ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[OAR-2004-0080, FRL-7851-9]

RIN 2060-AF00

National Emission Standards for Hazardous Air Pollutants: Appendix A - Test Methods; Method 301 for the Field Validation of Pollutant Measurement Methods from Various Waste Media

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: This action proposes to amend procedures for validating alternative emissions test methods, to rewrite the EPA's Method 301 in plain language, reorganize the method for clarity, correct technical errors, and revise the technical procedures. The revisions to the technical procedures include replacing quantitation limits with detection limits, revising the bias acceptance criteria and eliminating the correction factors, revising the precision acceptance criteria, and allowing analyte spiking as an option even when there is an existing test method.

DATES: Comments. Comments must be received on or before [INSERT DATE 60 DAYS AFTER PUBLICATION IN THE FEDERAL REGISTER].

Public Hearing. If anyone contacts the EPA requesting a public hearing by [INSERT DATE 20 DAYS AFTER PUBLICATION IN THE FEDERAL REGISTER], a public hearing will be held on [INSERT DATE 30 DAYS AFTER PUBLICATION IN THE FEDERAL REGISTER].

ADDRESSES: Comments. Submit your comments, identified by Docket ID No. OAR-2004-0080, by one of the following methods.

- Federal eRulemaking Portal: http:///www.regulations.gov. Follow the on-line instructions for submitting comments.
- Agency Website: http://www.epa.gov/edocket. EDOCKET, EPA's electronic public docket and comment system, is EPA's preferred method for receiving comments. Follow the on-line instructions for submitting comments.
- Mail: Air and Radiation Docket and Information Center (Mail Code 6102T), Attention Docket Number OAR-2004-0080, Room B108, U.S. EPA, 1301 Constitution Avenue, NW., Washington, DC 20460. The EPA requests that a separate copy also be sent to the contact person listed below (see FOR FURTHER INFORMATION CONTACT). Send submissions containing such proprietary or confidential business information (CBI) directly to the following address, and not to the public docket, to ensure that proprietary or CBI is not inadvertently placed in the public docket: Attention: Mr. Roberto Morales, U.S. Environmental Protection Agency, OAQPS Document Control Officer, 109 TW Alexander Drive, Room C404-02, RTP, NC, 27711.
- Hand Delivery: Air and Radiation Docket and Information Center (Mail Code 6102T), Attention Docket Number OAR-2004-0080, Room B102, U.S. EPA, 1301 Constitution Avenue, NW, Washington, DC 20460. Such deliveries are only accepted during the Docket's normal hours of operation, and special arrangements should be made for deliveries of boxed information. The EPA requests a separate copy also be sent to the contact person listed below (see FOR

FURTHER INFORMATION CONTACT).

Instructions. Direct your comments to Docket ID No. OAR-2004-0080. The EPA's policy is that all comments received will be included in the public docket without change and may be made available online at http://www.epa.gov/edocket, including any personal information provided, unless the comment includes information claimed to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Do not submit information that you consider to be CBI or otherwise protected through EDOCKET, regulations.gov websites, or e-mail. The EPA EDOCKET and the Federal regulations.gov websites are "anonymous access" systems, which means the EPA will not know your identity or contact information unless you provide it in the body of your comment. If you send an e-mail comment directly to the EPA without going through EDOCKET OR regulations.gov, your e-mail address will be automatically captured and included as part of the comment that is placed in the public docket and made available on the internet. If you submit an electronic comment, the EPA recommends that you include your name and other contact information in the body of your comment and with any disk or CD-ROM you submit. If the EPA cannot read your comment due to technical difficulties and cannot contact you for clarification, the EPA may not be able to consider your comment. Electronic files should avoid the use of special characters, any form of encryption, and be free of any defects or viruses. For additional information about EPA's public docket visit EDOCKET on-line or see the Federal Register of May 31, 2002 (67 FR 38102).

Docket. All documents in the docket are listed in the EDOCKET index at http://www.epa.gov/edocket. Although listed in the index, some information is not

publicly available, i.e., 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 hardcopy form. Publicly available docket materials are available either electronically in EDOCKET or in hard copy at the EPA Docket Center (Air Docket), EPA West, Room B-108, 1301 Constitution Avenue, NW., Washington, DC 20004. The Docket Center is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566-1744, and the telephone number for the Air Docket is (202) 566-1742.

Public Hearing. People interested in presenting oral testimony or inquiring as to whether a hearing is to be held should contact Ms. Corlis McCormick, Source Measurement Technology Group, Emission Measurement Center (D243-02), U.S. Environmental Protection Agency, Research Triangle Park, NC, 27711, telephone number: (919) 541-5545, at least 2 days in advance of the public hearing. People interested in attending the public hearing must also call Ms. McCormick to verify the time, date, and location of the hearing. The public hearing will provide interested parties the opportunity to present data, views, or arguments concerning the proposed changes to Method 301. If a public hearing is held, it will be held at 10:00 a.m. in the EPA's Auditorium in Research Triangle Park, North Carolina, or at an alternate site nearby.

FOR FURTHER INFORMATION CONTACT: For information concerning the proposed standards, contact Mr. Gary McAlister, Source Measurement Technology Group, Emission Measurement Center (D243-02), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number: (919) 541-1062, electronic mail address: mcalister.gary@epa.gov.

SUPPLEMENTARY INFORMATION:

Preamble Outline

The information in this preamble is organized as follows.

I. General Information

A. Does this Action Apply to Me?

Method 301 affects/applies to you if you want to propose a test method to meet an EPA requirement in absence of a validated method.

