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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Verification Protocol for Continuous Emission Monitors for Ammonia at a Power Production Facility

GENERIC VERIFICATION PROTOCOL

FOR

CONTINUOUS EMISSION MONITORS FOR AMMONIA AT A POWER PRODUCTION FACILITY

September 2003

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FOREWORD

This generic verification protocol is based upon a peer-reviewed specific test/quality assurance (QA) plan entitled "Test/QA Plan for Verification of Continuous Emission Monitors for Ammonia at a Coal-Fired Facility" (dated June 2003). The test/QA plan was developed with vendor and stakeholder input by the ETV Advanced Monitoring Systems (AMS) Center. Peer reviewers for the test/QA plan were John Higuchi of the South Coast Air Quality Management District and AMS Center stakeholders Ernie Bouffard and Tom Logan. In preparing this generic verification protocol, specific names of individuals involved, technology vendors and technologies, test dates, and similar details in the test/QA plan were revised to be generic. The experimental design in the protocol is the same as that in the peer-reviewed test/QA plan.

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ACRONYMS

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
CEM	continuous emission monitor
CO	carbon monoxide
CO_2	carbon dioxide
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification
ft	foot
H_2O	water
IC	ion chromatography
ISE	ion selective electrode
NIST	National Institute of Standards and Technology
NO_x	nitrogen oxide
O_2	oxygen
PE	performance evaluation
ppmv	parts per million volume
QA	quality assurance
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
RA	relative accuracy
RSD	relative standard deviation
SCR	selective catalytic control
SO_2	sulfur dioxide
TSA	technical systems audit

1 INTRODUCTION

1.1 Test Description

This protocol provides generic procedures for the development of a test/quality assurance (QA) plan and verification test for continuous emission monitors (CEMs) used to measure gaseous ammonia in source emissions. Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency's (EPA) Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants have an independent and credible assessment of what they are buying and permitting.

Verification tests are coordinated by Battelle, of Columbus, OH, which is EPA's partner for the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring methods for contaminants and natural species in air, water, and soil. In performing the verification test, Battelle will follow procedures specified in this protocol and will comply with quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).[1]

1.2 Test Objective

The objective of the verification test described in this protocol is to verify the performance of commercial ammonia CEMs by comparing them to reference ammonia measurements and by challenging them with ammonia standard gases. Testing can be conducted in facilities such as a full-scale coal-fired or gas turbine power plant using nitrogen oxide (NO_x) selective catalytic reduction (SCR) control technology.

1.3 Roles and Responsibilities

Verification tests are performed by Battelle in cooperation with EPA, the vendors whose CEMs are being verified, and a host facility. The organization chart is shown in Figure 1. The specific responsibilities of these individuals and organizations are detailed in the following paragraphs.

1.3.1 Battelle

The AMS Center's Verification Test Coordinator has overall responsibility for ensuring that the technical goals, schedule, and budget established for the verification test are met. More specifically, the Verification Test Coordinator shall

- Serve as Battelle's primary point of contact for vendor and test facility representatives
- Coordinate with the host facility to conduct the verification test, including establishing a subcontract as necessary
- Ensure that the procedures in this protocol are followed during the verification test
- Prepare draft verification reports and verification statements, revise according to reviewer comments, and be responsible for distribution of final copies
- Coordinate with the host facility, including collection and review of facility data
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Ensure that vendor confidentiality is maintained.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees the various stages of the verification test. The Verification Testing Leader shall

