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METHOD 301—FIELD VALIDATION OF POLLUTANT MEASUREMENT METHODS FROM VARIOUS WASTE MEDIA

USING METHOD 301

1.0 What is the purpose of Method 301?

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

2.0 When must I use Method 301?

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

3.0 What does Method 301 include?

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

3.2 *Definitions.*

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

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

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

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

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

4.0 How do I perform Method 301?

First, you introduce a known concentration of an analyte or compare the alternative test method against a validated test method to determine the alternative test method's bias. Then, you collect multiple, collocated simultaneous samples to determine the alternative test method's precision. Alternatively, though it is not required, we allow validation testing over a broad range of concentrations over an extended time period to determine precision of a proposed alternative method. Sections 5.0 through 17.0 describe the procedures in detail.

REFERENCE MATERIALS

5.0 What reference materials must I use?

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

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

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

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

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

SAMPLING PROCEDURES

6.0 What sampling procedures must I use?

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

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

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

6.3 *Spiking Procedure.*

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

6.3.2 *Gaseous Analyte with Sample Container (Bag or Canister).* Spike the sample containers after completion of each test run with an amount equal to the concentration in the applicable emission limitation or standard in the subpart of 40 CFR part 63 (or the expected sample concentration where there is no standard). The final concentration of the analyte would be approximately equal to the analyte concentration in the stack plus the applicable emission standard (corrected for spike volume). The volume amount of analyte must be less than 10 percent of the sample volume.

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

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

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

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

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

of the probe tip configuration is approximately five percent or more of the stack or duct cross-sectional area.

7.0 How do I ensure sample stability?

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

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

7.3 *Storage and Sampling Procedures for Testing Other Waste Media (e.g., Soil/Sediment, Solid Waste, Water/Liquid).* You must analyze half of the replicate samples at the proposed minimum storage time and the other half at the proposed maximum storage time or within two weeks of the initial analysis to identify the effect of storage times on analyte samples. The minimum storage time should be as soon as possible, but no longer than seven days after collection of the sample.

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

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

Where:

d_i = difference between the results of the ith sample.

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

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

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

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

Where:

d_i = The difference between the results of the ith sample, $R_{mini} - R_{maxi}$.

d_m = The mean of the paired sample differences.

n = Total number of paired samples.

7.4.2 *t Test.* Test the difference in the results for statistical significance by calculating the t-statistic and determining if the mean of the differences between the initial results and the results after storage is significant at the 95 percent confidence level and n − 1 degrees of freedom. Calculate the value of the t-statistic using Equation 301-3.

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

Where:

n = The total number of paired samples.

Compare the calculated t-statistic with the critical value of the t-statistic from Table 2. If the calculated t-value is less than the critical value, the difference is not statistically significant; thus, the sampling and analysis procedure ensures stability, and you may submit a request for validation of the proposed alternative test method. If the calculated t-value is greater than the critical value, the difference is statistically significant, and you must repeat the procedures in Section 7.2 or 7.3 with new samples using shorter proposed maximum storage times.

BIAS AND PRECISION

8.0 What are the requirements for bias?

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

9.0 What are the requirements for precision?

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

10.0 What calculations must I perform for isotopic spiking?

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

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

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

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.

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:

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

n = Number of isotopically spiked samples, 12.

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

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

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 6.2 and 6.4 as required, this critical value is 2.201 for the 11 degrees of freedom. If the calculated t-value is less than the critical value, the bias is not statistically significant, and the bias of the candidate test method is acceptable. If the calculated t-value is greater than the critical value, the bias is statistically significant, and you must evaluate the relative magnitude of the bias using Equation 301-7.

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

Where:

B_R = Relative bias.

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

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

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

Where:

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

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

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

If you are using quadruplet replicate sampling systems to compare an alternative test method to a validated method, then you must analyze the data according to the provisions in this section. If the data from the alternative test method fail either the bias or precision test, the data and the alternative test method are unacceptable. If the Administrator determines that the affected source has highly variable emission rates, the Administrator may require additional precision checks.

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

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

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

Where:

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

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

P_{1i} = First measured value with the alternative test method in the i-th sample.

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

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

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

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

Where:

B = Bias − mean of the d_i 's.

VS = Mean measured by the validated method.

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

11.2 *Precision.* Compare the estimated variance (or standard deviation) of the alternative test method to that of the validated method. If a significant difference is determined using the F test, the alternative test method and the results are rejected. If the F test does not show a significant difference, then the alternative test method has acceptable precision. Use the value furnished with the method. Calculate the estimated variance of the validated method using Equation 301-11.

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

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

Where:

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

n = Number of samples and the degrees of freedom.

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

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

Where:

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

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

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

12.0 What calculations must I perform for analyte spiking?

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

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

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

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

Where:

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

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

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

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

CS = Calculated value of the spiked level.

