6560-50-P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[EPA-HQ-OAR-2016-0069; FRL----]

RIN 2060-AT17

Revisions to Method 301: Field Validation of Pollutant Measurement Methods from Various Waste Media

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: In this action, the Environmental Protection Agency (EPA) proposes editorial and technical revisions to the EPA's Method 301 "Field Validation of Pollutant Measurement Methods from Various Waste Media" in order to correct and update the method. In addition, the EPA is clarifying the applicability of Method 301 as well as its utility to other regulatory provisions. The proposed revisions include ruggedness testing for validation of test methods for application at multiple sources, determination of limit of detection for all method validations, incorporating procedures for determining the limit of detection, revising the sampling requirements for the comparison procedure, adding storage and sampling procedures for sorbent sampling systems, and clarifying acceptable statistical

results for candidate test methods. We also propose to clarify the applicability of Method 301 to 40 Code of Federal Regulations (CFR) parts 59, 60, 61, 63, and 65, and to add equations to clarify calculation of the correction factor, standard deviation, estimated variance of a validated test method, standard deviation of differences, and t-statistic for all validation approaches.

Changes made to the Method 301 field validation protocol under this proposed action would apply only to methods submitted to the EPA for approval after the effective date of this action. **DATES:** Comments. Comments must be received on or before [**insert date 60 days after date of publication in the *Federal Register***].

Public Hearing. If anyone contacts the EPA requesting a public hearing by [**insert date [10] days after date of publication in the *Federal Register***], the EPA will hold a public hearing on [**insert date [30] days after date of publication in the *Federal Register***] from 1:00 p.m. (Eastern Standard Time) to 5:00 pm (Eastern Standard Time) at the U.S. Environmental Protection Agency building located at 109 T.W. Alexander Drive, Research Triangle Park, NC 27711. Information regarding a hearing will be posted at *http://www3.epa.gov/ttn/emc/methods/*.

ADDRESSES: Submit your comments, identified by Docket ID No. EPA-HQ-OAR-2016-0069, to the Federal eRulemaking Portal: *http://www.regulations.gov*. Follow the online instructions for

submitting comments. Once submitted, comments cannot be edited or withdrawn. The EPA may publish any comment received to its public docket. Do not submit electronically any information you consider to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute.

Multimedia submissions (audio, video, etc.) must be accompanied by a written comment. The written comment is considered the official comment and should include discussion of all points you wish to make. The EPA will generally not consider comments or comment contents located outside of the primary submission (*i.e.*, on the Web, Cloud, or other file sharing system). For additional submission methods, the full EPA public comment policy, information about CBI or multimedia submissions, and general guidance on making effective comments, please visit *http://www2.epa.gov/dockets/commenting-epa-dockets*.

FOR FURTHER INFORMATION CONTACT: For information concerning this proposal, contact Ms. Kristen J. Benedict, Office of Air Quality Planning and Standards, Air Quality Assessment Division (E143-02), Environmental Protection Agency, Research Triangle Park, NC 27711; telephone number: (919) 541-1394; fax number: (919) 541-0516; email address: *benedict.kristen@epa.gov*.

SUPPLEMENTARY INFORMATION:

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I. General Information

A. Does this action apply to me?

Method 301 affects/applies to you, under 40 CFR 63.7(f) or 40 CFR 65.158(a)(2)(iii), when you want to use an alternative to a required test method to meet an applicable requirement or when there is no required or validated test method. In addition, the validation procedures of Method 301 are an appropriate tool for demonstration of the suitability of alternative test methods under 40 CFR 59.104 and 59.406, 40 CFR 60.8(b), and 40 CFR 61.13(h)(ii). If you have any questions regarding the

applicability of the proposed changes to Method 301, contact the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

B. What should I consider as I prepare my comments?

Submitting CBI: 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 marked as CBI will not be disclosed except in accordance with procedures set forth in Title 40 CFR part 2.

Do not submit information that you consider to be CBI or otherwise protected through *http://www.regulations.gov* or email. Send or deliver information identified as CBI to: OAQPS Document Control Officer (Room C404-02), U.S. EPA, Research Triangle Park, NC 27711, Attention Docket ID No. EPA-HQ-OAR-2016-0069.

If you have any questions about CBI or the procedures for claiming CBI, please consult the person identified in the **FOR FURTHER INFORMATION CONTACT** section.

Docket: 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.*, CBI or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, will be publicly available only in hard copy. Publicly available docket materials are available either electronically in *http://www.regulations.gov* or in hard copy at the EPA Docket Center, EPA/DC, EPA WJC West Building, Room 3334, 1301 Constitution Ave., NW, Washington, DC. This Docket Facility 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.

C. Where can I get a copy of this document and other related information?

In addition to being available in the docket, an electronic copy of the proposed method revisions is available on the Technology Transfer Network (TTN) Web site at *http://www3.epa.gov/ttn/emc/methods/*. The TTN provides information and technology exchange in various areas of air pollution control.

II. Background

The EPA originally published Method 301 (Appendix A to 40 CFR part 63, Test Methods) on December 29, 1992 (57 FR 61970), as a field validation protocol method to be used to validate new test methods for hazardous air pollutants in support of the Early Reductions Program of Part 63 when test methods were unavailable. On March 16, 1994, the EPA incorporated Method 301 into 40 CFR 63.7 (59 FR 12430) as a means to validate a candidate test method as an alternative to a test method specified in a standard or for use where no test method is provided in a standard. To date, subsequent revisions of Method 301 have not distinguished requirements for source-specific applications of a candidate method versus application of a candidate test method at multiple sources. The EPA's Method 301 specifies procedures for determining and documenting the bias and precision of a test method that is a candidate for use as an alternative to a test method specified in an applicable regulation, or for use as a means for showing compliance with a regulatory standard in absence of a validated test method. Method 301 is required for these purposes under 40 CFR 63.7(f) and 40 CFR 65.158(a)(2)(iii), and would be considered an appropriate tool for demonstration and validation of alternative methods under 40 CFR 59.104 and 59.406, 40 CFR 60.8(b), and 40 CFR 61.13(h)(ii). The procedures specified in Method 301 are

applicable to various media types (*e.g.*, sludge, exhaust gas, wastewater).

Bias (or systemic error) is established by comparing measurements made using a candidate test method against reference values, either reference materials or a validated test method. Where needed, a correction factor for source-specific application of the method is employed to eliminate/minimize bias. This correction factor is established from data obtained during the validation test. Methods that have bias correction factors outside a specified range are considered unacceptable. Method precision (or random error) must be demonstrated to be as precise as the validated method for acceptance or less than or equal to 20 percent when the candidate method is being evaluated using reference materials.