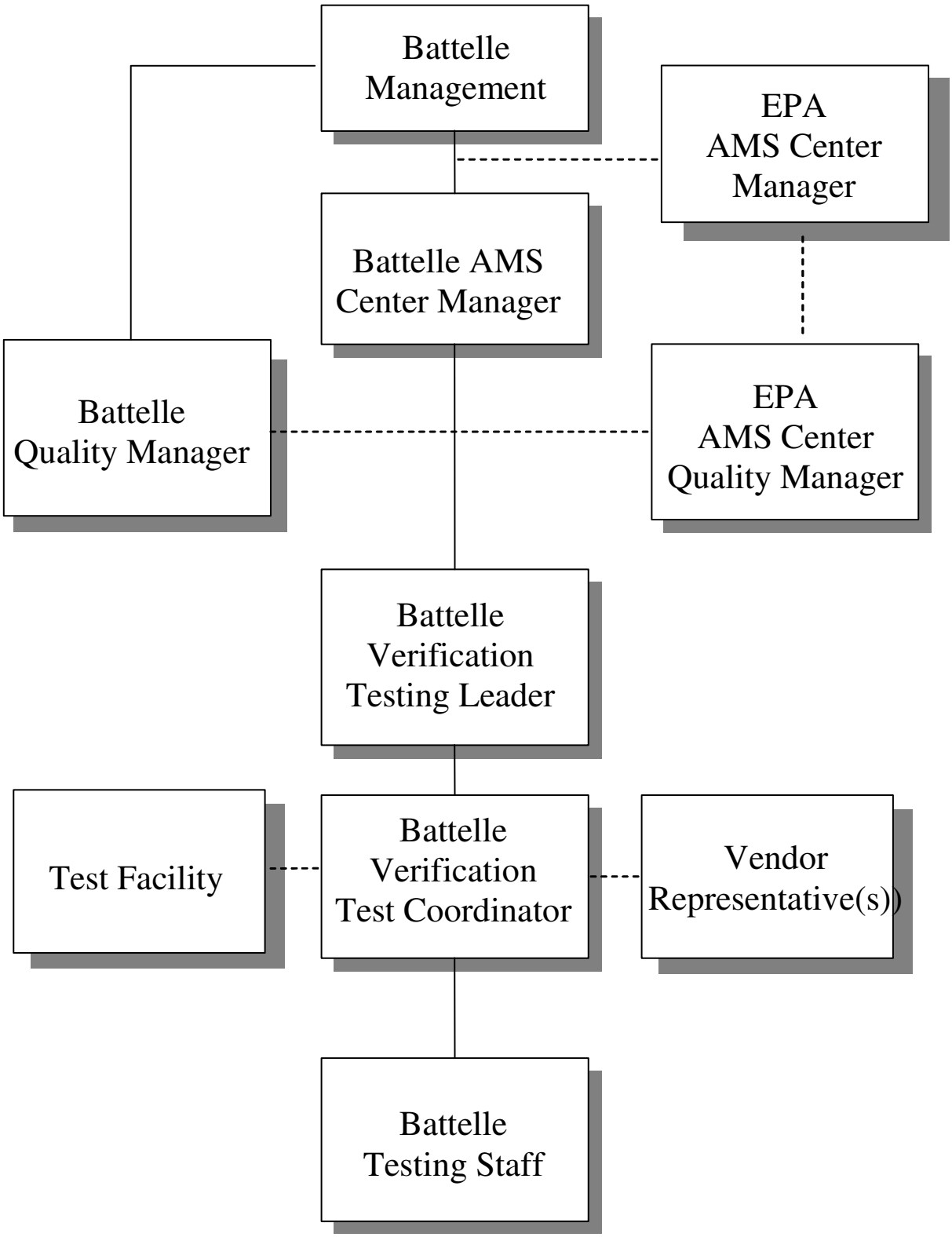

Figure 1. Oganization Chart for the Ammonia CEM Verification Test

- Support the Verification Test Coordinator (as necessary) in organizing the test
- Review the draft verification reports and statements.

The Battelle AMS Center Manager shall

- Review the draft verification reports and statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with the EPA AMS Center Manager and EPA AMS Center Quality Manager.

The Battelle Quality Manager for the verification test shall

- Conduct a pre-test QA review of the subcontracted reference sampling/analysis laboratory, if such a laboratory is employed in the verification
- Conduct a technical systems audit (TSA) once during the verification test
- Review results of performance evaluation audit(s) specified in this protocol
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Issue a stop work order if internal audits indicate that data quality is being compromised; notify Battelle's AMS Center Manager if such an order is issued
- Provide a summary of the audit activities and results for the verification reports
- Review the draft verification reports and statements
- Ensure that all quality procedures specified in this protocol and in the QMP[(1)] are followed.

Battelle testing staff will support the Verification Test Coordinator. These staff shall

- Assist in planning for the test, and making arrangements for the installation of the CEMs
- Assist vendors and host facility staff as needed during the CEM installation and verification testing
- Assure that test procedures and data acquisition are conducted according to this protocol or a specific test/QA plan
- Contribute to the planning of statistical treatment of the CEMs data as needed
- Perform statistical calculations specified in this protocol on the analyzer data as needed
- Provide results of statistical calculations and associated discussion for the verification reports as needed
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to statistics and data reduction as needed.

1.3.2 Vendors

Vendor representatives shall

- Document acceptance of the test procedures specified in this protocol prior to the test
- Provide an ammonia CEM for the duration of the verification test
- Commit or train a technical person to operate, maintain, and repair the CEM throughout the verification test
- Participate in verification testing, including providing data acquisition for their CEMs
- Provide to Battelle staff the data from their CEM at the conclusion of each test day
- Review their respective draft verification reports and statements.

1.3.3 EPA

EPA's AMS Center Quality Manager shall

- Perform, at EPA's option, one external technical systems audit during the verification test
- Notify EPA's AMS Center Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing the results of the external audit, if one is performed
- Review the draft verification reports and statements.

