

**PPS -001: Preliminary Performance Specifications
for Ammonia Continuous Emission Monitors (CEMs)**

1.0 Scope and Application

1.1 Analytes. This performance specification is applicable for the measurement of ammonia (NH₃, CAS No. 7664-41-7) in stack or process gas streams.

1.2 Applicability. This performance specification is for evaluating the acceptability of NH₃ continuous emission monitoring systems (CEMs) at the time of installation, or soon thereafter, and whenever specified in the regulations.

2.0 Summary of Performance Specification

Procedures for measuring CEMs relative accuracy and calibration drift are described. CEM installation and measurement locations, and data reduction procedures are also included.

3.0 Definitions

3.1 Calibration Drift (CD). The difference in the CEM output readings from an established reference value after a stated period of operation during which no maintenance, repair, or adjustment of the CEM was performed.

3.2 Continuous Emission Monitoring System (CEM). The total equipment required for the determination of ammonia concentration. The sample interface, gas analyzer, and data recorder are major subsystems of the CEM.

3.3 Relative Accuracy (RA). The absolute mean difference between the gas concentration determined by the CEM and the value determined from a reference method (RM), plus the 2.5 percent error confidence coefficient of a series of tests, divided by the mean of the RM tests, or

the applicable emission limit, as appropriate. (See Section 12.2.1.4)

3.4 Gas Cell. A gas containment cell that can be evacuated or pressurized with the sample gas. It can be configured in the same path with the source and reflector/detector of the CEM, or configured externally such that the light path through the cell is separate from that passing through the stack or duct.

3.5 Path CEM. A CEM that measures the gas concentration along a path of greater than 10% of the equivalent diameter of the stack or duct cross section.

3.6 Point CEM. A CEM that measures the gas concentration either at a single point or along a path of less than 10% of the equivalent diameter of the stack or duct cross section.

4.0 Interferences [Reserved]

5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEM user's manual and materials recommended by the reference method should be consulted for specific precautions to be taken.

6.0 Measurement Location

6.1 CEM Measurement Location. The CEM should be installed at an accessible location where the pollutant concentration measurements are directly representative, or can be corrected so as to be representative, of the total emissions from the affected facility or at the measurement

location cross section. It is suggested that the measurement location be at least two equivalent diameters downstream from the nearest control device, the point of ammonia injection, or other point at which a change in the pollutant concentration or emission rate may occur, and at least one half an equivalent diameter upstream from the effluent exhaust or control device.

6.1.1 Point CEMs. The measurement point should be (1) no less than 1.0 meter from the stack or duct wall, or (2) within or centrally located over the centroidal area of the stack or duct cross section.

6.1.2 Path CEMs. The effective measurement path should (1) be totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area, or (3) be centrally located over any part of the centroidal area.

6.2 Reference Method Measurement Location. Select, as appropriate, an accessible RM measurement point at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least one half of an equivalent diameter upstream from the effluent exhaust or control device. The CEMs and RM locations need not be the same, but should both allow representative sampling of the pollutant concentration.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control

These procedures shall be used for routine periodic, quarterly, or semiannual QA/QC

checks on the operation of the CEM. Some procedures test only the analytical program and are not intended as a test of the sampling system.

9.1 Field Audit Sample. This sample can serve as a check on both the sampling system and the analytical system. The audit sample is a source of known NH_3 concentrations (typically a compressed gas standard), that should be at a concentration that results in a CEM response that is approximately equal to the NH_3 concentration in the flue gas or at least 2 ppmv, whichever is greater. The audit sample is to be provided by the auditor(s) conducting the field audit. The audit sample must be traceable to a NIST (SRM or NTRM) or to an NMI (Netherlands Metrology Institute) (PRM) approved analytical standard with an analytical accuracy of no greater than $\pm 3\%$. The field audit should be conducted in a blind format, i.e., the concentration of the audit gas should not be revealed to the CEM operator until after the successful completion of the audit procedures.

9.2 Audit Test Procedure. For point CEMs, use the audit gas to spike the flue gas as described in Section 11.2.1.1. For path CEMs, spike the audit gas into the gas cell as described in Section 11.2.2.1. The audit sample must be traceable to a NIST (SRM or NTRM) or to an NMI (Netherlands Metrology Institute) (PRM) approved analytical standard with an analytical accuracy of no greater than $\pm 3\%$. Measure a series of spiked and unspiked samples using these procedures and analyze the results according to Section 12.1. The calculated bias should be below 10%.