Additionally, the EPA recognized that there were a number of ways Method 301 could be clarified while reviewing submitted data and answering questions from facilities, environmental labs, and technology vendors on the application and requirements of the method.

III. Summary of Proposed Revisions

In this action, we propose clarifications to the applicability and utility of Method 301 to additional regulatory provisions, and propose technical revisions and editorial

changes intended to clarify and update the requirements and procedures specified in Method 301.

A. Technical Revisions

1. Applicability of Ruggedness Testing and Limit of Detection Determination

In the current version of Method 301, the procedures for conducting ruggedness testing in sections 3.1 and 14.0, and for determining the limit of detection (LOD) in sections 3.1 and 15.0, are optional procedures that are not required for validation of a candidate test method. In this action, we propose to amend sections 3.1 and 14.0 to require ruggedness testing when using Method 301 to validate a candidate test method intended for application to multiple sources. Ruggedness testing would continue to be optional for validation of methods intended for source-specific applications. We also propose to amend sections 3.1 and 15.0 to require determination of the LOD for validation of all methods (*i.e.*, those intended for both source and multi-source application). Additionally, we propose clarifications to the LOD definition in section 15.1.

Ruggedness testing of a test method is a laboratory study to determine the sensitivity of the method by measuring its capacity to remain unaffected by small, but deliberate variations in method parameters such as sample collection rate and sample recovery temperature to provide an indication of its

reliability during normal usage. Requiring ruggedness testing and determination of the LOD for validation of a candidate test method that is intended for use at multiple sources will further inform the EPA's determination of whether the candidate test method is valid across a range of source emission matrices, varying method parameters, and conditions. Additionally, conducting an LOD determination for source-specific validations will account for the sensitivity of the candidate test method to ensure it meets applicable regulatory requirements.

2. Limit of Detection Procedures

The EPA proposes revisions to the requirements for determining the LOD specified in section 15.2 and Table 301-5 (Procedure I) to incorporate procedures of the EPA's proposed revisions to 40 CFR part 136, appendix B (80 FR 8955). The proposed revisions address laboratory blank contamination and account for intra-laboratory variability, consistent with the proposed changes to 40 CFR part 136. We propose to require Procedure I of Table 301-5 for determining an LOD when an analyte in a sample matrix is collected prior to an analytical measurement or the estimated LOD is no more than twice the calculated LOD.

For the purposes of this proposed rule, LOD would be equivalent to the calculated method detection limit (MDL) determined using the procedures specified in proposed 40 CFR

part 136, appendix B. Through this proposed change, laboratories would be required to consider media blanks when performing LOD calculations. If the revisions to 40 CFR part 136, appendix B are finalized as proposed prior to a final action on this proposal, we will cross-reference appendix B. If appendix B is finalized before this action and the revisions do not incorporate the procedures as described above, the EPA intends to incorporate the specific procedures for determining the LOD in the final version of Method 301 consistent with this proposal. If appendix B is not finalized before these proposed revisions, the EPA also intends to incorporate the specific procedures directly into Method 301. Other than the proposed revisions to 40 CFR part 136, appendix B, as discussed above, changes addressed under that rulemaking are outside the scope of this proposed action.

3. Storage and Sampling Procedures

Currently, the number of samples required by Method 301 when using a quadruplicate sampling system for conducting the analyte spiking procedure and for conducting the comparison procedure is not consistent. In this action, we propose revisions to section 11.1.3 and Table 301-1 to require six sets of quadruplicate samples (a total of 24 samples for the analyte spiking or comparison procedures) rather than four sets. This proposed revision will ensure the bias and precision

requirements are consistent in the method and decrease the amount of uncertainty in the calculations for bias and precision when comparing an alternative test method with a validated method. Bias and precision (standard deviation and variance) are all inversely related to the number of sampling trains (sample results) used to estimate the difference between the alternative test method and the validated method. As the number of trains goes up, the bias and precision estimates go down. Larger data sets provide better estimates of the standard deviation or variance and the distribution of the data. The proposed revision to collect a total of 24 samples when using the analyte spiking approach is also consistent with the number of samples required for the isotopic spiking approach. The 12 samples collected when conducting the isotopic spiking approach are equivalent to the 24 samples collected using the analyte spiking approach because the isotopic labelling of the spike allows each of the 12 samples to yield two results, one for an unspiked sample and one for a spiked sample.

In this action, we also propose revisions to section 9.0 to specify that either paired sampling or quadruplicate sampling systems may be used for isotopic spiking, while only quadruplicate sampling systems may be used to establish precision for analyte spiking or when comparing an alternative method to a validated method.

For validations conducted by comparing the candidate test method to a validated test method, we propose to add: (1) storage and sampling procedures for sorbent systems requiring thermal desorption to Table 301-2; and (2) a new Table 301-4 to provide a look-up table of F values for the one-sided confidence level used in assessing the precision of the candidate test method. We also propose an amendment to the reference list in section 18.0 to include the source of the F values.

4. Bias Criteria for Multi-Source versus Source-Specific Validation

In this action, we propose clarification to sections 8.0, 10.3, and 11.1.3 to specify that candidate test methods intended for use at multiple sources must have a bias less than or equal to 10 percent. We propose that candidate test methods with a bias greater than 10 percent, but less than 30 percent, apply only at the source at which the validation testing was conducted and that data collected in the future be adjusted for bias using a source-specific correction factor. A source-specific correction factor is not necessarily appropriate for use at multiple sources. This proposed change provides flexibility for source-specific Method 301 application while limiting the acceptance criteria for use of the method at multiple sources. We believe that the Method 301 results from a single source are

not sufficient to allow us to establish a correction factor that can be applied at multiple sources.

5. Relative Standard Deviation Assessment

In this action, we propose amendments to sections 9.0 and 12.2 to clarify the interpretation of the relative standard deviation (RSD) when determining the precision of a candidate test method using the analyte spiking or isotopic spiking procedures. For a test method to be acceptable, we propose that the RSD of a candidate test method must be less than or equal to 20 percent. Accordingly, we propose to remove the sampling provisions for cases where the RSD is greater than 20 percent, but less than 50 percent. Poor precision makes it difficult to detect potential bias in a test method. For this reason, we are proposing an acceptance criteria of less than or equal to 20 percent for analyte and isotopic spiking sampling procedures.