B. What Should I Consider as I Prepare My Comments for the EPA?

1. Submitting CBI. Do not submit this information to the EPA through EDOCKET, regulations.gov, or e-mail. Clearly mark the part or all of the information that you claim to be CBI. For CBI information in a disk or CD ROM that you mail to the

EPA, mark the outside of the disk or CD ROM as CBI and then identify electronically within the disk or CD ROM the specific information that is claimed as CBI. In addition to one complete version of the comment that includes information claimed as CBI, a copy of the comment that does not contain the information claimed as CBI must be submitted for inclusion in the public docket. Information so marked will not be disclosed except in accordance with procedures set forth in 40 CFR Part 2.

2. Tips for Preparing Your Comments. When submitting comments, remember to:

i. Identify the rulemaking by docket number and other identifying information (e.g., subject heading, Federal Register proposal publication date and reference page number(s)).

ii. Follow directions - The EPA may ask you to respond to specific questions or organize comments by referencing a Code of Federal Regulations (CFR) part or section number.

iii. Explain why you agree or disagree; suggest alternatives and provide substitute language for your requested changes.

iv. Describe any assumptions and provide any technical information and/or data that you used.

v. If you estimate potential costs or burdens, explain how you arrived at your estimate in sufficient detail to allow for it to be reproduced.

vi. Provide specific examples to illustrate your concerns, and suggest alternatives.

vii. Explain your views as clearly as possible, avoiding the use of profanity or

personal threats.

viii. Make sure to submit your comments by the specified comment period deadline.

Commenters wishing to submit proprietary information for consideration must clearly distinguish such information from other comments and clearly label it as CBI. Send submissions containing such proprietary information directly to the following address, and not to the public docket, to ensure that proprietary information is not inadvertently placed in the docket: Attention: Mr. Roberto Morales, U.S. Environmental Protection Agency, OAQPS Document Control Officer, 109 TW Alexander Drive, Room C404-02, RTP, NC, 27711. The EPA will disclose information identified as CBI only to the extent allowed by the procedures set forth in 40 CFR Part 2. If no claim of confidentiality accompanies a submission when it is received by the EPA, the information may be made available to the public without further notice to the commenter.

C. Availability of the Proposed Rule

In addition to being available in the docket, an electronic copy of the proposed changes to Method 301 is also available on the Internet through the Technology Transfer Network (TTN). Following signature, a copy of Method 301 will be posted on the TTN's policy and guidance page for newly proposed or promulgated rules http://www.epa.gov/ttn/oarpg. The TTN provides information and technology exchange in various areas of air pollution control. If more information regarding the TTN is needed, call the TTN HELP line at (919) 541-5384.

II. Introduction

Today's action proposes to amend EPA's Method 301; Field Validation of

Pollutant Measurement Methods from Various Waste Media. Method 301 can be found in Appendix A of 40 CFR, Part 63 (Test Methods). Method 301 was promulgated with 40 CFR, Part 63, Subpart D (Regulations Governing Compliance Extensions for Early Reductions of Hazardous Air Pollutants)(58 FR 27338, June 13, 1991) pursuant to Section 112 of the Clean Air Act (as amended in 1990). You would use Method 301 whenever you propose to use a test method to meet an EPA requirement in absence of a validated method. 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 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.

Today's action proposes to amend those provisions by correcting technical errors, and simplifying and clarifying procedures. Section II of this preamble discusses the proposed Method 301 rule, and Section III presents the administrative requirements for this action.

III. What Changes Are We Proposing?

A. Use Plain Language

In compliance with President Clinton's June 1, 1998, Executive Memorandum on Plain Language in government writing, Method 301 has been rewritten in plain language.

The use of plain language clarifies the requirements of Method 301, thus, reducing the burden (time) associated with understanding the Method. When Method 301 refers to "you," it means the owner or operator of the affected source.

B. Reorganize Method 301

We have reorganized the information in Method 301 to make it easier to follow the requirements and to understand the relationships among the various requirements. The reorganization did not create new requirements, but it does incorporate various corrections to technical errors and technical revisions. These corrections and revisions, as well as the rationale for the changes, are discussed in Sections III C and D of this preamble.

Section 17.0 of today's rule (What detection limits must I use?) shall apply instead of Section 9.0 (Practical Quantitation Limits) of the promulgated Method 301 rule. We have retained all other sections from the promulgated Method 301, but you will find them in new places. Where necessary for clarity, we have put the information from one section of Promulgated Method 301 into several new sections. Some information has been put into tables at the end of the Method. Section 2.0 presents new information. It has been added to explain when you must use Method 301 and to identify the requirement for receiving written approval from the Administrator before using the alternative test method. Table 1 of this preamble specifies where the sections in the promulgated Method 301 are found in the proposed Method 301 rule.

The equations of the promulgated Method 301 have also been amended. Some of the promulgated equations have been modified; some have been replaced by other equations, and some have simply been renumbered or reordered. The technical reasons

for the changes to the equations are discussed in Section III. D of this preamble. Table 2 indicates whether each equation in the proposed amended rule has changed from the promulgated rule. Equations 301-5 and 301-10 (correction factors when using isotopic spiking and paired sampling systems with a validated test method comparison) of promulgated Method 301 rule have been removed for the reasons discussed in Section III D of this preamble.

Table 1. Comparison of Sections in Proposed Method 301. to Those in Promulgated Method 301.

