2.

11.1.3 t Test. Calculate the t -statistic using Equation 301-3, where n is the total number of test sample differences (d_i). For the quadruplet sampling system procedure in Section 6.1 and Table 1, n equals four. Compare the calculated t -statistic with the critical value of the t -statistic, and determine if the bias is significant at the 95 percent confidence level. When four runs are conducted, as specified in Section 6.2 and Table 1, the critical value of the t -statistic is 3.182 for three degrees of freedom. If the calculated t -value is less than the critical value, the bias is not statistically significant and the data are acceptable. If the calculated t -value is greater than the critical value, the bias is statistically significant, and you must evaluate the relative magnitude of the bias using Equation 301-10.

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$$B_R = \left| \frac{B}{VS} \right| \times 100\% \quad \text{Eq. 301-10}$$

Where:

B = Bias - mean of the d_i 's.

VS = mean measured by the validated method.

If the relative bias is less than or equal to 10 percent, the bias of the candidate test method is acceptable and no correction factors are required. If the relative bias is greater than 10 percent but less than 30 percent, and if you correct all future data collected with the method for the magnitude of the bias, the bias of the candidate test method is acceptable. If either of the preceding two cases applies, you may continue to evaluate the method by calculating its precision. If not, the candidate method will not meet the requirements of Method 301.

11.2 Precision. Compare the estimated variance (or standard deviation) of the alternative test method to that of the validated method. If a significant difference is determined using the F test, the alternative test method and the results are rejected. If the F test does not show a significant

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difference, then the alternative test method has acceptable precision. Use the value furnished with the method. Calculate the estimated variance of the validated method using Equation 301-11.

11.2.1 Alternative Test Method Variance. Calculate the estimated variance of the alternative test method, S_p^2 , according to Equation 301-11.

$$S_p^2 = \frac{\sum_i^n d_i^2}{2n} \quad \text{Eq. 301-11}$$

Where:

d_i = The difference between the i-th pair of samples collected with the alternative test method.

n = number of samples and the degrees of freedom.

11.2.2 F Test. Determine if the estimated variance of the alternative test method is greater than that of the validated method by calculating the F-value using Equation 301-12.

$$F = \frac{S_p^2}{S_v^2} \quad \text{Eq. 301-12}$$

Where:

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S_p^2 = The estimated variance of the alternative method.

S_v^2 = The estimated variance of the validated method.

Compare the experimental F value with the one-sided confidence level for F. The one-sided confidence level of 95 percent for F is 6.388 when the procedure specified in Section 6.1 and Table 1 for quadruplet trains is followed. If the calculated F is outside the critical range, the difference in precision is significant, and the data and the candidate test method are unacceptable.

12.0 What calculations must I perform for analyte spiking?

You must analyze the data for analyte spike testing according to this section.

12.1 Bias Analysis. Test the bias for statistical significance at the 95 percent confidence level by calculating the t-statistic.

12.1.1 Bias. Determine the bias using the results from the analysis of the spiked field samples, the unspiked field samples, and the calculated value of the spike using Equation 301-13.

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$$d_i = \frac{(S_{1i} + S_{2i})}{2} - \frac{(M_{1i} + M_{2i})}{2} - CS \quad \text{Eq. 301-13}$$

Where:

S_{1i} = First measured value of the i th spiked sample.

S_{2i} = Second measured value of the i th spiked sample.

M_{1i} = First measured value of the i th unspiked sample.

M_{2i} = Second measured of the i th unspiked sample.

CS = Calculated value of the spiked level.

12.1.2 Standard Deviation of the Differences. Calculate the standard deviation of the differences, SD_d , using Equation 301-2.

12.1.3 t Test. Calculate the t-statistic using Equation 301-3, where n is the total number of test sample differences (d_i). For the quadruplet sampling system procedure in Table 1, n equals six. Compare the calculated t-statistic with the critical value of the t-statistic, and determine if the bias is significant at the 95 percent confidence level. When six runs are conducted, as specified in Table 1, the two-sided confidence level critical value is 2.571 for the five degrees of freedom.

If the relative bias is less than or equal to 10 percent with no

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correction factors, or the bias is greater than 10 percent but less than 30 percent with the use of correction factors, then the data are acceptable. Proceed to evaluate precision of the candidate test method.

$$B_R = \left| \frac{B}{VS} \right| \times 100\% \quad \text{Eq. 301-10}$$

Where:

B = Bias - mean of the d_i 's.