EPA's AMS Center Manager shall

- Notify the Battelle AMS Center Manager to facilitate a stop work order if the external audit indicates that data quality is being compromised
- Review the draft verification reports and statements
- Oversee the EPA review process on the verification reports and statements
- Coordinate the submission of verification reports and statements for final EPA approval.

1.3.4 Host Facility

The responsibilities of the host facility shall be to

- Coordinate the operation of the host facility for the purposes of ETV testing
- Coordinate the installation of vendors' equipment at the host facility
- Communicate needs for safety and other training of staff working at the host facility
- Provide on-site staff to assist during testing

- Provide calibrated facility monitoring equipment
- Provide data on facility operations during testing, for the verification reports
- Provide input in responding to any issues raised in assessment reports and audits related to facility operations
- Review draft verification reports and statements.

1.3.5 Reference Sampling/Analysis Subcontractor(s)

If reference measurements for ammonia are to be conducted by subcontractors to Battelle, the responsibilities of such subcontractors shall be to

- Adhere to the quality requirements in this protocol
- Assemble trained technical staff to conduct reference method sampling for the verification test
- Cooperate in a pre-test QA review to be conducted by the Battelle Quality Manager
- Oversee and conduct laboratory analysis of the reference method samples as appropriate
- Report reference method analytical and quality assurance results to Battelle in an agreed-upon format
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to reference method sampling and analysis.

2 EXPERIMENTAL DESIGN

2.1 Introduction

This protocol is applicable to the verification testing of commercial CEMs for determining gaseous ammonia in combustion source emissions, specifically measuring ammonia from a full-scale coal-fired or gas turbine power plant employing NO_x SCR technology. The

overall objective of the verification test described is to evaluate the performance of new ammonia CEMs operating continuously over a relatively short test period.

The performance parameters to be addressed by the verification test include

- Accuracy
- Comparability
- Linearity
- Precision
- Calibration drift
- Zero drift
- Response time
- Data completeness
- Operational factors.

Accuracy shall be assessed for the CEMs being verified by determining the degree of agreement with known concentrations of compressed ammonia gas standards. Comparability shall be assessed through the degree of agreement with a reference method. Precision shall be assessed in terms of the repeatability of the ammonia measurements under stable test conditions. Calibration drift, zero drift, linearity, and response time shall be assessed using commercial compressed gas standards of ammonia. The effort expended in installing and maintaining each CEM shall be documented and used to assess ease of use. The amount of time each CEM is operational and the maintenance activities performed over the verification test period shall be recorded and reported, to help assess data completeness.

2.2 Site Description

The verification test shall be conducted at a power plant employing NO_x SCR technology. The CEMs to be tested will be installed at the exit of the SCR and upstream of the air heater.

Access to the flue gas for the CEMs and for wet chemical reference sampling should be available through ports in the duct at the testing location. Appropriate ports should be available for CEMs requiring cross-duct access. The ammonia concentration should be determined at multiple points across the entire duct cross section, either prior to or after testing, to assess the degree of stratification. In the event that the reference and CEM sampling ports cannot be closely collocated, the data from this mapping of ammonia across the duct can be used to correct for any stratification between sampling ports. During the test period, the boiler and SCR should operate continuously.

2.3 General Design

The verification test developed from this protocol shall be conducted over a period of approximately five weeks. Approximately two weeks prior to testing should be available for installing the commercial CEMs at the facility and conducting a shakedown run of all the CEMs before the verification test begins.

Testing shall not begin until all of the reference method equipment is ready and the facilities are operating normally. Similarly, it is desirable that all the commercial CEMs be fully operational to participate in the verification test.

The ammonia CEM testing shall involve continuous monitoring of ammonia by the CEMs over the entire test period with reference method sampling conducted on each weekday during the first and fifth weeks of the test period. A total of 15 duplicate reference samples shall be collected during both the first and fifth weeks. The average CEM readings during these periods shall be used for comparisons with the ammonia concentrations measured from the reference method samples. During each day of reference method sampling, a zero and span check shall be conducted on the CEMs by challenging each with zero air and an ammonia gas standard. These zero/span checks shall be used to assess drift of the CEMs during the test period.

During the third week of testing, each of the CEMs shall be challenged independently with a series of runs involving dynamic spiking of compressed ammonia gas standards. The results of these runs will be used to assess accuracy of the CEMs as well as the linearity in instrument response.

Throughout the verification test, each CEM undergoing testing shall be operated by the CEM vendor's own staff or by on-site staff trained by the vendor. However, the intent of the testing is for the CEM to operate continuously in a manner simulating operation at a power production facility. As a result, once the verification test has begun, no adjustment or recalibration will be performed, other than what would be conducted automatically by the CEM in normal unattended operation. Repair or maintenance procedures may be carried out at any time, but testing will not be interrupted; and data completeness will be reduced if such activities prevent collection of CEM data required for verification.