6. Applicability of Method 301

Currently, Method 301 states that it is applicable for determining alternative test methods for standards under 40 CFR part 63 (National Emission Standards for Hazardous Air Pollutants for Source Categories). Although 40 CFR 65.158(a)(2)(iii) specifically cross-references Method 301, Method 301 has not previously been revised to reference Part 65. For Parts 63 and 65, Method 301 must be used for establishing an alternative test method. In this action, we propose revisions

clarifying that Method 301 is applicable to both parts 63 and 65 and that Method 301 is also appropriate for validating alternative test methods for use under the following parts under Title 40 of the Clean Air Act:

- Part 59 (National Volatile Organic Compound Emission Standards for Consumer and Commercial Products)
- Part 60 (Standards of Performance for New Stationary Sources)
- Part 61 (National Emission Standards for Hazardous Air Pollutants)

We believe that the Method 301 procedures for determining bias and precision provide a suitable technical approach for assessing candidate or alternative test methods for use under these regulatory parts as the testing provisions are very similar to those under Parts 63 and 65. To accommodate the expanded applicability and suitability, we propose to revise the references in sections 2.0, 3.2, 5.0, 13.0, 14.0, and 16.1 to refer to all five regulatory parts.

7. Equation Additions

In this action, we propose to clarify the procedures in Method 301 by adding the following equations:

- Equation 301-8 in section 10.3 for calculating the correction factor
- Equation 301-11 in section 11.1.1 and Equation 301-19 in section 12.1.1 for calculating the numerical bias

- Equation 301-12 in section 11.1.2 and Equation 301-20 in section 12.1.2 for determining the standard deviation of differences
- Equation 301-13 in section 11.1.3 and Equation 301-21 in section 12.1.3 for calculating the t-statistic
- Equation 301-15 in section 11.2.1 to estimate the variance of the validated test method
- Equation 301-23 in section 12.2 for calculating the standard deviation.

We also propose revisions to the denominator of Equation 22 to use the variable "CS" rather than "VS." Additionally, we propose revisions to the text of Method 301, where needed, to list and define all variables used in the method equations. These proposed changes are intended to improve the readability of the method and ensure that required calculations and acceptance criteria for each of Method 301's three validation approaches are clear.

B. Clarifying and Editorial Changes

In this action, we propose minor edits throughout the text of Method 301 to clarify the descriptions and requirements for assessing bias and precision, to ensure consistency when referring to citations within the method, to renumber equations and tables (where necessary), and to remove passive voice.

We propose edits to clarify several definitions in section 3.2. In the definition of "Paired sampling system," we propose a minor edit to note that the system is collocated. For the

definition of “Quadruplet sampling system,” we propose to replace the term “Quadruplet” with “Quadruplicate” and to add descriptive text to the definition to provide examples of replicate samples. We are also proposing companion edits throughout the method text to reflect the change in terminology from “quadruplet” to “quadruplicate.” Additionally, we propose clarifying edits to the definition of “surrogate compound.”

We also propose replacing the term “alternative test method” with “candidate test method” in section 3.2 and throughout Method 301 to maintain consistency when referring to a test method that is subject to the validation procedures specified in Method 301.

Additionally, the EPA proposes the following updates and corrections by:

- Updating the address for submitting waivers in section 17.2.
- Adding the t-value for 11 degrees of freedom to Table 301-2.
- Correcting the t-value for four degrees of freedom in Table 301-2.

IV. Request for Comments

The EPA specifically requests public comments on the expanded applicability of Method 301 to 40 CFR part 59 and to note the suitability of Method 301 for validation of alternative test methods under 40 CFR parts 60 and 61. In addition, we

specifically request comment on the following proposed technical amendments to Method 301:

A) Requiring ruggedness testing and determination of LOD for validation of test methods intended for multi-source and source-specific applications.

B) Incorporating the procedures specified in the proposed revisions to 40 CFR part 136, appendix B into the Method 301 procedures for determining LOD.

C) Revising the sampling requirements for the method comparison procedure to require six sets of quadruplicate samples rather than four sets, and adding storage and sampling procedures for sorbent systems that require thermal desorption.

D) Clarifying that candidate test methods that are intended for use at multiple sources must have a bias less than or equal to 10 percent and that test methods, where the bias is greater than 10 percent but less than to 30 percent, are applicable only on a source-specific basis with the use of a correction factor.

E) Clarifying that the RSD of a candidate test method validated using the analyte spiking or isotopic spiking

procedure must be less than or equal to 20 percent for the method to be acceptable.

F) Adding equations to calculate the: 1) correction factor (if required) when using isotopic spiking; 2) standard deviation when using the analyte spiking procedure; 3) estimated variance of validated test method when using the comparison procedure; and 4) standard deviation of differences and t-statistic when using the analyte spiking or comparison procedures.

V. Statutory and Executive Order Reviews

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

This proposed action is not a significant regulatory action and was, therefore, not submitted to the Office of Management and Budget (OMB) for review.

B. Paperwork Reduction Act (PRA)

This proposed action does not impose an information collection burden under the PRA. The revisions being proposed in this action to Method 301 do not add information collection requirements, but make corrections and updates to existing testing methodology.

C. Regulatory Flexibility Act (RFA)

I certify that this proposed action will not have a significant economic impact on a substantial number of small entities under the RFA. This action will not impose any requirements on small entities. The proposed revisions to Method 301 do not impose any requirements on regulated entities beyond those specified in the current regulations, nor do they change any emission standard. We have therefore concluded that this proposed action will have no net regulatory burden for all directly regulated small entities.

D. Unfunded Mandates Reform Act (UMRA)

This proposed action does not contain any unfunded mandate of $100 million or more as described in UMRA, 2 U.S.C. 1531–1538. The proposed action imposes no enforceable duty on any state, local or tribal governments or the private sector.

E. Executive Order 13132: Federalism

This proposed 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.

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

This proposed action does not have tribal implications, as specified in Executive Order 13175. This proposed action would

correct and update the existing procedures specified in Method 301. Thus, Executive Order 13175 does not apply to this proposed action.

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

The EPA interprets Executive Order 13045 as applying only to those regulatory actions that concern environmental health or safety risks that the EPA has reason to believe may disproportionately affect children, per the definition of "covered regulatory action" in section 2-202 of the Executive Order. This proposed action is not subject to Executive Order 13045 because it does not concern an environmental health risk or safety risk.

H. Executive Order 13211: Actions that Significantly Affect Energy Supply, Distribution, or Use

This proposed action is not subject to Executive Order 13211, because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act (NTTAA)

This proposed action involves technical standards. The agency previously identified ASTM D4855-97 (Standard Practice for Comparing Test Methods) as being potentially applicable in previous revisions of Method 301, but determined that the use of ASTM D4855-97 was impractical (Section V in 76 FR 28664).