Proposed New Section		Promulgated Method Section	
	Using Method 301		
1.0	What is the purpose of Method 301?	1.1	Applicability
2.0	When must I use Method 301?	None	
3.0	What does Method 301 include?	1.1.2	
4.0	How do I perform Method 301?	1.2	Principle
	Reference Materials and Performance Audits		
5.0	What reference materials must I use?	3.0	Reference Materials
6.0	How do I conduct the performance audit?	4.0	EPA Performance Audit Materials
	Sampling Procedures		
7.0	What sampling procedures must I use?	5.0	Procedure for Determination of Bias and Precision in the Field
8.0	How do I ensure sample stability?	8	Procedure for Sample Stability in Bias and Precision Evaluations
	Bias and Precision		
9.0	What are the requirements for bias?	1.2.1	Bias
10.0	What are the requirements for precision?	1.2.2	Precision
11.0	What calculations must I perform for isotopic sampling?	6.1	Isotopic Sampling
12.0	What calculations must I perform for comparison with a validated method if I am using paired sampling systems?	6.2.1	Comparison with a validated method: Paired Sampling Systems
13.0	What calculations must I perform for comparison with a validated method if I am using quadruplet replicate sampling systems?	6.2.2	Comparison with a validated method: Quadruplet Replicate Sampling Systems
14.0	What calculations must I perform for analyte spiking?	6.3	Analyte Spiking
15.0	How do I conduct followup tests?	11	Followup Testing
	Optional Requirements		
16.0	How do I use and conduct ruggedness testing?	7	Ruggedness Testing
17.0	What detection limits must I use?	9	Practical Limit of Quantitation

Table 1. Comparison of Sections in Proposed Method 301. to Those in Promulgated Method 301.

Proposed New Section		Promulgated Method Section	
	Other Requirements and Information		
18.0	How do I apply for approval to use an alternative method?	10	Field Validation Report Requirements
19.0	How do I request a waiver?	1.1.1 and 12	Procedure for Obtaining a Waiver
20.0	What definitions apply to this method?	2	Definitions
21.0	Where can I find additional information?	13	Bibliography

Table 2. Equations in Proposed Method 301

The following equation in proposed Method 301. . .		is...	The following equation in promulgated Method 301...
301-1	Difference in Sample Results	new	
301-7	Relative Magnitude of Bias	new	
301-9	Relative Magnitude of Bias for Comparing Against Validated Methods Using Paired Sampling Systems	new	
Equations When Using Isotopic Spiking			
301-4	Numerical Value of Bias	a revision of	301-1
301-5	Standard Deviation	the same as	301-2
301-6	t Test	a replacement for	301-3 and 301-4
301-8	Relative Standard Deviation	a revision of	301-6
Equations When Comparing Against Validated Method Using Paired Sampling Systems			
301-2	Standard Deviation	for paired sampling systems, a replacement for	301-2
301-3	t Test	the same as	301-9
301-10	Variance	a replacement for	301-7
301-11	Pooled Variance	new	
301-12	Alternative Test Method Variance	a replacement for	301-9a
301-13	F test	the same as	301-8
Equations When Comparing Against Validated Method Using Quadruplet Replicate Sampling Systems			
301-14	Bias	the same as	301-12
301-15	Alternative Test Method Variance	the same as	301-11
Equations When Using Analyte Spiking			
301-16	Bias	the same as	301-14
301-17	t Test	a replacement for	301-4
301-18	Standard Deviation for Spiked Samples	a revision of	301-13
301-19	Standard Deviation for Unspiked Samples	a replacement for	301-13 and 301-6

The following equation in proposed Method 301. . .		is...	The following equation in promulgated Method 301...
301-20	F test	new	
301-21	Pooled Standard Deviation	a replacement for	301-15

C. Correct Technical Errors

Some of the equations in promulgated Method 301 are incorrect. We are proposing to correct these equations with today's action. For a discussion of new equations due to technical revisions, see Section III D of this preamble. We revised several equations to clarify their intent. Under the new numbering system, the revised equations are 301-4 (numerical value of bias), 301-6 (t Test), 301-8 (relative standard deviation), 301-18 (standard deviation for spiked samples), and 301-19 (standard deviation for unspiked samples). These changes were editorial/defining changes and not technical changes. For example, we added or changed subscripts or redefined a variable.

We added Equations 301-1, 301-7, and 301-9. Equation 301-1 is used to calculate the difference in minimum and maximum storage times under the new sample stability procedures. Equation 301-7 is used to calculate relative magnitude of bias for isotopic spiking. This new equation was needed when we dropped the use of correction factors. Likewise, Equation 301-9 was needed for calculating relative magnitude of bias when comparing against a validated method using paired sampling systems.

We also added Equation 301-11 and changed Equations 301-12, 301-17, 301-18, and 301-19 to correct technical errors in promulgated Method 301. Equations 301-11 (Pooled Variance) and 301-12 (Alternative Test Method Variance) are being proposed to correct a technical error in the promulgated method. Addition and subtraction can only be performed on the variance. It cannot be performed on the standard deviation. The proposed Equation 301-11 is a new equation that calculates the pooled variance of both methods when comparing against validated methods using paired sampling systems. The proposed Equation 301-12 replaces the standard deviation with the variance.

Equations 301-17 (calculation of the test "t-statistic") and 301-21 (calculation of the pooled standard deviation) were changed because the divisor was wrong. Equation 301-20 (F test) was added so that the tester could determine if the spiked and unspiked samples had the same precision, thereby allowing them to be pooled to calculate the overall precision.

The proposed Equation 301-2 (Standard Deviation) replaces the promulgated Equation 301-2 when comparing against validated methods using paired sampling systems. The text in promulgated 6.2.1.4 directs the analyst to determine the mean of the paired sample differences by substituting d_m (mean of the paired sample differences) and d_i (standard deviation of the differences) for S_i and S_m in the proposed Equation 301-2. We created the proposed Equation 301-2 to incorporate these changes.

D. Make Technical Revisions

We are proposing 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,

(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.

1. Practical Limit of Quantitation. We are proposing to replace the determination of the PLQ with a procedure to determine the Limit of detection (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.

The PLQ is defined as the level or concentration at which the precision of a test method reaches an acceptable value. There are several problems with this concept. The first is the idea that there is an absolute value for acceptable precision. To a certain extent, a tester can compensate for imprecision by collecting additional data so there is no absolute level at which the imprecision of a test method becomes so great that the method is no longer useful. This concept works best when the precision of the test method is independent of the concentration of the analyte being measured. As the concentration of the analyte increases, the imprecision of the method as a percentage of the measured quantity decreases. In this case, the relative imprecision will actually decrease as the quantity measured increases.