2.4 Test Conditions

Actual concentrations of parameters and gaseous constituents typical of the flue gas stream at the host facility during the testing period shall be measured. When reference method sampling is being conducted, the fuel loading and ammonia injection rate shall be held as constant as possible throughout the entire sampling period (e.g., fuel loading rate within ± 10%, and ammonia injection rate within ± 10%) to allow comparisons of CEM data to reference method data under constant conditions. During normal operation, the ammonia concentrations in the flue gas should be at or below 2 parts per million volume (ppmv); and, during dynamic spiking, the range of concentrations should be changed to be between approximately 0 and 10 ppmv.

2.5 Test Procedures

The CEMs undergoing verification shall be installed between the exit of the SCR and the inlet of the air heaters. Ports for the reference method sampling shall be located on the same duct as the CEMs as close as possible to the sampling locations of the CEMs. The sampling ports shall be assigned so that no CEM is affected by the operation of any other CEM or by the reference method sampling. In situ CEMs should be installed with either an in-line gas cell or an external gas cell that can be used for calibration and dynamic spiking purposes. Likewise the extractive systems should be installed with a means of spiking compressed gas into the sampling probe upstream of the in-line filter.

At either the beginning or the end of each test day during the first and fifth weeks of testing, the CEMs undergoing testing shall be supplied (one at a time) with zero gas and then with a commercial compressed gas standard containing ammonia. After reaching equilibrium, the response to each gas shall be recorded for use in assessing the zero and calibration drift of the CEMs.

During the second and fourth weeks of the test, the CEMs will continue to operate continuously, though no zero/span checks or reference sampling will take place.

2.5.1 Reference Method

During testing, wet chemical reference samples shall be collected during the first and fifth weeks, using a time-integrated method for measurement of ammonia in flue gas. At the time of writing this generic protocol, the EPA Conditional Test Method (CTM 027)[(2)] was similar to a draft American Society for Testing and Materials (ASTM) method[(3)] that is designed specifically for measuring low levels of ammonia, typical of slip concentrations from SCR applications. There are, however, some notable differences between the two methods. The primary difference involves sample analysis rather than sample collection. The draft ASTM method[(3)] calls for analysis by ion selective electrode (ISE) whereas the EPA method[(2)] calls for analysis by ion

chromatography (IC). Other differences between the draft ASTM method and EPA CTM027 include different concentrations and volumes of the sulfuric acid solution in impingers 1 and 2 of the sampling train. The draft ASTM method calls for a smaller volume of a more dilute acid solution. This is more appropriate than the approach recommended in EPA CTM027 for measuring low levels of ammonia, so the ASTM acid volumes and concentration shall be substituted in the EPA CTM027 method for this verification test.

During verification testing, reference sampling shall be conducted simultaneously with two trains collocated with the CEMs being tested. The sampling duration for each run will typically be between 30 and 60 minutes. Thus, each of the three reference sampling periods during a test day will provide two reference ammonia samples for comparison to the CEM data. Unique sample identification numbers shall be implemented so that final data used for verification can be traced back through the analytical process to the original sample. Field blank samples also shall be recovered from one blank sampling train on each of three days during each week that reference method samples are collected. Before sample recovery, that blank train shall be transported to the sampling location. As possible, different train equipment will be used for the blank train on different days. Additionally, on each of three days during each week of reference sampling, one sample train shall be spiked with ammonia solution to serve as a field spike sample.

Samples will be recovered from the reference method trains within two hours of sample collection. Each of the reference samples will be split into two portions, with one portion analyzed on-site by the draft ASTM method[3] and the second portion analyzed in the laboratory by the EPA CTM027[2]. The ISE analysis shall be conducted within two hours of sample recovery using available on-site facilities. The front and back impingers shall be analyzed separately on-site by ISE. If no breakthrough has occurred (<10% of front end detected on the second impinger), the solutions will be combined for IC analysis. The results of the on-site analysis by ISE will not be used for verification of the CEMs. Rather they will be used to assess the ammonia levels being sampled and to ensure that the reference sampling is being performed properly. Samples for IC analysis shall be stored at 4°C ± 2°C (not frozen) and shall be shipped

on blue ice to the analytical laboratory within one week of sample collection. After receipt at the laboratory, the samples shall be stored at 4°C ± 2°C until analysis and shall be analyzed within two weeks of collection. Just prior to IC analysis, the samples shall be removed from refrigerated storage and allowed to slowly warm to room temperature.