9.3. Routine Zero and Span. The CEM must be checked using high and zero span gases on a daily basis. The span gas for routine use must be vendor certified ammonia calibration gas that is traceable to a NIST (SRM or NTRM) or to an NMI (Netherlands Metrology Institute) (PRM) approved analytical standard with an analytical accuracy of no greater than $\pm 3\%$. The zero span gases supplied should be vendor certified to contain less than 1 ppm ammonia. Zero and span gases are to be supplied to the CEM inlet, in the case of point CEMs, or to an optical gas cell, in the case of path CEMs. The ammonia gas standards used must be of appropriate concentrations

for the intended use, i.e., of comparable concentration to flue gas NH₃ levels for use with point CEMs, and of concentration to be comparable to flue gas ammonia levels after adjustment for the gas cell path length, in use with path CEMs.

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1. Initial Validation. The performance of path or point NH₃ CEMs can be validated following installation using guidelines found in EPA Method 301. The method provides two options for CEM performance validation: 1) comparison against a validated reference method or 2) through the analysis of a series of dynamic analyte spikes. These two techniques are described in more detail below. Validation testing is used for initial certification upon installation of a new system. Subsequent periodic performance evaluations can be performed with analyte spiking. Performance of the CEM is checked initially, then periodically afterward as required by the EPA, by analyzing audit gases.

11.2. Validation

11.2.1. Point CEMs. Use EPA Method 301 type sampling to validate the point NH₃ CEM. According to Method 301, either comparison to a reference method (RM) or analyte spiking may be used to validate a CEM's performance. For point NH₃ CEMs, the former is discussed in Section 11.2.1.4 and the latter discussed below.

A general outline of the spike procedure is as follows:

- (1) a spike gas mixture of known concentration is preheated to at least the temperature of the inlet;
- (2) the spike gas is introduced at the sampling inlet, upstream of any particulate filter, to insure that the spike is carried through all sampling components downstream of the inlet;

- (3) the spike gas is introduced to the flue gas sample at a ratio of approximately 1 part spike to 9 parts flue gas (or more dilute);
- (4) the dilution factor may be determined by comparing the total flow (sample & spike) to the spike flow alone.

The flue gas concentration of NH_3 is unimportant as long as the spiked component can be measured, the dilution ratio is known, and the flue gas (including interferences) is similar in composition to that expected under test conditions.

Validation can be performed using a single point NH_3 CEM analyzing unspiked and spiked samples sequentially (Section 11.2.1.1). However, flue gas concentrations that vary rapidly may confound the assessment of CEM bias using this sequential method. Thus it is recommended that two separate sampling inlets be used with one CEM, where one line carries unspiked flue gas and the other the flue-gas diluted spike mixture (Section 11.2.1.2). Yet even with two sampling lines, measurement of bias might still be problematic, because variations in the flue gas concentration may occur on timescales much shorter than the time between consecutive measurements. Alternatively, two point NH_3 CEMs can be operated side-by-side, one measuring spiked sample, the other unspiked flue-gas (Section 11.2.1.3). In that approach, one of the CEMs must have been previously validated, to serve as the basis for validation of the second CEM. In this arrangement spiked and unspiked measurements can be synchronized so as to minimize the affect of temporal variation of NH_3 in the unspiked flue gas on the determination of CEM bias. *(Note that none of the procedures outlined above adequately address the acquisition of measurements having the best possible precision, or measurement of reproducibility between spiked or between unspiked measurements. Four instruments running simultaneously are required to achieve adequate bias and precision results.)*

According to the guidelines set forth in EPA Method 301, a validation spiking run consists of at least 24 independent analytical results, 12 spiked and 12 unspiked. At a minimum, five volumes of air must pass through the sampling system between measurements used in the statistical analysis, i.e. measurements must be independent to be included in the analysis. Stated another way, an interval of time equal to five time constants must elapse between two measurements for them to be taken as independent, where the time constant is given by:

time constant (min) = total volume of sampling inlet (L)/sample flow rate (L/min).

The results are analyzed following procedures outlined in Sections 12.1 and 12.2 to determine if the validation requirements have been fulfilled. In lieu of 24 independent 'point' measurements, averaged results over the spiking periods can be used in the statistical workup to aid in the determination of CEM bias. A series of measurements of spiked gas are combined over a given time interval (five minutes, for instance) to produce an average result. Similarly, a series of measurements of the unspiked gas are acquired and averaged for the same length of time. Allow five time constants between successive averaging intervals. Use the 12 spiked and 12 unspiked average concentrations obtained for the statistical determination of bias. Note that using long averaging intervals may improve determination of bias but confound any measurement of precision given long term variations in the analyte concentration in the flue gas.