However, for most environmental measurements, it appears that the 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, the PLQ has no meaning.

The LOD is the minimum level or concentration of an analyte that produces a signal or response that is distinguishable from the signal or response produced when no analyte is present. This is a measurable quantity that can be determined regardless of the method's precision or whether that precision varies with the level of the analyte. For all of these reasons, we believe that the LOD is a more useful parameter to characterize a test method's performance.

2. Bias Acceptance Criteria. We are also proposing to change the acceptance criteria for the bias in a proposed alternative method from $\pm$ 30% to $\pm$ 10% and

concurrently to eliminate the requirement for correcting all data collected with the method. We believe that twelve pairs of results from a single source are not sufficient to allow us to establish a correction factor that can or should be applied to all future uses of the method. In addition, keeping track of correction factors to ensure that they are applied to future uses of the method is a huge administrative burden both for the users of the method and the regulatory agencies who oversee its use. If we do not use correction factors, method biases of up to 30 percent are undesirably large. Therefore, we are proposing to reduce the acceptable bias to ± 10% and eliminate the requirement to correct the data. With this change, the bias of alternative methods will be acceptable; the criteria for using the alternative test method at similar sources will be clear, and the administrative burden will be reduced.

3. Precision Acceptance Criteria. We are proposing to change the acceptance criteria for method precision when using analyte spiking from ± 50% to ± 20%. In addition, we are proposing to eliminate the requirement for different numbers of replicate samples depending on the method's relative precision. All future testing using an alternative test method at similar sources will require only three replicate samples. The requirement in the existing procedure was an attempt to compensate for the poorer precision of some candidate alternative test methods by increasing the amount of data that the user was required to collect. While more data does compensate for the imprecision of any future data collected with the method, allowing candidate alternative test methods with poor precision creates other problems. One problem is that poor precision makes it more difficult to detect potential bias in a test method. For this reason, we are proposing to tighten the acceptance criteria for the precision of candidate

alternative test methods.

4. Analyte Spiking. We are also proposing to allow the tester to use analyte spiking to evaluate an alternative test method even when there is an existing compliance test method. If the NESHAP specifies a test method, promulgated Method 301 requires the tester to evaluate an alternative method by direct comparison. We believe that this is too restrictive in some cases. For example, a change in process technology may cause a previously unbiased test method to develop an interference that biases its results. If the tester is required to compare the alternative test method to the existing test method, the alternative method could never demonstrate acceptable performance if it were unbiased. We believe that it is sufficient for an alternative method to demonstrate acceptable performance by using the analyte spiking procedure and that this is a reasonable alternative to direct comparison.

5. Sample Stability. Finally, we are proposing 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. New Section 8.4 includes 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 have also added Table 1 to 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 promulgated Method 301.

III. What Are The Administrative Requirements?

A. Executive Order 12866 - Regulatory Planning and Review

Under Executive Order 12866 (58 FR 51735, October 4, 1993), the EPA must determine whether the regulatory action is "significant" and, therefore, subject to review by the Office of Management and Budget (OMB) and the requirements of the Executive Order. The Executive Order defines "significant regulatory action" as one that is likely to result in a rule that may:

(1) Have an annual effect on the economy of $100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities;

(2) Create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;

(3) Materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or

(4) Raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

It has been determined that this proposed regulatory action is not a "significant regulatory action" under the terms of Executive Order 12866 and is, therefore, not subject to OMB review.

B. Paperwork Reduction Act

This action does not impose or change the information collection burden under the provisions of the Paperwork Reduction Act 44 U.S.C. 3501, et seq. Burden means

the total time, effort, or financial resources expended by persons to generate, maintain, retain, or disclose or provide information to or for a Federal agency. This includes the time needed to review instructions; develop, acquire, install, and utilize technology and systems for the purposes of collecting, validating, and verifying information, processing and maintaining information, and disclosing and providing information; adjust the existing ways to comply with any previously applicable instructions and requirements; train personnel to be able to respond to a collection of information; search data sources; complete and review the collection of information; and transmit or otherwise disclose the collection of information.

An agency may not conduct or sponsor, and a person is not required to respond to a collection of information unless it displays a currently valid OMB control number. The OMB control numbers for EPA's regulations are listed in 40 CFR Part 9 and 48 CFR Chapter 15.

C. Regulatory Flexibility Act (RFA)

The 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 the purposes of assessing the impacts of today's proposed rule on small entities, small entity is defined as: (1) A small business that meets the definitions for small business based on the Small Business Association (SBA) size standards which, for

this proposed action, are operations that have fewer than 1,000 employees; (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-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of today's proposed rule on small entities, I certify that this proposed action will not have a significant economic impact on a substantial number of small entities. In determining whether a rule has significant economic impact on a substantial number of small entities, the impact of concern is any significant adverse economic impact on small entities since the primary purpose of the regulatory flexibility analysis is to identify and address regulatory alternatives "which minimize any significant economic impact of the proposed rule on small entities," (5 U.S.C. 603 and 604). Thus, an agency may certify that a rule will not have a significant economic impact on a substantial number of small entities if the rule relieves regulatory burden, or otherwise has a positive economic effect on all of the small entities subject to the rule. This proposed rule will not impose any requirements on small entities. This rule establishes procedures for using alternative methods. As such, small entities and other sources are not required to comply with this proposed rule, but may elect to use Method 301. The proposed rule offers additional flexibility to all sources, including small entities that may be subject to requirements under the CAA. Additionally, this proposed amended rule clarifies and simplifies the procedures for using alternative methods. We continue to be interested in the potential impacts of the proposed rule on small entities and welcome comments on issues related to such impacts.