At the ammonia concentrations to be used in the verification test, it is expected from previous results[4] that the precision of duplicate reference method results will be within about 35% relative percent difference. It is expected that day-to-day reproducibility of ammonia levels in the facility will also be within that range. Thus, during normal operation it is expected that the ammonia levels will be consistent to ± 35% throughout each week of testing. As a result, the entire set of reference method results, not merely those from a single test day, shall be considered in screening for reference data quality. The reference method results shall be reviewed before verification comparisons are made to identify individual statistical outliers from the full set of reference method results. That is, the reference method results will be screened for two factors:

- Precision of results from collocated sampling trains
- Consistency of results with previous and later results at the respective sampling location.

Identification of outliers will be based on statistical tests such as a t-test comparison of means or a Q-test evaluation of divergent results. In any case where rejection of a reference result is suggested, an effort shall be made to find an assignable cause for the divergent result. Reference method results that are identified as statistical outliers on any of these criteria shall be reported, but shall not be used for verification. The intent of this approach is to provide a valid set of reference data for verification purposes, while also illustrating the degree of variability of the reference method.

2.5.2 Dynamic Spiking

During the third week of testing, each of the CEMs shall be challenged with a series of dynamic spiking runs. During these runs the ammonia concentrations shall be increased by approximately 2, 5, and 8 ppmv above the flue gas concentration. At each spike concentration, a series of runs will be conducted including 12 spiked and 12 unspiked sample measurements. These measurements shall be performed by sampling pairs of spiked samples, followed by sampling pairs of unspiked samples. Prior to measurement, each CEM shall be readied by purging the gas cell (for in situ analyzers) with at least 10 volumes of zero air or by purging the sampling probe (for extractive CEMs) with at least 10 volumes of sample gas. After this purging is completed, a standard ammonia gas mixture will be introduced, at a measured flow rate, to the gas cell (for in situ analyzers), or to the sampling probe (for extractive CEMs). The CEM readings of the spiked sample shall be recorded after at least 10 volumes of gas have passed through the gas cell or sampling probe. A second spiked sample shall be measured after at least five volumes of gas have passed through the sample cell or sampling probe after the measurement of the first spiked sample. After the second spiked sample is measured, a pair of unspiked samples shall be measured following the same procedure as the spiked samples, with the exception that zero air will be substituted for the ammonia spike gas. The procedures for the collection of the spiked and unspiked samples shall be conducted a total of six times at each of the spike concentrations to obtain 12 spiked and 12 unspiked samples at each concentration.

For the in situ CEMs, these dynamic spiking runs shall be conducted by flowing compressed ammonia gas standards into the in-line or external gas cell to achieve the desired ammonia concentrations. The ammonia and the zero air will be supplied as described above or until the CEM readings reach equilibrium, at which point the measured concentration and the spike gas flow rate will be recorded. The volume/length of the gas cell, the optical pathlength, and the known concentration of the gas standard shall be used to calculate the theoretical increase in cross-stack concentration introduced during the run.

For the extractive CEMs, the dynamic spiking shall be conducted by injecting ammonia gas into the probe tip upstream of the particulate filter such that the ammonia passes through as much of the sampling system as possible. The ammonia gas standard should mix with the flue gas at a ratio of approximately one part spike gas to nine parts flue gas or more dilute. The flow rate of the compressed gas and the dilution ratio of the spike gas shall be used to calculate the theoretical increase in concentration introduced during the spiking.

2.5.3 Data Comparisons

Table 1 summarizes the data that will be used for the verification comparisons. The results of the dynamic spiking shall be used to assess accuracy of the CEM results relative to calculated ammonia concentrations determined from the spike gas concentration and flow rate. For each spiking run, the difference between the ammonia concentration measured by the CEM and the calculated ammonia concentration from spiking will be determined. The differences will be used to assess accuracy of the CEM results.

For comparison to the reference method results, the measurements from each of the CEMs will be separately averaged over each of the individual reference sampling periods. Comparability with the reference method shall be assessed by comparing the averaged CEM results during the reference sampling periods with the reference results from the respective periods. A total of 30 ammonia reference sampling runs should be made in the verification test (15 during each of the first and fifth weeks of testing), with two reference method sampling trains operating simultaneously in each sampling run. Thus a total of 60 reference samples will be used to evaluate comparability of the CEMs relative to the reference method.

Linearity of the CEM response shall be assessed from the dynamic spiking results. The measured ammonia concentrations and the calculated ammonia concentrations will be used to assess linearity in the range from the background concentration to approximately 8 ppmv above background. A total of 72 data points (36 background and 12 each at 2, 5, and 8 ppmv above background) will be used for this assessment.