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

The EPA believes that this action is not subject to Executive Order 12898 (59 FR 7629, February 16, 1994) because it does not establish an environmental health or safety standard. This action would make corrections and updates to an existing protocol for assessing the precision and accuracy of alternative test methods to ensure they are comparable to the methods otherwise required; thus, it does not modify or affect the impacts to human health or the environment of any standards for which it may be used.

Revisions to Method 301: Field Validation of Pollutant Measurement Methods from Various Waste Media

List of Subjects in 40 CFR Part 63

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

_____
Dated:

_____
Gina McCarthy,
Administrator.

For the reasons stated in the preamble, the EPA proposes to amend title 40, chapter I of the Code of the Federal Regulations 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

1.0 What is the purpose of Method 301?

Method 301 provides a set of procedures for the owner or operator of an affected source, to validate a candidate test method as an alternative to a required test method based on established precision and bias criteria. These validation procedures are applicable under 40 CFR part 63 or 65 when a test method is proposed as an alternative test method to meet an applicable requirement or in the absence of a validated method. Additionally, the validation procedures of Method 301 are appropriate for demonstration of the suitability of alternative test methods under 40 CFR parts 59, 60, and 61. If, under 40 CFR part 63 or 60, you choose to propose a validation method other than Method 301, you must submit and obtain the Administrator’s approval for the candidate validation method.

2.0 What approval must I have to use Method 301?

If you want to use a candidate test method to meet requirements in a subpart of 40 CFR part 59, 60, 61, 63, or 65, you must also request approval to use the candidate test method according to the procedures in Section 16 of this method and the appropriate section of the part (§59.104, §59.406, §60.8(b), §61.13(h)(ii), §63.7(f), or §65.158(a)(2)(iii)). You must receive the Administrator's written approval to use the candidate test method before you use the candidate test method to meet the applicable federal requirements. In some cases, the Administrator may decide to waive the requirement to use Method 301 for a candidate test method to be used to meet a requirement under 40 CFR part 59, 60, 61, 63, or 65 in absence of a validated test method. Section 17 of this method describes the requirements for obtaining a waiver.

3.0 What does Method 301 include?

3.1 Procedures. Method 301 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. Bias is established by comparing the results of sampling and analysis against a reference value. Bias may be adjusted on a source-specific basis using a correction factor and data obtained during the validation test. Precision may be determined using a paired sampling system or quadruplicate sampling system for isotopic

spiking. A quadruplicate sampling system is required when establishing precision for analyte spiking or when comparing a candidate test method to a validated method. If such procedures have not been established and verified for the candidate test method, Method 301 contains procedures for ensuring sample stability by developing sample storage procedures and limitations and then testing them. Method 301 also includes procedures for ruggedness testing and determining detection limits. The procedures for ruggedness testing and determining detection limits are required for candidate test methods that are to be applied to multiple sources and optional for candidate test methods that are to be applied at a single source.

3.2 Definitions.

Affected source means an affected source as defined in the relevant part and subpart under Title 40 (*e.g.,* 40 CFR parts 59, 60, 61, 63, and 65).

Candidate test method means the sampling and analytical methodology selected for field validation using the procedures described in Method 301. The candidate test method may be an alternative test method under 40 CFR part 59, 60, 61, 63, or 65.

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

Quadruplicate sampling system means a sampling system capable of obtaining four replicate samples (*e.g.,* two pairs of measured data, one pair from each method when comparing a candidate test method against a validated test method, or analyte spiking with two spiked and two unspiked samples) that are collected as close as possible in sampling time and sampling location.

Surrogate compound means a compound that serves as a model for the target compound(s) being measured (*i.e.*, similar chemical structure, properties, behavior). The surrogate compound can be distinguished by the candidate test method from the compounds being analyzed.

4.0 How do I perform Method 301?

First, you use a known concentration of an analyte or compare the candidate test method against a validated test method to determine the bias of the candidate test method. Then, you collect multiple, collocated simultaneous samples to determine the precision of the candidate test method. Additional procedures, including validation testing over a broad range of concentrations over an extended time period are used to expand the applicability of a candidate test method to multiple sources. Sections 5.0 through 17.0 of this method describe the procedures in detail.

5.0 What reference materials must I use?

You must use reference materials (a material or substance with one or more properties that 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 59, 60, 61, 63, or 65 requires. If you want to expand the applicable range of the candidate test method, you must conduct additional test runs using analyte concentrations higher and lower than the applicable emission limitation or the anticipated level of the target analyte. You must obtain information about your analyte according to the procedures in Sections 5.1 through 5.4 of this method.

5.1 Exhaust Gas Test Concentration. You must obtain a known concentration of each analyte from an independent source such as a specialty gas manufacturer, specialty chemical company, or chemical laboratory. You must also obtain the manufacturer’s certification of traceability, uncertainty, and stability for the analyte concentration.

5.2 Tests for Other Waste Media. You must obtain the pure liquid components of each analyte from an independent manufacturer. The manufacturer must certify the purity, traceability, uncertainty, and shelf life of the pure liquid components. You must dilute the pure liquid components in the

same type medium or matrix 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 compound that contains a unique element (*e.g.,* 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 concentration of the isotopically-labeled analyte must be more than five times the concentration of the naturally-occurring analyte.

Sampling Procedures

6.0 What sampling procedures must I use?

You must determine bias and precision by comparison against a validated test method, using isotopic spiking, or using analyte spiking (or the equivalent). Isotopic spiking can only be used with candidate test methods capable of measuring multiple isotopes simultaneously such as test methods using mass spectrometry or radiological procedures. You must collect

samples according to the requirements specified in Table 301-1 of this method. You must perform the sampling according to the procedures in Sections 6.1 through 6.4 of this method.

6.1 Isotopic Spiking. Spike all 12 samples with isotopically-labelled analyte at an analyte mass or concentration level equivalent to the emission limitation or standard specified in the applicable regulation. If there is no applicable emission limitation or standard, spike the analyte at the expected level of the samples. Follow the applicable spiking procedures in Section 6.3 of this method.

6.2 Analyte Spiking. In each quadruplicate set, spike half of the samples (two out of the four samples) with the analyte according to the applicable procedure in Section 6.3 of this method. You should spike at an analyte mass or concentration level equivalent to the emission limitation or standard specified in the applicable regulation. If there is no applicable emission limitation or standard, spike the analyte at the expected level of the samples. Follow the applicable spiking procedures in Section 6.3 of this method.