D. Unfunded Mandates Reform Act

Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), Public Law 1044, establishes requirements for Federal agencies to assess the effects of their regulatory actions on State, local, and tribal governments and the private sector. Under Section 202 of the UMRA, the EPA generally must prepare a written statement, including cost-benefit analysis, for proposed and final rules with "Federal mandates" that may result in expenditures to State, local, and tribal governments, in the aggregate, or to the private sector, of $100 million or more in any one year. Before promulgating an EPA rule for which a written statement is needed, Section 205 of the UMRA generally requires the EPA to identify and consider a reasonable number of regulatory alternatives and adopt the least costly, most cost-effective, or least burdensome alternative if the Administrator publishes with the final rule an explanation why that alternative was not adopted. Before EPA establishes any regulatory requirements that may significantly or uniquely affect small governments, including tribal governments, it must have developed under Section 203 of the UMRA a small government agency plan. The plan must provide for notifying potentially affected small governments, enabling official of affected small governments to have meaningful and timely input in the development of EPA regulatory proposals with significant Federal intergovernmental mandates, and informing, educating, and advising small governments on compliance with the regulatory requirements.

We have determined that today’s proposed amended rule does not contain Federal mandates for State, local, or tribal governments or the private sector. Therefore, this proposed amended rule is not subject to the requirements of Sections 202 and 205 of the

UMRA.

E. Executive Order 13132 - Federalism

Executive Order 13132, entitled "Federalism" (64 FR 43255, August 10, 1999), requires the EPA to develop an accountable process to ensure “meaningful and timely input by State and local officials in the development of regulatory policies that have federalism implications." "Policies that have federalism implications" is defined in the Executive Order to include regulations that 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."

Under Executive Order 13132, the EPA may not issue a regulation that has federalism implications, that imposes substantial direct compliance costs, and that is not required by statute, unless the Federal government provides the funds necessary to pay the direct compliance costs incurred by State and local governments, or the EPA consults with State and local officials early in the process of developing the proposed regulation. The EPA also may not issue a regulation that has federalism implications and that preempts State law unless the Agency consults with State and local officials early in the process of developing the proposed regulation.

Today’s proposed amended rule will not have federalism implications. They 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. Today’s proposed amended rule clarifies and simplifies the procedures for using alternative methods. Thus, the requirements of Section 6 of the Executive Order do not apply.

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

Executive Order 13175, entitled “Consultation and Coordination with Indian Tribal Governments” (65 FR 67249, November 9, 2000), requires EPA to develop an accountable process to ensure “meaningful and timely input by tribal officials in the development of regulatory policies that have tribal implications.” The proposed amended rule does not have tribal implications, as specified in Executive Order 13175. The proposed action serves to clarify and simplify procedures for using alternative methods. Therefore, Executive Order 13175 does not apply to the proposed amended rule.

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

Executive Order 13045, “Protection of Children from Environmental Health Risks and Safety Risks” (62 FR 19885, April 23, 1997), applies to any rule that the EPA determines is: (1) "economically significant" as defined under E.O. 12866; and (2) concerns an environmental health or safety risk that the EPA has reason to believe may have a disproportionate effect on children. If the regulatory action meets both criteria, the EPA must evaluate the environmental health or safety effects of the planned rule on children and explain why the planned regulation is preferable to other potentially effective and reasonable alternatives considered by the EPA.

The EPA interprets Executive Order 13045 as applying only to those regulatory actions that are based on health or safety risks, such that the analysis required under Section 5-501 of the Executive Order has the potential to influence the regulation. The proposed amended rule is not subject to Executive Order 13045 because it is not

economically significant as defined in Executive Order 12866, and because this proposed amended rule is not based on health or safety risks. Thus, Executive Order 13045 does not apply to this proposed amended rule.

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

This rule is not subject to Executive Order 13211, "Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use" (66FR28355(May22, 2001)) because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act of 1995

Section 112(d) of the National Technology Transfer and Advancement Act of 1995 (NTTAA), Public Law No. 104-113, Section 12(d)915 U.S.C. 272 note), directs all Federal agencies to use voluntary consensus standards instead of government unique

standards in their regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical.

Voluntary consensus standards are technical standards (e.g., materials specifications, test methods, sampling procedures, and business practices, etc.) that are developed or adopted by one or more voluntary consensus standards bodies. Examples of organizations, generally regarded as voluntary consensus standards bodies, include the American Society for Testing and Materials (ASTM), the National Fire Protection Association (NFPA), and the Society of Automotive Engineers (SAE). The NTTAA

requires Federal agencies like EPA to provide Congress through OMB with explanations when an agency decides not to use available and applicable voluntary consensus standards. This proposed amended rule clarifies and simplifies, already promulgated, procedures for use of alternative standards. The intent of the Method 301 is to allow owners and operators of sources regulated by Part 63 standards the flexibility and option to use alternative standards. Today's proposed amended rule is intended to simplify and clarify the procedures for using alternative standards. Therefore, the EPA is not considering the use of any voluntary consensus standards with today's proposed action.

List of Subjects in 40 CFR Part 63

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

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Dated: December 16, 2004.

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Michael O. Leavitt,
Administrator.

For the reasons stated in the preamble, Title 40, Chapter I, Part 63, of the Code of the Federal Regulations is proposed to be 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. Part 63 is amended by revising Appendix A to read as follows:

Appendix A to Part 62 - Test Methods

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

Sec.

Using Method 301

1.0 What is the purpose of Method 301?

2.0 When must I use Method 301?

3.0 What does Method 301 include?

4.0 How do I perform Method 301?

Reference Materials and Performance Audits

5.0 What reference materials must I use?

6.0 How do I conduct the performance audit?

Sampling Procedures

7.0 What sampling procedures must I use?

8.0 How do I ensure sample stability?

Bias and Precision

9.0 What are the requirements for bias?

Using Method 301

1.0 What is the purpose of Method 301?

This method describes the minimum procedures that you, the owner or operator of an affected source subject to requirements under 40 CFR Part 63, must use to validate an alternative test method to a test method required in 40 CFR Part 63.