11.2.1.1. Validation with a single analyzer and sampling line. Connect the sampling system components and flush with at least 10 system volumes of unspiked flue gas. Begin sampling by recording two independent measurements of the unspiked flue gas (i.e., five system volumes of gas between independent measurements). Introduce the spike gas into the sample inlet, upstream of the particulate filter. Allow ten system volumes of gas to purge the system then record two measurements of the spiked flue gas. Turn off the spike flow and allow the system to purge again with 10 volumes of unspiked flue gas before beginning the procedure again. Repeat the above six times to record 24 total measurements. Spiked and unspiked measurements may be recorded in groups of four rather than in pairs. Analyze results as described in Sections 12.1 and 12.2. If the statistical analysis meets the validation criteria, then the validation is completed. If the validation criteria are not met, the problem may be the temporal variation in the unspiked flue gas concentrations may be faster than the interval between successive measurements. Several options are available to address this problem: (1) average results over longer time intervals to smooth out these short term variabilities; (2) modify the sample system to reduce its time constant by, for example, employing a system with lower total internal volume or increasing the sample flow rate; (3) using two sample trains; (4) using two CEMs simultaneously (one of which has been validated previously) to perform synchronized

measurements. This performance specification permits modifications to the sampling system to minimize its time constant if the other requirements of the validation sampling procedure are fulfilled.

11.2.1.2. Validation with a single CEM and two sampling lines. An alternative sampling scheme employs two separate sampling lines, one carrying spiked flue gas, the other carrying unspiked gas. The lines are connected to the CEM and additional pump by means of a four-way valve. The additional pump, operating at a flow rate similar to the flow rate of the CEM, is required so that the sampling line not currently being analyzed is constantly purged. In one position, the four way valve allows the flow of spiked gas to be drawn into the CEM by the CEM's internal vacuum pump, while at the same time the flow of unspiked gas is drawn through its separate sample line using the additional pump, the effluent of which is exhausted to vent. When the four-way valve's position is switched, the unspiked gas is diverted to the CEM and the spiked gas is diverted to vent. A rotameter or other flow indicating device is installed upstream of the valve on both sample lines.

To perform the validation, set the four-way valve to sample for unspiked flow. Introduce spiked gas into the inlet of the CEM. Before commencing recording measurements from either inlet line, allow at least ten volumes of sample gas to pass through the respective line. Begin with two independent measurements of unspiked flue gas. Switch the valve to allow the CEM to sample the spiked gas flow and send unspiked flow to vent. Allow sufficient time for the sample flow to purge the tubing downstream of the four way valve (5-10 time constants). Record two independent measurements of the spiked gas sample. Repeat above until 24 total independent measurements are recorded.

11.2.1.3. Synchronized measurements with two CEMs. Use two identical CEMs and sampling inlets to perform synchronized spiked and unspiked measurements. One CEM measures spiked flue gas, the other unspiked flue gas. Ensure that the time constants for both CEM configurations are approximately the same. Establish flow through both CEMs then begin the flow of spiking gas into the inlet of one of the inlets. Allow at least ten volumes of sample to pass through the sampling inlets before commencing sampling. Start recording

concentrations at the same time. Record at least 12 independent measurements with each system. In this approach one of the CEMs must have been previously validated, by the CEM vendor or the facility, so that its bias can be accounted for in validating the second CEM.

11.2.1.4. Comparison to a reference method (RM) using integrated sampling.

Obtain EPA approval that the chosen reference method qualifies as a RM for ammonia for the source to be tested. Follow the published procedures for the RM in preparing and setting up equipment and the sampling system, performing measurements, and reporting results. Conduct at least nine runs in which the NH₃ CEM and the RM are sampling simultaneously. Each run must be at least 30 minutes long. If more than nine runs are performed, up to three may be discarded so long as nine remain for validation purposes. The average NH₃ concentration values

from the CEM and RM for each run are used to calculate the relative accuracy of the CEM compared to the RM, as described in Section 12.2.1.

11.2.2. Path CEMs. Use EPA Method 301 type sampling for validation. According to Method 301, either comparison to a reference method (RM) or analyte spiking may be used to validate an instrument's performance. For path CEMs, the former approach is identical to that described for extractive CEMs in Section 11.2.1.4, and the latter approach is discussed below.