6.3 Spiking Procedure.

6.3.1 Gaseous Analyte with Sorbent or Impinger Sampling Train. Sample the analyte being spiked (in the laboratory or preferably in the field) at a mass or concentration that is approximately equivalent to the applicable emission limitation

or standard (or the expected sample concentration or mass where there is no standard) for the time required by the candidate test method, and then sample the stack gas stream for an equal amount of time. The time for sampling both the analyte and stack gas stream should be equal; however, you must adjust the sampling time to avoid sorbent breakthrough. You may sample the stack gas and the gaseous analyte at the same time. You must introduce the analyte as close to the tip of the sampling probe 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 analyte mass or concentration to yield a concentration approximately equivalent to the applicable emission limitation or standard (or the expected sample concentration or mass where there is no standard). Thus, the final concentration of the analyte in the sample container would be approximately equal to the analyte concentration in the stack gas plus the equivalent of the applicable emission standard (corrected for spike volume). The volume amount of spiked gas must be less than 10 percent of the sample volume of the container.

6.3.3 Liquid or Solid Analyte with Sorbent or Impinger Trains. Spike the sampling trains with an amount approximately equivalent to the mass or concentration in the applicable

emission limitation or standard (or the expected sample concentration or mass 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 must spike the sampling trains 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 analyte mass or concentration approximately equivalent to the applicable emission limitation or standard in the subpart (or the expected sample concentration or mass where there is no standard).

6.4 Probe Placement and Arrangement for Stationary Source Stack or Duct Sampling. To sample a stationary source, you must place the paired or quadruplicate probes according to the procedures in this subsection. You must place the probe tips in the same horizontal plane.

6.4.1 Paired Sampling Probes. For paired sampling probes, the first probe tip should be 2.5 centimeters (cm) from the outside edge of the second probe tip, with a pitot tube on the outside of each probe. Section 17.1 of Method 301 describes conditions for waivers. For example, the Administrator may approve a validation request where other paired arrangements for the pitot tubes (where required) are used.

6.4.2 Quadruplicate Sampling Probes. For quadruplicate 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 of the probe tips or two pitot tubes, where required, with their location on either side of the probe tip configuration. Section 17.1 of Method 301 describes conditions for waivers. For example, 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 Sample Storage and Threshold Procedures. If the candidate 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 candidate test method and you are not required to conduct the procedures specified in Section 7.2 or 7.3 of this method. If the candidate test method does not include such procedures, your candidate method must include 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 of this method. The minimum time period between collection and

storage must be as soon as possible, but no longer than 72 hours after collection of the sample. The maximum storage duration must not be longer than 2 weeks.

7.2 Storage and Sampling Procedures for Stack Test Emissions. You must store and analyze samples of stack test emissions according to Table 301-2 of this method. You may reanalyze the same sample at both the minimum and maximum storage durations for: (1) samples collected in containers such as bags or canisters that are not subject to dilution or other preparation steps, or (2) impinger samples not subjected to preparation steps that would affect stability of the sample such as extraction or digestion. For candidate test method samples that do not meet either of these criteria, you must analyze one of a pair of replicate samples at the minimum storage duration and the other replicate at the proposed storage duration but no later than 2 weeks of the initial analysis to identify the effect of storage duration on analyte samples. If you are using the isotopic spiking procedure, then you must analyze each sample for the spiked analyte and the native analyte.

7.3 Storage and Sampling Procedures for Testing Other Waste Media (*e.g.*, Soil/Sediment, Solid Waste, Water/Liquid). You must analyze one of each pair of replicate samples (half the total samples) at the minimum storage duration and the other replicate (other half of samples) at the maximum storage duration or

within two weeks of the initial analysis to identify the effect of storage duration on analyte samples. The minimum time period between collection and storage should be as soon as possible, but no longer than 72 hours after collection of the sample.

7.4 Sample Stability. After you have conducted sampling and analysis according to Section 7.2 or 7.3 of this method, compare the results at the minimum and maximum storage durations. 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} replicate pair of samples.

R_{mini} = Results from the i^{th} replicate sample pair at the minimum storage duration.

R_{maxi} = Results from the i^{th} replicate sample pair at the maximum storage duration.

For single samples that can be reanalyzed for sample stability assessment (*e.g.,* bag or canister samples and impinger samples that do not require digestion or extraction), the values for R_{mini} and R_{maxi} will be obtained from the same sample rather than replicate samples.

7.4.1 Standard Deviation. Determine the standard deviation 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:

SD_d = Standard deviation of the differences of the paired samples.

d_i = Difference between the results of the i^{th} replicate pair of samples.

d_m = 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 results at the minimum storage duration and the results after the maximum storage duration 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.

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

Where:

t = t-statistic.

d_m = The mean of the paired sample differences.

SD_d = Standard deviation of the differences of the paired samples.

n = Total number of paired samples.

Compare the calculated t-statistic with the critical value of the t-statistic from Table 301-3 of this method. If the calculated t-value is less than the critical value, the difference is not statistically significant. Therefore, the sampling, analysis, and sample storage procedures ensure

stability, and you may submit a request for validation of the candidate 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 of this method with new samples using a shorter proposed maximum storage duration or improved handling and storage procedures.

Determination of Bias and Precision

8.0 What are the requirements for bias?

You must determine bias by comparing the results of sampling and analysis using the candidate test method against a reference value. The bias must be no more than ± 10 percent for the candidate test method to be considered for application to multiple sources. A candidate test method with a bias greater than ± 10 percent and less than or equal to ± 30 percent can only be applied on a source-specific basis at the facility at which the validation testing was conducted. In this case, you must use a correction factor for all data collected in the future using the candidate test method. If the bias is more than ± 30 percent, the candidate test method is unacceptable.

9.0 What are the requirements for precision?

You may use a paired sampling system or a quadruplicate sampling system to establish precision for isotopic spiking. You must use a quadruplicate sampling system to establish precision

for analyte spiking or when comparing a candidate test method to a validated method. If you are using analyte spiking or isotopic spiking, the precision, expressed as the relative standard deviation (RSD) of the candidate test method, must be less than or equal to 20 percent. If you are comparing the candidate test method to a validated test method, the candidate test method must be at least as precise as the validated method as determined by an F test (see Section 11.2.2 of this method).

10.0 What calculations must I perform for isotopic spiking?

You must analyze the bias, RSD, precision, and data acceptance for isotopic spiking tests according to the provisions in Sections 10.1 through 10.4 of this method.

10.1 Numerical Bias. Calculate the numerical value of the bias using the results from the analysis of the isotopic spike in the field samples and the calculated value of the 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-labeled analyte in the samples.

CS = Calculated value of the isotopically-labeled spike level.