VS = mean measured by the validated method.

12.2 Precision. Calculate the standard deviation and the relative standard deviation of the candidate test method. The relative standard deviation of the candidate test method can be calculated using Equation 301-8.

13.0 How do I conduct tests at similar sources?

If the Administrator has approved the use of an alternative test method to a test method required in 40 CFR part 63 for an affected source, and the Administrator has approved the use of the alternative test method at your similar source according to the procedures in Section 17.1.1, you must meet the requirements in this section. You must have at least three

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replicate samples for each test that you conduct at the similar source. You must average the results of the samples to determine the pollutant concentration.

Optional Requirements

14.0 How do I use and conduct ruggedness testing?

If you want to use a validated test method at a concentration that is different from the concentration in the applicable emission limitation in the subpart of 40 CFR part 63 or for a source category that is different from the source category that the test method specifies, then you must conduct ruggedness testing according to the procedures in Citation 18.16 of Section 18.0 and submit a request for a waiver according to Section 17.1.1.

Ruggedness testing is a laboratory study to determine the sensitivity of a method to parameters such as sample collection rate, interferant concentration, collecting medium temperature, and sample recovery temperature. You conduct ruggedness testing by changing several variables simultaneously instead of changing one variable at a time. For example, you can determine the effect of seven variables in eight experiments instead of one.

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(W.J. Youden, Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33-36).

15.0 How do I determine the Limit of Detection for the alternative method?

15.1 Limit of Detection. The Limit of Detection (LOD) is the lowest level above which you may obtain quantitative results with an acceptable degree of confidence. For this protocol, the LOD is defined as three times the standard deviation, S_0 , at the blank level.

15.2 Purpose. The LOD will be used to establish the lower limit of the test method. If the estimated LOD is no more than twice the calculated LOD, use Procedure I in Table 4 to determine S_0 . If the LOD is greater than twice the calculated LOD, use Procedure II in Table 4 to determine S_0 . For radiochemical methods, use the Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual (i.e., use the minimum detectable concentration (MDC) and not the LOD) available at http://www.epa.gov/radiation/docs/marlap/402-b-04-001c-20_final.pdf.

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Other Requirements and Information

16.0 How do I apply for approval to use an alternative test method?

16.1 Submitting Requests. You must request to use an alternative test method according to the procedures in Section 63.7(f). You may not use an alternative test method to meet any requirement under 40 CFR part 63 until the Administrator has approved your request. The request must include a field validation report containing the information in Section 16.2. The request must be submitted to the Director, Air Quality Assessment Division, U.S. Environmental Protection Agency, C304-02, Research Triangle Park, NC 27711.

16.2 Field Validation Report. The field validation report must contain the information in Sections 16.2.1 through 16.2.8.

16.2.1 Regulatory objectives for the testing, including a description of the reasons for the test, applicable emission limits, and a description of the source.

16.2.2 Summary of the results and calculations shown in Sections 6.0 through 16, as applicable.

16.2.3 Analyte certification and value(s).

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16.2.4 Discussion of laboratory evaluations.

16.2.5 Discussion of field sampling.

16.2.6 Discussion of sample preparations and analysis.

16.2.7 Storage times of samples (and extracts, if applicable).

16.2.8 Reasons for eliminating any results.

17.0 How do I request a waiver?

17.1 Conditions for Waivers. If you meet one of the criteria in Sections 17.1.1 through 17.1.2, the Administrator may waive the requirement to use the procedures in this method to validate an alternative test method. In addition, if EPA currently recognizes an appropriate test method or considers the analyst's test method to be satisfactory for a particular source, the Administrator may waive the use of this protocol or may specify a less rigorous validation procedure.

17.1.1 Similar Sources. If the alternative test method that you want to use has been validated at another source and you can demonstrate to the Administrator's satisfaction that your affected source is similar to that source, then the

Administrator may waive the requirement for you to validate the

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alternative test method. One procedure you may use to demonstrate the applicability of the method to your affected source is by conducting a ruggedness test as described in Section 14.0.

17.1.2 Documented Methods. If the bias and precision of the alternative test method that you are proposing have been demonstrated through laboratory tests or protocols different from this method, and you can demonstrate to the Administrator's satisfaction that the bias and precision apply to your application, then the Administrator may waive the requirement to use this method or to use part of this method.

17.2 Submitting Applications for Waivers. You must sign and submit each request for a waiver from the requirements in this method in writing. The request must be submitted to the Director, Air Quality Assessment Division, U.S. Environmental Protection Agency, C304-02, Research Triangle Park, NC 27711.