11.2.2.1. Validation with a single CEM. A gas cell, of known pathlength and volume, is mounted outside the stack between the light source and receptor of the CEM and is maintained at a temperature near that expected of the flue gas. The analyte spike mixtures and/or zero air are introduced dynamically through this cell. The light path must pass through the cell and into the stack so that the analyte in both the flue gas and the cell can be measured simultaneously. The validation begins with the measurement of unspiked sample gas. Ensure that the gas cell is evacuated, or that zero gas is flowing through the gas cell, and allow at least ten cell volumes of analyte-free zero air to purge the gas cell. Collect measurements for two independent unspiked samples, where those two independent measurements are separated by at minimum five cell volumes of zero gas. After the unspiked samples are measured, a gas flow containing a known concentration of analyte is then provided to the gas cell, and two spiked sample measurements are recorded, allowing at least 10 volumes to purge the cell prior to recording the spiked sample measurements. Again, two independent measurements are separated by at minimum five cell volumes of spiked gas. Repeat this procedure six times so that 24 samples (12 unspiked, 12 spiked) are collected. During validation testing, the flue gas concentration of NH_3 is unimportant as long as the spiked component can be measured and the flue gas (including interferences) is similar in composition to that expected under test conditions.

Care must be taken to correct the measurement results for any difference in absorption coefficient caused by differences between the gas cell and flue gas temperatures. Maintenance of the cell within the range of flue gas temperature minimizes the need for such corrections.

11.2.2.2. Synchronized measurements with two analyzers. Use two identical CEMs installed such that the paths sampled by these CEMs are as nearly identical to each other as possible. Ammonia spike gas is introduced into the gas cell of one of the systems, whereas zero gas is introduced to the gas cell of the other system. Ensure that the time constants for both instrument configurations are approximately the same. Establish flow through the gas cells of each analyzer then begin the flow of spiking gas into the gas cell of one of the analyzers and zero gas into the gas cell of the other. Allow at least ten volumes of sample to pass through the sampling trains before commencing sampling. Start recording concentrations at the same time. Collect at least 12 independent samples with each system. As noted in Section 11.2.1.3 and elsewhere, one of the two CEMs must have been previously validated, so that it can serve as the basis for validation of the second CEM.

11.3. Calibration Drift. The CEM design should allow the determination of calibration drift (CD) at zero and high-level values. If this is not possible or practical the design must allow these determinations to be conducted at a low-level (i.e., between zero and 20 percent of the full-scale) and at a value between 50 percent and 100 percent of full-scale.

11.3.1. Calibration Drift Procedure. Determine the CD of the CEM once per day for seven consecutive days, while the source is being operated at least 50 percent of normal load, by means of reference gases, gas cells, or optical filters. Record the response of the CEM and subtract the response from the reference value.

12.0 Calculations and Data Analysis

12.1 Calculations for Validation by Analyte Spiking. Validation of CEM performance by analyte spiking is assessed by calculating the bias as described below. All data from the CEM must be on a consistent dry basis and, as applicable, on a consistent diluent basis.

12.1.1. Bias. Bias is calculated as follows:

$$B = S_m - M_m - CS \quad (1)$$

where

- B = Bias at the spike level
- S_m = Mean of the observed spiked sample concentrations
- M_m = Mean of the observed unspiked sample concentrations
- CS = Expected value of the spiked concentration.

For path CEMs, the expected concentration (CS) is calculated as:

$$CS = [NH_3]_s \cdot \frac{L_c}{L_D} \quad (2)$$

where $[NH_3]_s$ is the concentration of the spike gas, L_c is the length of the gas cell, and L_D is the pathlength that the CEM samples across the duct. For extractive CEMs, the expected concentration (CS) is calculated as

$$CS = [NH_3]_s \cdot \frac{F_s}{F + F_s} \quad (3)$$

where F_s is the flow rate of the spike gas and F is the flow rate of the flue gas. The sum of $F + F_s$ is the total sampling flow rate of the CEM.

12.1.2 Statistical Analysis of Validation Measurements. Arrange the independent measurements as in Table 1 of Appendix A. More than 12 pairs of measurements may be

analyzed. The statistical analysis follows EPA Method 301, Section 6.3. Calculate the differences, d_i , for each pair of spiked and each pair of unspiked measurements. Then calculate the standard deviation of the spiked pairs of measurements using Equation 4.

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}} \quad (4)$$

where,

d_i = the differences between pairs of spiked measurements

SD_s = the standard deviation of the d_i values

n = the number of spiked pairs, $2n = 12$ for the minimum of 12 spiked and 12 unspiked measurements.