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

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

Where:

SD = Standard deviation of the candidate test method.

S_i = Measured value of the isotopically-labeled analyte in the i^{th} field sample.

S_m = Mean of the measured values of the isotopically-labeled analyte in the samples.

n = Number of isotopically-spiked samples.

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 of this method and the numerical bias determined in Section 10.1 of this method.

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

t = Calculated t-statistic.

B = Bias at the spike level.

SD = Standard deviation of the candidate test method.

n = Number of isotopically spike samples.

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 (see Table 301-3 of this method). When you conduct isotopic spiking according to the procedures specified in Sections 6.1 and 6.3 of this method as required, this critical value is 2.201 for 11 degrees of freedom. If the

calculated t-value is less than or equal to 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.

$$B_R = \left|\frac{B}{CS}\right| x100\% \qquad \text{(Eq. 301-7)}$$

Where:

B_R = Relative bias.
B = Bias at the spike level.
CS = Calculated value of the spike level.

If the relative bias is less than or equal to 10 percent, the bias of the candidate test method is acceptable for use at multiple sources. If the relative bias is greater than 10 percent but less than or equal to 30 percent, and if you correct all data collected with the candidate test method in the future for bias using the source-specific correction factor determined in Equation 301-8, the candidate test method is acceptable only for application to the source at which the validation testing was conducted and may not be applied to any other sites. If either of the preceding two cases applies, you may continue to evaluate the candidate test method by calculating its precision.

If not, the candidate test method does not meet the requirements of Method 301.

$$CF = \left(\frac{1}{1 + \frac{B}{CS}} \right) \qquad \text{(Eq. 301-8)}$$

CF = Source-specific bias correction factor.

B = Bias at the spike level.

CS = Calculated value of the spike level.

If the CF is outside the range of 0.70 to 1.30, the data and method are considered unacceptable.

10.4 Precision. Calculate the RSD according to Equation 301-9.

$$RSD = \left(\frac{SD}{S_m} \right) \times 100 \qquad \text{(Eq. 301-9)}$$

Where:

RSD = Relative standard deviation of the candidate test method.

SD = Standard deviation of the candidate test method calculated in Equation 301-5.

S_m = Mean of the measured values of the spike samples.

The data and candidate 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 you are comparing a candidate test method to a validated method, then you must analyze the data according to the

provisions in this section. If the data from the candidate test method fail either the bias or precision test, the data and the candidate 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 candidate test method and the validated method (d_m). Calculate d_i according to Equation 301-10.

$$d_i = \frac{(V_{1i} + V_{2i})}{2} - \frac{(P_{1i} + P_{2i})}{2} \qquad \text{(Eq. 301-10)}$$

Where:

d_i = Difference in measured value between the candidate test method and the validated method for each quadruplicate sampling train.

V_{1i} = First measured value with the validated method in the i^{th} quadruplicate sampling train.

V_{2i} = Second measured value with the validated method in the i^{th} quadruplicate sampling train.

P_{1i} = First measured value with the candidate test method in the i^{th} quadruplicate sampling train.

P_{2i} = Second measured value with the candidate test method in the i^{th} quadruplicate sampling train.

Calculate the numerical value of the bias using Equation 301-11.

$$B = \frac{\sum_{i}^{n} d_i}{n} \qquad \text{(Eq. 301-11)}$$

Where:

B = Numerical bias.

d_i = Difference between the candidate test method and the validated method for the i^{th} quadruplicate sampling train.

n = Number of quadruplicate sampling trains.

11.1.2 Standard Deviation of the Differences. Calculate the standard deviation of the differences, SD_d, using Equation 301-12.

$$SD_d = \sqrt{\frac{\sum_{i}^{n} (d_i - d_m)^2}{(n-1)}} \qquad \text{(Eq. 301-12)}$$

Where:

SD_d = Standard deviation of the differences between the candidate test method and the validated method.

d_i = Difference in measured value between the candidate test method and the validated method for each quadruplicate sampling train.

d_m = Mean of the differences, d_i, between the candidate test method and the validated method.

n = Number of quadruplicate sampling trains.

11.1.3 T Test. Calculate the t-statistic using Equation 301-13.

$$t = \frac{|d_m|}{\left(\frac{SD}{\sqrt{n}}\right)} \qquad \text{(Eq. 301-13)}$$

Where:

t = Calculated t-statistic.

d_m = The mean of the differences, d_i, between the candidate test method and the validated method.

SD_d = Standard deviation of the differences between the candidate test method and the validated method.

n = Number of quadruplicate sampling trains.

For the procedure comparing a candidate test method to a validated test method listed in Table 301-1 of this method, 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 (see Table 301-3 of this method). When six runs are conducted, as specified in Table 301-1 of this method, the critical value of the t-statistic is 2.571 for five degrees of freedom. If the calculated t-value is less than or equal to 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 magnitude of the relative bias using Equation 301-14.

$$B_R = \left|\frac{B}{VS}\right| x\ 100\% \qquad \text{(Eq. 301-14)}$$

Where:

B_R = Relative bias.

B = Bias as calculated in Equation 301-11.

VS = Mean of measured values from the validated method.

If the relative bias is less than or equal to 10 percent, the bias of the candidate test method is acceptable. On a source-specific basis, if the relative bias is greater than 10 percent but less than or equal to 30 percent, and if you correct all data collected in the future with the candidate test method for the bias using the correction factor, CF, determined in Equation 301-8 (using VS for CS), the bias of the candidate test method is acceptable for application to the source at which the validation testing was conducted. If either of the preceding two cases applies, you may continue to evaluate the candidate test method by calculating its precision. If not, the candidate test method does not meet the requirements of Method 301.

11.2 Precision. Compare the estimated variance (or standard deviation) of the candidate test method to that of the validated test method according to Sections 11.2.1 and 11.2.2 of this method. If a significant difference is determined using the F test, the candidate test method and the results are rejected. If the F test does not show a significant difference, then the candidate test method has acceptable precision.

11.2.1 Candidate Test Method Variance. Calculate the estimated variance of the candidate test method according to Equation 301-15.

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

Where:

S_p^2 = Estimated variance of the candidate test method.

d_i = The difference between the i^{th} pair of samples collected with the candidate test method in a single quadruplicate train.

n = Total number of paired samples (quadruplicate trains).

Calculate the estimated variance of the validated test method according to Equation 301-16.

$$S_v^2 = \frac{\sum_i^n d_i^2}{2n} \qquad \text{(Eq. 301-16)}$$

Where:

S_v^2 = Estimated variance of the validated test method.

d_i = The difference between the i^{th} pair of samples collected with the validated test method in a single quadruplicate train.

n = Total number of paired samples (quadruplicate trains).