Table 1. Summary of Data to be Obtained in Ammonia CEM Verification Test

Performance Parameter	Objective	Comparison Based On	Total Number of Data Points for Verification
Accuracy	Determine degree of quantitative agreement with compressed gas standard	Dynamic spiking with ammonia gas standards	36
Comparability	Determine degree of quantitative agreement with reference method	Reference method results	60
Linearity	Determine linearity of response over a range of ammonia concentrations	Dynamic spiking with gas standards	72
Precision	Determine repeatability of successive measurements at fixed ammonia levels	Repetitive measurements under constant facility conditions measured over the duration of each reference method sampling run, and each dynamic spiking run Repetitive ammonia standard testing	66
Cal/Zero Drift	Determine stability of zero gas and span gas response over successive days	Zero gas and NH_3 gas standard	10
Response Time	Determine rise and fall time	Recording successive readings at start and end of sampling NH_3 gas standard	6

Precision of the CEMs shall be assessed based on the individual measurements performed by each CEM over the duration of each reference method sampling run. For example, if a CEM provides an updated measurement every five minutes; then, over a 25-minute sampling run, a total of five readings would be obtained. The average and standard deviation of those readings will be calculated to assess precision. This procedure will be applied to each of the 30 reference method sampling intervals and each of the 36 dynamic spiking runs at elevated ammonia concentrations.

Calibration and zero drift shall be verified based on challenging the CEMs with zero gas and with a compressed gas standard of ammonia on each test day during the first and fifth weeks

of the test. Thus up to 10 data points will be used to assess zero drift and an equal number to assess calibration drift. Calibration drift of the CEMs will be assessed at approximately 80% of full scale for each of the CEMs.

CEM response time shall be assessed once in each of the first, third, and fifth weeks of the test by recording successive CEM readings as the CEM responds to the ammonia gas standard or returns to baseline after analysis of that standard. The former readings will indicate the CEM rise time and the latter the CEM fall time.

No additional test activities will be required to determine the data completeness achieved by the CEMs. Data completeness shall be assessed by comparing the data recovered from each CEM to the amount of data that would be recovered upon completion of all portions of these test procedures.

Setup and maintenance needs shall be documented qualitatively, both through observation and through communication with the vendors (or their trained representatives) during the test. Factors to be noted include the frequency of scheduled maintenance activities, the down time of the CEM, and the number of staff operating or maintaining it during the verification test.

3 STATISTICAL CALCULATIONS

The statistical calculations to be used to verify CEM performance are described below. In all cases, measurement results from both the reference method and the CEMs undergoing testing are to be reported in units of ppmv on a dry basis at 20 °C, 1 atmosphere pressure, and the actual flue gas oxygen (O_2) content.

3.1 Relative Accuracy

The relative accuracy (RA) of the CEMs with respect to the ammonia gas standards will be assessed using Equation 1:

$$RA = \frac{\left|\bar{d}\right| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\% \quad (1)$$

where *d* refers to the difference between the calculated ammonia concentration from the dynamic spiking and the average of the CEM measurements recorded during the respective spiking periods, and *x* corresponds to the calculated spike concentration. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the 100(1 - α)th percentile of the distribution with n-1 degrees of freedom. The RA will be determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). The RA calculated in this way can be interpreted as an upper confidence bound for the relative bias of the CEM, i.e., $\frac{|\bar{d}|}{\bar{x}}$, where the superscript bar indicates the average value of the differences or of the reference values. RA shall be calculated separately at each of the spiking levels.

3.2 Comparability

The comparability of the CEM results and the EPA CTM027[(2)] reference method results shall be assessed using Equation 1, in which *d* represents the difference between the average of paired reference method results and the average of the CEM results from the period during which the paired reference method samples were collected, and *x* corresponds to the average of the paired reference method results. Comparability will be calculated using all EPA CTM 027[(2)] reference method sample results (assuming all reference method samples can be treated as independent results). The impact of the number of data points (n) on the RA value will be noted in the verification report.

3.3 Linearity

Linearity shall be assessed by a linear regression analysis of the dynamic spiking data using the calculated ammonia concentrations as the independent variable and the CEM results as the dependent variable. Linearity will be expressed in terms of slope, intercept, and coefficient of determination (r^2).

3.4 Precision

Precision shall be calculated in terms of the percent relative standard deviation (RSD) of a series of CEM measurements made over the duration of each reference method sampling run with ammonia injected at a constant level into the SCR zone and during each of the dynamic spiking runs. During each reference method sampling run, and during each dynamic spiking run, all readings from a CEM undergoing testing will be recorded, and the mean and standard deviation of those readings will be calculated. Precision (P) will then be determined as

$$P = \frac{SD}{\overline{X}} \times 100 \qquad (2)$$

where SD is the standard deviation of the CEM readings and $\overline{X}$ is the mean of the CEM readings. This calculation will be done for each CEM, using the CEM data collected during every reference method sampling run and dynamic spiking run. The verification report will note that the calculated precision is subject to the variability of the host facility, and not only to the CEM variability. Although no comparison among CEMs will be made, all CEM data from the periods of reference sampling will be reviewed to assess whether the consensus of the CEM data indicates an unusual variation in the test facility itself. If such a variation is indicated, that finding will be noted in all verification reports.