17.3 Information Application for Waiver. The request for a waiver must contain a thorough description of the test method, the intended application, and results of any validation or other supporting documents. The request for a waiver must contain, at This document is a prepublication version, signed by EPA Administrator, Lisa P. Jackson on 05/10/2011. We have taken steps to ensure the accuracy of this version, but it is not the official version.

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a minimum, the information in Sections 17.3.1 through 17.3.4. The Administrator may request additional information if necessary to determine whether this method can be waived for a particular application.

17.3.1 A Clearly Written Test Method. The method should be written preferably in the format of 40 CFR part 60, Appendix A Test Methods. It must include an applicability statement, concentration range, precision, bias (accuracy), and minimum and maximum storage time in which samples must be analyzed.

17.3.2 Summaries of previous validation tests or other supporting documents. If a different procedure from that described in this method was used, you must submit documents substantiating the bias and precision values to the Administrator's satisfaction.

17.3.3 Ruggedness Testing Results. You must submit results of ruggedness testing conducted according to Section 14.0, sample stability conducted according to Section 7.0, and detection limits conducted according to Section 15.0, as applicable. For example, you would not need to submit

ruggedness testing results if you will be using the method at
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the same concentration level as the concentration level at which it was validated.

17.3.4 Applicability Statement and Basis for Waiver Approval. Your discussion of the applicability statement and basis for approval of the waiver should address the following as applicable: applicable regulation, emission standards, effluent characteristics, and process operations.

18.0 Where can I find additional information?

You can find additional information in the references in Sections 18.1 through 18.16.

18.1 Albritton, J.R., G.B. Howe, S.B. Tompkins, R.K.M. Jayanty, and C.E. Decker. 1989. Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits, Status Report No. 11. Environmental Protection Agency Contract 68-02-4125. Research Triangle Institute, Research Triangle Park, NC. September.

18.2 ASTM Standard E 1169-89 (current version), "Standard Guide for Conducting Ruggedness Tests," available from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

18.3 DeWees, W.G., P.M. Grohse, K.K. Luk, and F.E. Butler. This document is a prepublication version, signed by EPA Administrator, Lisa P. Jackson on 05/10/2011. We have taken steps to ensure the accuracy of this version, but it is not the official version.

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1989. Laboratory and Field Evaluation of a Methodology for Speciating Nickel Emissions from Stationary Sources. EPA Contract 68-02-4442. Prepared for Atmospheric Research and Environmental Assessment Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. January.

18.4 International Conference on Harmonization of Technical Requirements for the Registration of Pharmaceuticals for Human Use, ICH-Q2A, "Text on Validation of Analytical Procedures," 60 FR 11260 (March 1995).

18.5 International Conference on Harmonization of Technical Requirements for the Registration of Pharmaceuticals for Human Use, ICH-Q2b, "Validation of Analytical Procedures: Methodology," 62 FR 27464 (May 1997)

18.6 Keith, L.H., W. Crummer, J. Deegan Jr., R.A. Libby, J.K. Taylor, and G. Wentler. 1983. Principles of Environmental Analysis. American Chemical Society, Washington, DC.

18.7 Maxwell, E.A. 1974. Estimating variances from one or two measurements on each sample. Amer. Statistician 28:96-97.

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18.8 Midgett, M.R. 1977. How EPA Validates NSPS Methodology. Environ. Sci. & Technol. 11(7):655-659.

18.9 Mitchell, W.J., and M.R. Midgett. 1976. Means to evaluate performance of stationary source test methods. Environ. Sci. & Technol. 10:85-88.

18.10 Plackett, R.L., and J.P. Burman. 1946. The design of optimum multifactorial experiments. Biometrika, 33:305.

18.11 Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Inc., pp. 79-81.

18.12 U.S. Environmental Protection Agency. 1978. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods. Publication No. EPA-600/4-77-027b. Office of Research and Development Publications, 26 West St. Clair St., Cincinnati, OH 45268.

18.13 U.S. Environmental Protection Agency. 1981. A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. Publication No. EPA-600/7-81-010. Available from

the U.S. EPA, Quality Assurance Division (MD-77), Research

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Triangle Park, NC 27711.

18.14 U.S. Environmental Protection Agency. 1991.
Protocol for The Field Validation of Emission Concentrations
From Stationary Sources. Publication No. 450/4-90-015.
Available from the U.S. EPA, Emission Measurement Technical
Information Center, Technical Support Division (MD-14), Research
Triangle Park, NC 27711.