11.2.2 The F test. Determine if the estimated variance of the candidate test method is greater than that of the validated method by calculating the F-value using Equation 301-17.

$$F = \frac{S_p^2}{S_v^2} \qquad \text{(Eq. 301-17)}$$

Where:

F = Calculated F value.

S_p^2 = The estimated variance of the candidate test method.

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

Compare the calculated F value with the one-sided confidence level for F from Table 301-4 of this method. The upper one-sided confidence level of 95 percent for $F_{(6,6)}$ is 4.28 when the procedure specified in Table 301-1 of this method for quadruplicate sampling trains is followed. If the calculated F value is greater than the critical F value, 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, which is defined as the mean of the differences between the spiked samples and the unspiked samples in each quadruplicate sampling train minus the spiked amount, using Equation 301-18.

$$d_i = \frac{(S_{1_i} + S_{2_i})}{2} - \frac{(M_{1i} + M_{2_i})}{2} - CS \qquad \text{(Eq. 301-18)}$$

Where:

d_i = Difference between the spiked samples and unspiked samples in each quadruplicate sampling train minus the spiked amount.

S_{1i} = Measured value of the first spiked sample in the i^{th} quadruplicate sampling train.

S_{2i} = Measured value of the second spiked sample in the i^{th} quadruplicate sampling train.

M_{1i} = Measured value of the first unspiked sample in the i^{th} quadruplicate sampling train.

M_{2i} = Measured value of the second unspiked sample in the i^{th} quadruplicate sampling train.

CS = Calculated value of the spike level.

Calculate the numerical value of the bias using Equation 301-19.

$$B = \frac{\sum_{i}^{n} d_i}{n} \qquad \text{(Eq. 301-19)}$$

Where:

B = Numerical value of the bias.

d_i = Difference between the spiked samples and unspiked samples in each quadruplicate sampling train minus the spiked amount.

n = Number of quadruplicate sampling trains.

12.1.2 Standard Deviation of the Differences. Calculate the standard deviation of the differences using Equation 301-20.

$$SD_d = \sqrt{\frac{\sum_i^n (d_i - d_m)^2}{n-1}} \qquad \text{(Eq. 301-20)}$$

Where:

SD_d = Standard deviation of the differences of paired samples.

d_i = Difference between the spiked samples and unspiked samples in each quadruplicate sampling train minus the spiked amount.

d_m = The mean of the differences, d_i, between the spiked samples and unspiked samples.

n = Total number of quadruplicate sampling trains.

12.1.3 T Test. Calculate the t-statistic using Equation 301-21, where n is the total number of test sample differences (d_i). For the quadruplicate sampling system procedure in Table 301-1 of this method, n equals six.

$$t = \frac{|d_m|}{\left(\frac{SD_d}{\sqrt{n}}\right)} \qquad \text{(Eq. 301-21)}$$

t = Calculated t-statistic.

d_m = Mean of the difference, d_i, between the spiked samples and unspiked samples.

SD_d = Standard deviation of the differences of paired samples.

n = Number of quadruplicate sampling trains.

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 quadruplicate runs are conducted, as specified in Table 301-1 of this method, the 2-sided confidence level critical value is 2.571 for the five

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 magnitude of the relative bias using Equation 301-22.

$$B_R = \left|\frac{B}{CS}\right| x\, 100\% \qquad \text{(Eq. 301-22)}$$

Where:

B_R = Relative bias.
B = Bias at the spike level from Equation 301-19.
CS = Calculated value at the spike level.

If the relative bias is less than or equal to 10 percent, the bias of the candidate test method is acceptable. On a source-specific basis, if the relative bias is greater than 10 percent but less than or equal to 30 percent, and if you correct all data collected with the candidate test method in the future for the magnitude of the bias using Equation 301-8, the bias of the candidate test method is acceptable for application to the tested source at which the validation testing was conducted. Proceed to evaluate precision of the candidate test method.

12.2 Precision. Calculate the standard deviation using Equation 301-23.

$$SD = \sqrt{\frac{\sum_{i}^{n} (S_i - S_m)^2}{(n-1)}} \qquad \text{(Eq. 301-23)}$$

Where:

SD = Standard deviation of the candidate test method.

S_i = Measured value of the analyte in the i^{th} spiked sample.

S_m = Mean of the measured values of the analyte in all the spiked samples.

n = Number of spiked samples.

Calculate the RSD of the candidate test method using Equation 301-9, where SD and S_m are the values from Equation 301-23. The data and candidate test method are unacceptable if the RSD is greater than 20 percent.

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 59, 60, 61, 63, or 65 for an affected source, and you would like to apply the alternative test method to a similar source, then you must petition the Administrator as described in Section 17.1.1 of this method.

14.0 How do I use and conduct ruggedness testing?

Ruggedness testing is an optional requirement for validation of a candidate test method that is intended for the source where the validation testing was conducted. Ruggedness testing is required for validation of a candidate test method

intended to be used at multiple sources. If you want to use a validated test method at a concentration that is different from the concentration in the applicable emission limitation under 40 CFR part 59, 60, 61, 63, or 65, 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 Reference 18.16 of Section 18.0 of this method and submit a request for a waiver for conducting Method 301 at that different source category according to Section 17.1.1 of this method.

Ruggedness testing is a study that can be conducted in the laboratory or the field to determine the sensitivity of a method to parameters such as analyte concentration, sample collection rate, interferent concentration, collection 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 only eight experiments. (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 candidate test method?

Determination of the Limit of Detection (LOD) as specified in Sections 15.1 and 15.2 of this method is required for source-specific method validation and validation of a candidate test method intended to be used for multiple sources.

15.1 Limit of Detection. The LOD is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. For this protocol, the LOD is defined as three times the standard deviation, S_o, at the blank level.

15.2 Purpose. The LOD establishes the lower detection limit of the candidate test method. You must calculate the LOD using the applicable procedures found in Table 301-5 of this method. For candidate test methods that collect the analyte in a sample matrix prior to an analytical measurement, you must determine the LOD using Procedure I in Table 301-5 of this method by calculating a method detection limit (MDL) as described in proposed 40 CFR part 136, appendix B. For the purposes of this section, the LOD is equivalent to the calculated MDL. 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://www2.epa.gov/radiation/marlap-manual-and-supporting-documents*.