An additional precision assessment may be made by sampling an ammonia standard from the probe inlet for one hour. These repeated measurements may be reported along with the precision assessment made from measuring the flue gases.

3.5 Calibration and Zero Drift

Calibration and zero drift shall be reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the CEM in the daily sampling of the same ammonia standard gas and of zero gas. Up to 10 ammonia standard readings, and up to 10 zero readings, will be used for this calculation. This calculation, along with the range of the data, will indicate the day-to-day variation in zero and standard readings.

3.6 Response Time

Response time shall be assessed in terms of both the rise and fall times of each ammonia CEM when sampling the ammonia gas standard. Rise time (i.e., 0% to 95% response time) will be determined by recording all CEM readings as the gas supplied to the CEM is switched from zero gas to the ammonia standard. Once a stable response has been achieved with the gas standard, the fall time (i.e., the 100% to 5% response time) will be determined in a similar way, by recording all CEM readings as the gas supplied is switched from the ammonia standard back to zero gas. For CEMs that provide periodic rather than continuous readings, determination of rise and fall times may involve interpolation between readings.

Rise and fall times shall each be determined once for each CEM in each of the first, third, and fifth weeks of the test. Thus a total of six data points will be obtained relevant to response time for each CEM. Rise and fall times will be reported in units of seconds.

4 MATERIALS AND EQUIPMENT

4.1 Gases and Chemicals

4.1.1 High Purity Nitrogen/Air

The high purity gases used for zeroing the CEMs shall be commercial ultra-high purity (i.e., minimum 99.999% purity) air or nitrogen.

4.1.2 Ammonia Standard Gases

Compressed gas standards containing ammonia shall be obtained for use in the calibration checks and the dynamic spiking activities of the CEMs. These will consist of ammonia in a nitrogen matrix, at levels appropriate to achieve increases above background concentrations of approximately 2, 5, and 8 ppmv during dynamic spiking and for use in the calibration checks performed during the first and last weeks of testing. Multiple cylinders of uniform concentration will be obtained, if required to meet the gas consumption rates of the CEMs during the test.

4.2 Reference Method

4.2.1 Sampling Trains

The glassware, filters, and associated equipment for performance of the reference method[2] sampling shall be supplied by the subcontractor and will meet the requirements of the EPA conditional test method for ammonia measurement. Multiple trains will be supplied so that six trains (i.e., three sampling runs with two trains each) may be sampled in a single day, in addition to at least three blank trains and three spiked trains per week.

4.2.2 Analysis Equipment

Laboratory equipment for sample recovery and analysis shall include all chemicals and solutions for preparation of the samples for analysis as well as for the analysis of the samples. An ISE will be provided for on-site analysis, and an IC will be available for laboratory analysis.

4.3 Facility Monitoring Equipment

Monitoring equipment should include monitors for major flue gas constituents [(O_2, carbon dioxide (CO_2)] and for chemical contaminants [(CO, NO_x, sulfur dioxide (SO_2)], as well as sensors for temperature and pressure and may include ammonia CEM systems already installed at the facility. These devices are considered part of the host facility for purposes of this test, and will be operated by the host facility during this verification according to normal facility procedures.

4.4 Equipment Used for Performance Evaluation Audits

Performance evaluation (PE) audits shall be performed for the temperature and pressure measurements in the flue gas. Those PE audits will be performed by conducting a parallel measurement using an independent monitoring device. The devices to be used may include the following:

- Thermocouple temperature indicator
- Aneroid barometer
- Magnehelic differential pressure indicator
- Flow meter
- Balance.

These devices will have been calibrated by the manufacturer or by Battelle's Instrument Laboratory within the six months immediately preceding the verification test or calibrated on site

as necessary. In addition, a calibrated set of weights shall be used to audit the balance used to weigh impingers from the reference method trains (used for determining flue gas H_2O content).

A National Institute of Standards and Technology (NIST)-traceable ammonia standard solution will also be used to spike three blank reference method trains, in each of the first and fifth weeks of the test to assess the overall ammonia measurement. NIST-traceable ammonia standards will be used to prepare blind audit samples to assess the performance of both the ISE and the IC.

5 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance/quality control (QA/QC) activities include providing blank sampling trains (three per week) and blank sampling materials (filters, reagent solution blanks) in the field. Documentation of these activities is required in the verification data file. Deviation from the reference method[2] will occur as a result of using the concentrations and volumes identified in the draft ASTM method[3] for solutions used in the impingers.

5.1 Equipment Calibrations

5.1.1 Host Facility Equipment

Monitoring devices shall be calibrated by host facility staff according to normal facility procedures. All calibration results must be documented for inclusion in the verification test data files and verification report.