18.15 Wernimont, G.T., "Use of Statistics to Develop and
Evaluate Analytical Methods," AOAC, 1111 North 19th Street, Suite
210, Arlington, VA 22209. USA, 78-82 (1987).

18.16 Youden, W.J. Statistical techniques for
collaborative tests. Statistical Manual of the Association of
Official Analytical Chemists, Association of Official Analytical
Chemists, Washington, DC, 1975, pp. 33-36.

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Table 1 of Appendix A. Sampling Procedures

If you are...	You must collect...
comparing against a validated method	9 sets of replicate samples using a paired sampling system (a total of 18 samples) or 4 sets of replicate samples using a quadruplet sampling system (a total of 16 samples). In each sample set, you must use the validated test method to collect and analyze half of the samples.
using isotopic spiking (can only be used for procedures requiring mass spectrometry)	a total of 12 replicate samples. You may collect the samples either by obtaining 6 sets of paired samples or 3 sets of quadruplet samples.
using analyte spiking	a total of 24 samples using the quadruplet sampling system (a total of 6 sets of replicate samples).

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Table 2 of Appendix A. Critical Values of t for the Two Tailed 95 Percent Confidence Limit

Degrees of freedom	t_{95}
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228

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Table 3 of Appendix A. Storage and Sampling Procedures for Stack Test Emissions

If you are...	With...	Then you must...
using isotopic or analyte spiking procedures	sample container (bag or canister) and impinger sampling systems	analyze 6 of the samples within 7 days and then analyze the same 6 samples at the proposed maximum storage time or 2 weeks after the initial analysis.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest 6 of the samples within 7 days and extract or digest 6 other samples at the proposed maximum storage time or 2 weeks after the first extraction or digestion. Analyze an aliquot of the first 6 extracts (digestates) within 7 days and proposed maximum storage times or 2 weeks after the initial analysis. This will allow analysis of extract storage impacts.
	sorbent sampling systems that require thermal	analyze 6 samples within 7 days. Analyze another set of 6 samples at the proposed

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**Table 3 of Appendix A. Storage and Sampling Procedures
for Stack Test Emissions**

If you are...	With... desorption	Then you must... maximum storage time or within 2 weeks of the initial analysis.
comparing an alternative test method against a validated test method	sampling method that does not include sorbent and impinger sampling systems that require extraction or digestion	analyze half of the samples (8 or 9) within 7 days and half of the samples (8 or 9) at the proposed maximum storage time or within 2 weeks of the initial analysis.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest 6 of the samples within 7 days and extract or digest 6 other samples at the proposed maximum storage time or within 2 weeks of the first extraction or digestion. Analyze an aliquot of the first 6 extracts (digestates) within 7 days and at the proposed maximum storage times or within 2 weeks of the initial analysis. This will allow analysis of

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**Table 3 of Appendix A. Storage and Sampling Procedures
for Stack Test Emissions**

If you are...	With...	Then you must...
		extract storage impacts.

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Table 4 of Appendix A. Procedures for Estimating S_0 .

If the estimated LOD (LOD_1 , expected approximate LOD concentration level) is no more than twice the calculated LOD, use Procedure I as follows. Estimate the LOD (LOD_1) and prepare a test standard at this level. The test standard could consist of a dilution of the analyte described in Section 5.0.	If the estimated LOD (LOD_1 , expected approximate LOD concentration level) is greater than twice the calculated LOD, use Procedure II as follows. Prepare two additional standards (LOD_2 and LOD_3) at concentration levels lower than the standard used in Procedure I (LOD_1).
Using the normal sampling and analytical procedures for the method, sample and analyze this standard at least 7 times in the laboratory.	Sample and analyze each of these standards (LOD_2 and LOD_3) at least 7 times.
Calculate the standard deviation, S_1 , of the measured values.	Calculate the standard deviation (S_2 and S_3) for each concentration level.
Calculate the LOD_0 (referred to as the calculated LOD) as 3 times S_1 , where $S_0 = S_1$.	Plot the standard deviations of the three test standards (S_1 , S_2 and S_3) as a function of concentration.
	Draw a best-fit straight line through the data points and extrapolate to zero concentration. The standard deviation at zero concentration is S_0 .
	Calculate the LOD_0 (referred to as the calculated LOD) as 3 times S_0 .

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