Other Requirements and Information

16.0 How do I apply for approval to use a candidate test method?

16.1 Submitting Requests. You must request to use a candidate test method according to the procedures in §63.7(f) or similar sections of 40 CFR parts 59, 60, 61, and 65 (§59.104, §59.406, §60.8(b), §61.13(h)(ii), or §65.158(a)(2)(iii)). You cannot use a candidate test method to meet any requirement under these parts until the Administrator has approved your request. The request must include a field validation report containing the information in Section 16.2 of this method. You must submit the request to the Group Leader, Measurement Technology Group, U.S. Environmental Protection Agency, E143-02, 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 of this method.

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 16.0 of this method, as applicable.

16.2.3 Reference material certification and value(s).

16.2.4 Discussion of laboratory evaluations.

16.2.5 Discussion of field sampling.

16.2.6 Discussion of sample preparation 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 Section 17.1.1 or 17.1.2 of this method, the Administrator may waive the requirement to use the procedures in this method to validate an alternative or other candidate test method. In addition, if the EPA currently recognizes an appropriate test method or considers the candidate 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 or other candidate test method that you want to use was validated for source-specific application at another source and you can demonstrate to the Administrator’s satisfaction that your affected source is similar to that validated source, then the Administrator may waive the requirement for you to validate the alternative or other candidate test method. One procedure you may use to demonstrate the applicability of the method to your affected source is to conduct a ruggedness test as described in Section 14.0 of this method.

17.1.2 Documented Methods. If the bias and precision of the alternative or other candidate 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 Group Leader, Measurement Technology Group, U.S. Environmental Protection Agency, E143-02, Research Triangle Park, NC 27711.

17.3 Information Application for Waiver. The request for a waiver must contain a thorough description of the candidate 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 Sections 17.3.1 through 17.3.4 of this method. 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 candidate test method should be written preferably in the format of 40 CFR part 60, Appendix A, Test Methods. Additionally, the candidate test must include an applicability statement, concentration range,

precision, bias (accuracy), and minimum and maximum storage durations in which samples must be analyzed.

17.3.2 Summaries of Previous Validation Tests or Other Supporting Documents. If you use a different procedure from that described in this method, 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 of this method, sample stability conducted according to Section 7.0 of this method, and detection limits conducted according to Section 15.0 of this method, as applicable. For example, you would not need to submit ruggedness testing results if you will be using the method at the same affected source and level at which it was validated.

17.3.4 Applicability Statement and Basis for Waiver Approval. Discussion of the applicability statement and basis for approval of the waiver. This discussion should address as applicable the following: 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 18.17 of this method.

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 Conshohoken, PA 19428.

18.3 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.

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.

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 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. In: Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33-36.

18.17 NIST/SEMATECH (current version), “e-Handbook of Statistical Methods,” available from NIST, *http://www.itl.nist.gov/div898/handbook/*.

Table 301-1. Sampling Procedures

If you are...	**You must collect...**
Comparing the candidate test method against a validated method	A total of 24 samples using a quadruplicate sampling system (a total of six sets of replicate samples). In each quadruplicate sample set, you must use the validated test method to collect and analyze half of the samples.

Table 301-1. Sampling Procedures

If you are...	You must collect...
Using isotopic spiking (can only be used with methods capable of measurement of multiple isotopes simultaneously)	A total of 12 samples, all of which are spiked with isotopically-labeled analyte. You may collect the samples either by obtaining six sets of paired samples or three sets of quadruplicate samples.
Using analyte spiking	A total of 24 samples using the quadruplicate sampling system (a total of six sets of replicate samples – two spiked and two unspiked).

Table 301-2. 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) or impinger sampling systems that are not subject to dilution or other preparation steps	Analyze six of the samples within 7 days and then analyze the same six samples at the proposed maximum storage duration or 2 weeks after the initial analysis.
	Sorbent and impinger sampling systems that require extraction or digestion	Extract or digest six of the samples within 7 days and extract or digest six other samples at the proposed maximum storage duration or 2 weeks after the first extraction or digestion. Analyze an aliquot of the first six extracts (digestates) within 7 days and proposed maximum storage duration or 2 weeks after the initial analysis. This will allow analysis of extract storage impacts.
	Sorbent sampling systems that	Analyze six samples within 7 days. Analyze another

Table 301-2. Storage and Sampling Procedures for Stack Test Emissions

If you are...	With...	Then you must...
	require thermal desorption	set of six samples at the proposed maximum storage time or within 2 weeks of the initial analysis.
Comparing a candidate test method against a validated test method	Sample container (bag or canister) or impinger sampling systems that are not subject to dilution or other preparation steps	Analyze at least six of the candidate test method samples within 7 days and then analyze the same six samples at the proposed maximum storage duration or within 2 weeks of the initial analysis.
	Sorbent and impinger sampling systems that require extraction or digestion	Extract or digest six of the candidate test method samples within 7 days and extract or digest six other samples at the proposed maximum storage duration or within 2 weeks of the first extraction or digestion. Analyze an aliquot of the first six extracts (digestates) within 7 days and an aliquot at the proposed maximum storage durations or within 2 weeks of the initial analysis. This will allow analysis of extract storage impacts.
	Sorbent systems that require thermal desorption	Analyze six samples within 7 days. Analyze another set of six samples at the proposed maximum storage duration or within 2 weeks of the initial analysis.

Table 301-3. 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	2.777
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
11	2.201

Table 301-4. Upper Critical Values of the F Distribution for the 95 Percent Confidence Limit

Numerator (k_1) and denominator (k_2) degrees of freedom	$F\{F>F_{.05}(k_1,k_2)\}$
1,1	161.4
2,2	19.0
3,3	9.3
4,4	6.39
5,5	5.05
6,6	4.28
7,7	3.79
8,8	3.44
9,9	3.18
10,10	2.98

Table 301-5. Procedures for Estimating S_o

If the estimated LOD (LOD_1, expected approximate LOD concentration level) is no more than twice the calculated LOD or an analyte in a sample matrix was collected prior to	If the estimated LOD (LOD_1, expected approximate LOD concentration level) is greater than twice the calculated LOD, use Procedure II as follows.

Table 301-5. Procedures for Estimating S_o

an analytical measurement, use Procedure I as follows.	
Procedure I Determine the LOD by calculating a method detection limit (MDL) as described in proposed 40 CFR Part 136, Appendix B.	Procedure II Prepare two additional standards (LOD_2 and LOD_3) at concentration levels lower than the standard used in Procedure I (LOD_1).
	Sample and analyze each of these standards (LOD_2 and LOD_3) at least seven times.
	Calculate the standard deviation (S_2 and S_3) for each concentration level.
	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_o.
	Calculate the LOD_0 (referred to as the calculated LOD) as 3 times S_o.