2.0 When must I use Method 301?

If you want to request to use an alternative test method to meet requirements in a

subpart of 40 CFR Part 63, you must use Method 301 to validate the alternative test method. You must request approval to use the alternative test method according to the procedures in Section 18 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. Section 19 describes the requirements for obtaining a waiver.

3.0 What does Method 301 include?

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.

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. Sections 5.0 through 17.0 describe these procedures in detail.

Reference Materials and Performance Audits

5.0 What reference materials must I use?

You must use reference materials (that is, analytes) 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. The additional runs must be conducted according to the ruggedness procedures in 16.0. You must use the analytes according to the procedures in 5.1 through 5.4.

5.1 Exhaust Gas Tests. 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 stability data for the analyte concentration and recommendations for recertification.

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. You must verify the accuracy of the concentration of each diluted analyte by comparing its response to the pure liquid components.

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.

6.0 How do I conduct the performance audit?

6.1 Getting Performance Audit Material. If EPA has performance audit material for the analytes that you are testing, you must use it to assess method bias. You can get a list of performance audit materials at http://www.epa.gov/ttn/emc/email.html#audit or by contacting EMC at (919) 541-5545. You must request the performance audit material at least 30 days before the validation test.

6.2 Sampling and Analyzing Performance Audit Material. You must sample and analyze the performance audit material three times according to the instructions provided with the audit sample. You must submit the three results with the field validation report. Although there are no acceptance criteria for these performance audit results, you and the Administrator may use them to assess the relative error of sample recovery, sample preparation, and analytical procedures and then consider the relative error in evaluating the measured emissions.

Sampling Procedures

7.0 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. Isotopic sampling can only be used for procedures requiring mass spectrometry. You must collect samples according to the requirements in Table 1. You must perform the sampling according to the procedures in Sections 7.1 through 7.5.

7.1 Comparison Against a Validated Test Method. If you are comparing the results from the validated test method, it is recommended that you conduct a performance audit according to the procedures in Section 6.

7.2 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 7.4.1 through 7.4.2 for the applicable waste medium.

7.3 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 7.4.

7.4 Spiking Procedure.

7.4.1 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.

7.4.2 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 shall approximate the level of the emission concentration in the stack. The volume amount of analyte shall be less than 10 percent of the sample volume.

7.4.3 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.

7.4.4 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).

7.5 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 7.5. You must place the probes in the same horizontal plane.

7.5.1 For Paired Sample Probes, the sample 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 are used.

7.5.2 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 in the center or two pitot tubes 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 5 percent or more of the stack or duct cross-sectional area.

8.0 How do I ensure sample stability?

8.1 Developing Storage and Analysis Procedures. If the alternative test method includes well-established procedures supported by experimental data for sample storage and the time 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 8.2 or 8.3. 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 8.2 or 8.3. The minimum storage time should be as soon as possible, but no longer than 24 hours after collection of the sample. The maximum storage time should be four weeks or less.

8.2 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.

8.3 Storage and Sampling Procedures for Testing Other Waste Media. You must analyze half of the replicate samples at the proposed minimum storage time and the other half at the proposed maximum storage time to identify the effect of storage times on analyte samples. The minimum storage time should be as soon as possible, but no longer

than 24 hours after collection of the sample. The maximum storage time should be two weeks or less.

8.4 Sample Stability. After you have conducted sampling and analysis according to 8.2 or 8.3, compare the results at the minimum and maximum storage times. Calculate the difference in the results using Equation 301-1.

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

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.

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

$$SD_d = \sqrt{\frac{\sum_{i}^{N} (d_i - d_m)^2}{n-1}} \qquad \text{Eq. 301-2}$$

Where:

V_m = validated method

P_m = proposed alternative test method

d_i = The difference between the i-th pair of samples, V_m - P_m

d_m = The mean of the paired sample differences.

n = total number of paired samples

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

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

Where: n is 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 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 8.2 or 8.3 with new samples using shorter proposed maximum storage times.

Bias and Precision

9.0 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% for the alternative test method to be acceptable.

10.0 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 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. 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.

11.0 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 11.1 through 11.3.

11.1. 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.

$$B = S_m - CS \qquad \text{Eq. 301-4}$$

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.

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

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

Where:

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

n = Number of isotopically spiked samples, 12.

11.3 t Test. Test the bias for statistical significance by calculating the t-statistic using Equation 301-6. Use the standard deviation determined in Section 11.2 and the numerical bias determined in section 11.1.

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

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 7.2 and 7.4 as required, this critical value is 2.201 for the eleven 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 301-7.

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

Where:

B_R = Relative bias.

If the relative bias is less than or equal to 10 percent, then the data are acceptable. You may proceed to evaluate the precision. If not the candidate method will not meet the requirements of Method 301.

11.4 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 is 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.

12.0 What calculations must I perform for comparison with a validated method if I am using paired sampling systems?

You must analyze the data for comparison with a validated method according to Section 12. Conduct these procedures to determine if an alternative test method produces results equivalent to a validated method. If the data from the alternative test method fail either the bias or precision test, the data and the alternative test method are unacceptable.

12.1 Bias Analysis.

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

12.1.2 t Test. Test the bias for statistical significance by calculating the t-statistic and determine if the mean of the differences between the alternative test method and the validated method is significant at the 95 percent confidence level. Calculate the value of the t-statistic using Equation 301-3. For the spiking procedure for paired sampling systems, according to Section 7.1 and Table 1, n equals nine.