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

12.1.3 *t Test.* Calculate the t-statistic using Equation 301-3, where n is the total number of test sample differences (d_i). For the quadruplet sampling system procedure in Table 1, n equals six. Compare the calculated t-statistic with the critical value of the t-statistic, and determine if the bias is significant at the 95 percent confidence level. When six runs are conducted, as specified in Table 1, the two-sided confidence level critical value is 2.571 for the five degrees of freedom. If the relative bias is less than or equal to 10 percent with no correction factors, or the bias is greater than 10 percent but less than 30 percent with the use of correction factors, then the data are acceptable. Proceed to evaluate precision of the candidate test method.

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

Where:

B = Bias − mean of the d_i's.

VS = Mean measured by the validated method.

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

13.0 How do I conduct tests at similar sources?

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

OPTIONAL REQUIREMENTS

14.0 How do I use and conduct ruggedness testing?

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

Ruggedness testing is a laboratory study to determine the sensitivity of a method to parameters such as sample collection rate, interferant concentration, collecting medium temperature, and sample recovery temperature. You conduct ruggedness testing by changing several variables simultaneously instead of changing one variable at a time. For example, you can determine the effect of seven variables in eight experiments instead of one. (W.J. Youden, Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33-36).

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

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

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

OTHER REQUIREMENTS AND INFORMATION

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

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

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

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

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

16.2.3 *Analyte certification and value(s).*

16.2.4 *Discussion of laboratory evaluations.*

16.2.5 *Discussion of field sampling.*

16.2.6 *Discussion of sample preparations and analysis.*

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

16.2.8 *Reasons for eliminating any results.*

17.0 How do I request a waiver?

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

17.1.1 *Similar Sources.* If the alternative test method that you want to use has been validated at another source and you can demonstrate to the Administrator's satisfaction that your affected source is similar to that source, then the Administrator may waive the requirement for you to validate the alternative test method. One procedure you may use to demonstrate the applicability of the method to your affected source is by conducting a ruggedness test as described in Section 14.0.

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

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

17.3 *Information Application for Waiver*. The request for a waiver must contain a thorough description of the test method, the intended application, and results of any validation or other supporting documents. The request for a waiver must contain, at a minimum, the information in Sections 17.3.1 through 17.3.4. The Administrator may request additional information if necessary to determine whether this method can be waived for a particular application.

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

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

17.3.3 *Ruggedness Testing Results.* You must submit results of ruggedness testing conducted according to Section 14.0, sample stability conducted according to Section 7.0, and detection limits conducted according to Section 15.0, as applicable. For example, you would not need to submit ruggedness testing results if you will be using the method at the same concentration level as the concentration level at which it was validated.

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

18.0 Where can I find additional information?

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

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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).

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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.

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TABLE 1 TO APPENDIX A—SAMPLING PROCEDURES

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

TABLE 2 TO APPENDIX A—CRITICAL VALUES OF T FOR THE TWO TAILED 95 PERCENT CONFIDENCE LIMIT

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

TABLE 3 TO APPENDIX A—STORAGE AND SAMPLING PROCEDURES FOR STACK TEST EMISSIONS

If you are . . .	With . . .	Then you must . . .
using isotopic or analyte spiking procedures	sample container (bag or canister) and impinger sampling systems	analyze 6 of the samples within 7 days and then analyze the same 6 samples at the proposed maximum storage time or 2 weeks after the initial analysis.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest 6 of the samples within 7 days and extract or digest 6 other samples at the proposed maximum storage time or 2 weeks after the first extraction or digestion. Analyze an aliquot of the first 6 extracts (digestates) within 7 days and proposed maximum storage times or 2 weeks after the initial analysis. This will allow analysis of extract storage impacts.
	sorbent sampling systems that require thermal desorption	analyze 6 samples within 7 days. Analyze another set of 6 samples at the proposed maximum storage time or within 2 weeks of the initial analysis.
comparing an alternative test method against a validated test method	sampling method that does not include sorbent and impinger sampling systems that require extraction or digestion	analyze half of the samples (8 or 9) within 7 days and half of the samples (8 or 9) at the proposed maximum storage time or within 2 weeks of the initial analysis.
	sorbent and impinger sampling systems that require extraction or digestion	extract or digest 6 of the samples within 7 days and extract or digest 6 other samples at the proposed maximum storage time or within 2 weeks of the first extraction or digestion. Analyze an aliquot of the first 6 extracts (digestates) within 7 days and at the proposed maximum storage times or within 2 weeks of the initial analysis. This will allow analysis of extract storage impacts.

TABLE 4 TO APPENDIX A—PROCEDURES FOR ESTIMATING S_o

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