Calculate the relative standard deviation (RSD) as a percentage using SD_s and the mean of the spiked concentrations, S_m . The RSD must be $< 50\%$.

$$RSD = \frac{SD}{S_m} \cdot 100 \quad (5)$$

Repeat the calculations in equations (4) and (5) to determine SD_u and RSD , respectively for the unspiked samples. Calculate the standard deviation of the mean (SD) using SD_s and SD_u using Equation 6.

$$SD = \sqrt{SD_s^2 + SD_u^2} \quad (6)$$

The t-statistic to test the bias for statistical significance is calculated as follows:

$$t = \frac{|B|}{SD} \quad (7)$$

where the bias, B , is given in Section 12.1. For 11 degrees of freedom, and a one-tailed distribution, Method 301 requires $t < 2.201$. There is no limitation on the number of measurements but there must be at least 12 independent spiked and 12 independent unspiked measurements. Refer to the t -distribution (Table 2) at the 95% confidence level and appropriate degrees of freedom for the critical t -value when more than 12 sets of independent measurements

are made. If the t -statistic indicates the bias to be statistically significant, then analytical measurements must be multiplied by the correction factor, CF , given by:

$$CF = \frac{1}{1 + \frac{B}{CS}} \quad (8)$$

12.2 Calculations for Validation by Comparison to Reference Method. Validation of CEM performance by comparison to a reference method is assessed by calculating the relative accuracy as described below.

12.2.1. Relative Accuracy. Relative accuracy is determined from the sum of the arithmetic mean of the differences between the CEM results and the RM results and the 2.5% confidence coefficient, divided by the mean of the RM results.

12.2.1.1. Arithmetic mean of differences. Calculate the arithmetic mean of the differences between the CEM results and the RM results as:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^n d_i \quad (9)$$

where

n is the number of data points, and

d_i is the difference between the CEM result and the RM result for the i^{th} test run.

12.2.1.2. Standard deviation. Calculate the standard deviation of the differences, S_d , as follows:

$$S_d = \left[\frac{\sum_{i=1}^n d_i^2 - \frac{\left(\sum_{i=1}^n d_i\right)^2}{n}}{n-1} \right] \quad (10)$$

12.2.1.3. Confidence coefficient. Calculate the 2.5 percent error confidence coefficient (one-tailed), CC , as:

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \quad (11)$$

where $t_{0.975}$ = t -value for the number of samples (see Table 2 in Appendix A).

12.2.1.4. Relative accuracy. Calculate the RA of a set of data as follows:

$$RA = \frac{[|\bar{d}| + CC]}{\overline{RM}} \times 100 \quad (12)$$

where

$|\bar{d}|$ is the absolute value of the mean differences (d_i),

CC is the confidence coefficient, and

\overline{RM} is the mean of the RM values. In cases where the average emissions for the test period are less than 50% of the applicable standard, substitute the emission standard value in the denominator in place of \overline{RM} .

The *RA* of the CEM must be no greater than 35%, when the mean RM values are used in the denominator of Equation 12, or no greater than 20% when the applicable emission standard is used in the denominator of Equation 12. These criteria are chosen for consistency with other Performance Specifications, and can be revised based on the performance information specific to NH₃ CEMs and NH₃ reference methods.

12.3. Calibration Drift. Calculate the CD of the CEM as:

$$CD = \frac{(C - M)}{S} \times 100 \quad (13)$$

where *C* is the calibration value of the reference gas, gas cell, or optical filter, *M* is the measured response of the CEM, and *S* is the full-scale value.

The calibration of the CEM must not drift or deviate from the calibration value of the reference gas, gas cell, or optical filter by more than 2.5 percent of the full-scale value. These criteria are chosen for consistency with other Performance Specifications, and can be revised based on the performance information specific to NH₃ CEMs.

13.0 References [Reserved]

14.0 Appendix A. Tables

Table 1. Arrangement of Validation Measurements for Statistical Analysis.

Measurement	Time	Spiked Reading (ppm)	Difference Spiked (d)	Unspiked Reading (ppm)	Difference Unspiked (d)
1		S_1	$S_2 - S_1$	U_1	$U_2 - U_1$
2		S_2		U_2	
3		S_3	$S_4 - S_3$	U_3	$U_4 - U_3$
4		S_4		U_4	
5		S_5	$S_6 - S_5$	U_5	$U_6 - U_5$
6		S_6		U_6	
7		S_7	$S_8 - S_7$	U_7	$U_8 - U_7$
8		S_8		U_8	
9		S_9	$S_{10} - S_9$	U_9	$U_{10} - U_9$
10		S_{10}		U_{10}	
11		S_{11}	$S_{12} - S_{11}$	U_{11}	$U_{12} - U_{11}$
12		S_{12}		U_{12}	
Average					

Table 2. t-Values

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.3003	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

^a The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.