Compare the calculated t-statistic with the critical value of the t-statistic. When nine runs are conducted, as specified in Section 7.1 and Table 1, the critical value of the t-statistic is 1.397 for eight 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 301-9. If the relative bias is less than or equal to 10 percent, then the data are acceptable. Proceed to evaluate precision.

$$B_R = \left| \frac{B}{VS} \right| \quad x \quad 100\% \qquad \text{Eq. 301-9}$$

Where:

B = Bias = mean of the d_i's

VS = mean measured by the validated method

12.2. Precision. Compare the variance 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 difference, then the alternative test method has acceptable precision. This procedure requires that you know the standard deviation of the validated method, SD_v. Use the value furnished with the method. If the standard deviation of the validated method is not available, the paired replicate sampling procedure may not be used.

12.2.1 Variance. Calculate the variance of the validated method, S_v^2, using Equation 301-10.

$$S_v^2 = SD_v^2 \qquad \text{Eq. 301-10}$$

Where:

SD_v = Standard deviation provided with the validated method.

12.2.2 Pooled Variance. Calculate the pooled variance of both methods, S^2_{pooled}, according to Equation 301-11.

$$S^2_{pooled} = \frac{\sum_i^N d_i^2}{2(n-1)} \qquad \text{Eq. 301-11}$$

Where:

d_i = The difference between the i-th pair of validated and alternative method samples.

n = The number of pairs of samples.

12.2.3 Alternative Test Method Variance. Calculate the variance of the alternative test method, S^2_p, from the S^2_{pooled} using Equation 301-12.

$$S^2_p = S^2_{pooled} - S^2_v \qquad \text{Eq. 301-12}$$

(If $S^2_v > S^2_{pooled}$, let $S^2_p = S^2_{pooled}/2$).

12.2.4 The F test. Determine if the variance of the alternative test method is significantly different from that of the validated method by performing the F test. Calculate the experimental F-value using Equation 301-13.

$$F = \frac{S_p^2}{S_v^2} \qquad \text{Eq. 301-13}$$

Compare the experimental F value with the critical range of F at a 95 percent confidence level. When the procedure specified in Section 7.1 and Table 1 for paired trains is followed as required, the critical range is 0.291 to 3.44. If the calculated F is outside the critical range, the difference in precision is significant and the data and alternative test method are unacceptable.

13.0 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 13.0. 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.

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

13.1.1 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 301-14.

$$d_i = \frac{(V_{1_i} + V_{2_i})}{2} - \frac{(P_{1_i} + P_{2_i})}{2} \qquad \text{Eq. 301-14}$$

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 in the i-th sample.

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

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

13.1.3 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 7.1 and Table 1, n equals four. Compare the calculated t-statistic with the critical value from 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 7.2 and Table 1, the critical value of the t-statistic is 1.638 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 301-9. If the relative bias is less than or equal to 10 percent, then the data are acceptable. Proceed to evaluate precision of the alternative test method.

13.2 Precision. Compare the variance 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 difference, then the alternative test method has acceptable precision. This procedure requires the standard deviation of the validated method, SD_v, to be known. Use the value furnished with the method. If there are no published values, calculate the variance of the validated method using Equation 301-15.

13.2.1 Alternative Test Method Variance. Calculate the variance of the alternative test method, S_p^2, according to Equation 301-15.

$$S_p^2 = \frac{\Sigma d_i^2}{2n} \qquad \text{Eq. 301-15}$$

Where:

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

13.2.2 The F test. Determine if the variance of the alternative test method is greater than that of the validated method by calculating the F-value using Equation 301-13. Compare the experimental F value with the critical range of F. The critical range is 0.264 to 3.79 for the 95 percent confidence level when the procedure specified in Section 7.1 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 alternative test method are unacceptable.

14.0 What calculations must I perform for analyte spiking?

You must analyze the data for analyte spike testing according to Section 14.

14.1 Bias Analysis.

14.1.1 Bias. Calculate the numerical value of 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 301-16.

$$B = S_m - M_m - CS \qquad \text{Eq. 301-16}$$

Where:

B = Bias at the spike level.

S_m = Mean of the spiked samples.

M_m = Mean of the unspiked samples.

CS = Calculated value of the spiked level.

14.1.2 T Test. Test the bias for statistical significance by calculating the t-statistic using Equation 301-17 and comparing it with the critical value of the two-sided t-distribution at the 95 percent confidence level and n-2 degrees of freedom. This critical value is 2.228 for the ten degrees of freedom.

$$t = \frac{|B|}{\sqrt{\frac{S_u^2 + S_s^2}{12}}} \qquad \text{Eq. 301-17}$$

Where:

$S^2_u = (SD_u)^2$, SD_u is calculated in Equation 301-19.

$S^2_s = (SD_s)^2$, SDs is calculated in Equation 301-18.

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 301-7. If the relative bias is less than or equal to 10 percent, then the data are acceptable. You may proceed to evaluate precision.

14.2 Precision. Calculate the standard deviation and the RSD of the alternative test method.

14.2.1 Spiked Samples. Calculate the difference, d_i, between the pairs of the spiked alternative test method measurements for each replicate sample set. Determine

the standard deviation (SD_s) of the spiked values using Equation 301-18.

$$SD_s = \sqrt{\frac{\Sigma\, d_{is}^{\,2}}{2n}} \qquad \text{Eq. 301-18}$$

Where: d_{is} = Difference between the i-th pair of spiked samples.

n = Number of paired samples.

14.2.2 Unspiked Samples. Calculate the standard deviation of the unspiked values using Equation 301-19.

$$SD_u = \sqrt{\frac{\Sigma\, d_{iu}^{\,2}}{2n}} \qquad \text{Eq. 301-19}$$

Where: d_{iu} = Difference between the i-th pair of unspiked samples.

n = Number of paired samples.

14.2.3 Pooled Standard Deviation. Calculate the pooled standard deviation of the spiked and unspiked samples if the standard deviations are not significantly different. Test for this difference using Equation 301-20.

$$F = \frac{S_u^{\,2}}{S_s^{\,2}} \qquad \text{Eq. 301-20}$$

Where S_u^2 and S_s^2 are defined in Equation 301-17.

For the case where n = 6 and a 95 percent confidence level, the standard deviations may be pooled if the calculated F lies between 0.139 and 7.146. Calculate the pooled standard deviation (SD_{pooled}) using Equation 301-21.

$$SD_{pooled} = \sqrt{\frac{S_s^2 + S_u^2}{2}} \qquad \text{Eq. 301-21}$$

If the variances are significantly different and cannot be pooled, use the standard deviation of the spiked samples for the bias analysis in Section 14.1.2.

14.2.4 Relative Standard Deviation. Calculate the RSD of the alternative test method using Equation 301-8 and the pooled standard deviation determined from Section 14.2.3. If the pooled standard deviation or the standard deviation from the unspiked samples is used, S_m is the mean of the unspiked samples. If the standard deviation of the spiked samples is used, S_m is the mean of the spiked samples. The data and alternative test method are unacceptable if the RSD is greater than 20 percent.

15.0 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 19.1.1, you must meet the requirements in this section. You must have at least three 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

16.0 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 10 of Section 18.0 and submit a request for a waiver according to 19.1.1.

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

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

17.1 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 3 times the standard deviation, S_o, at the blank level. This LOD corresponds to an uncertainty of ±30% at the 99 percent confidence level.

17.2 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_o. If the LOD is greater than twice the calculated LOD, use

Procedure II in Table 4 to determine S_o.

Other Requirements and Information

18.0 How do I apply for approval of an alternative test method?

18.1 Submitting Requests. You must request to use an alternative test method according to the procedures in §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 reporting containing the information in 18.2. The request must be submitted to the Director, Emissions Monitoring and Analysis Division, U.S. Environmental Protection Agency, C304-02, Research Triangle Park, NC 27711.

18.2 Field Validation Report. The field validation report must contain the information in 18.2.1 through 18.2.9.

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

18.2.2 Summary of the results and calculations shown in Sections 7.0 through 17, as applicable.

18.2.3 Analyte certification and value(s).

18.2.4 Laboratory demonstration of the quality of the spiking system.

18.2.5 Discussion of laboratory evaluations.

18.2.6 Discussion of field sampling.

18.2.7 Discussion of sample preparations and analysis.

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

18.2.9 Reasons for eliminating any results.

19.0 How do I request a waiver?

19.1 Conditions for Waivers. If you meet one of the criteria in 19.1.1 through 19.1.3, the Administrator may waive the requirement to use the procedures in this method to validate an alternative test method. In addition, if the 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.

19.1.1 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 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 16.0.

19.1.2 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.

19.1.3 Conditional Test Methods. If the alternative test method has been demonstrated to be valid at several sources, you may ask the Administrator to designate the alternative test method as a conditional test method. If the Administrator has designated a test method as a conditional test method and you are using the conditional method within its stated applicability, you do not have to validate it according to the

procedures in this method. You can find a list of conditional test methods at http://www.epa.gov/ttn/emc/ctm.html.

19.2 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, Emissions Monitoring and Analysis Division, U.S. Environmental Protection Agency, C304-02, Research Triangle Park, NC 27711.

19.3 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 a minimum, the information in 19.3.1 through 19.3.4. The Administrator may request additional information if necessary to determine whether this method can be waived for a particular application.

19.3.1 A Clearly Written Test Method. The method should be written preferably in the format of 40 CFR 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.

19.3.2 Summaries (see Section 18.3) 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.

19.3.3 Ruggedness Testing Results. You must submit results of ruggedness testing conducted according to Section 16, sample stability conducted according to Section 8, and detection limits conducted according to Section 17, as applicable. For

example, you would not need to submit ruggedness testing results if you will be using the method at the same concentration level as the concentration level at which it was validated.

19.3.4 Applicability Statement and Arguments for Waiver Approval. Discussion of the applicability statement and arguments for approval of the waiver. This discussion should address as applicable the following: applicable regulation, emission standards, effluent characteristics, and process operations.

20.0 What definitions apply to this method?

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 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.

21.0 Where can I find additional information?

You can find additional information in the references in paragraphs 21.1 through

21.12.

21.1 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.

21.2 DeWees, W.G., P.M. Grohse, K.K. Luk, and F.E. Butler. 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.

21.3 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.

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

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

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

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

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

21.9 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.

21.10 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 Triangle Park, NC 27711.

21.11 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.

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

Table 1 of Appendix A. Sampling Procedures

If you are...	You must collect...
comparing against a validated method	nine sets of replicate samples using a paired sampling system (a total of 18 samples) or four 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 six sets of paired samples or three 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).

Table 2. of Appendix A. Critical Values of t for the two tailed 95 percent confidence limit

Degrees of freedom	t_{95}
1	3=078
2	1=886
3	1=638
4	1=533
5	1=476
6	1=44
7	1=415
8	1=397
9	1=383
10	1=372

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 six of the samples at the proposed minimum storage time and then analyze the same six samples at the proposed maximum storage time.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest six of the samples at the proposed minimum storage time and extract or digest six other samples at the proposed maximum storage time. Analyze an aliquot of the first six extracts (digestates) at both the proposed minimum and proposed maximum storage times. This will allow analysis of extract storage impacts.
	sorbent sampling systems that require thermal desorption	analyze six samples at the proposed minimum storage time. Analyze another set of six samples at the proposed maximum storage time.
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) at the proposed minimum storage time and half of the samples (8 or 9) at the proposed maximum storage time.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest six of the samples at the proposed minimum storage time and extract or digest six other samples at the proposed maximum storage time. Analyze an aliquot of the first six extracts (digestates) at both the proposed minimum and proposed maximum storage times. This will allow analysis of extract storage impacts.

Table 4. to Appendix A. Procedures for Estimating S_o

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