5.1.2 Reference Method Sampling Equipment

Equipment to collect the reference samples shall be calibrated according to the procedures described in the reference method[2]. All calibration results must be documented for inclusion in the verification test data files and verification report.

5.1.3 Analytical Equipment

Analysis of the reference samples shall be conducted both on-site using an ISE and in a laboratory using IC. The ISE analysis will be used only for initial QA purposes to ensure that the ammonia levels in the duct are within the expected range and to ensure that the reference sampling is being conducted properly. The ISE shall be calibrated according to the manufacturer's recommendations using at least three different solutions prepared from NIST-traceable ammonia standards. Immediately after calibration, at least three standard solutions will be reanalyzed using the ISE. If the ISE reading does not agree between the standard concentration of the solutions within 10%, the calibration will be repeated. The calibration will be conducted on-site daily during each week of reference sampling and will include ammonia concentrations that will bracket the concentrations expected in the reference samples.

The equipment used for the IC analysis shall be calibrated by staff of the laboratory performing the analysis. The calibration will be conducted according to the manufacturer recommendations and the requirements of the reference method[2] and will include concentrations of ammonia standard solutions that bracket the expected concentration of the sample solutions. The calibration will be acceptable if the r^2 of the calibration curve is >0.95. All calibration results must be documented for inclusion in the verification test data files and verification report.

5.1.4 Calibration Check/Dynamic Spiking Equipment

The dry gas meter used to measure the spike gas flow rate during the calibration checks and the dynamic spiking activities shall be calibrated against a NIST-traceable flow transfer standard. The date of the calibration will be within one year of the date of the dynamic spiking activities.

5.2 QA/QC Samples

5.2.1 Field Blanks

During each week of reference method sampling, a total of three sampling trains shall be used as field blank samples. These trains will be prepared and transported to the sampling location, but will not be used to collect a sample of flue gas. The trains will then be disassembled, and the field blank solutions will be analyzed on-site by ISE to ensure that the background concentration as a result of on-site handling and exposure is negligible relative to the ammonia content of the samples. If background levels are greater than 10% of the sample concentrations, no additional reference sampling will be conducted until the cause of the contamination is identified and rectified. The field blank solutions will also be analyzed in the laboratory by IC.

5.2.2 Laboratory Blanks

Laboratory blank solutions shall be prepared for both ISE and the IC analysis. The solutions will be analyzed prior to analysis of the reference samples. A laboratory blank solution will be analyzed after every 10^{th} reference method sample to ensure no drift in the ISE or IC instrumentation. If the blank levels are greater than 10% of the expected sample concentrations, the cause of the contamination will be identified and rectified, all analyses performed after the

most recent acceptable blank will be invalidated, and analysis of those samples will be repeated (if possible).

5.2.3 Laboratory Spikes

Laboratory spike solutions shall be prepared with concentrations approximately equal to ammonia concentrations expected from the collection of a 5 ft^3 sample of flue gas with 2 ppmv ammonia. These solutions will be prepared for both ISE and the IC analysis using NIST-traceable ammonia solutions. The solutions will be analyzed prior to analysis of the reference samples. A laboratory spike solution will be analyzed after every 10^{th} reference method sample to ensure that there is no drift in the ISE or IC instrumentation. If the measured concentrations are not within ±10% of the spike concentration, the cause of the discrepancy will be investigated and rectified if possible. If such a discrepancy is observed, all analyses performed after the most recent acceptable spike will be invalidated; and analysis of those samples will be repeated (if possible).

5.3 Assessment and Audits

5.3.1 Technical Systems Audits

Battelle's ETV Quality Manager shall perform a TSA once during the performance of the verification test. The purpose of this TSA is to ensure that the verification test is performed in accordance with this protocol, the test/QA plan, the Battelle AMS Center QMP[(1)], and all associated methods and standard operating procedures. In this audit, the Battelle Quality Manager will review the reference sampling and analysis methods used, compare actual test procedures to those specified in this protocol, and review data acquisition and handling procedures.

At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to testing staff at the time of the audit and documented in a TSA report.

5.3.2 Performance Evaluation Audit

A PE audit shall be conducted to assess the quality of the measurements made in the verification test. This audit addresses only those measurements that factor into the data used for verification, i.e., the CEMs being verified and the vendors operating these CEMs are not the subject of the PE audit. This audit will be performed once during the verification test and must be performed by analyzing a standard or comparing to a reference that is independent of standards used during the testing. For most of the key measurements, this audit will be done by comparing data from the facility equipment to that from a second analyzer or monitor operated simultaneously. Comparisons will be made for temperature, pressure, and balance. In addition, the balance used to determine flue gas H_2O content by means of the reference method impinger samples will be checked with a calibrated set of weights different from those used to calibrate the balance for use. Table 2 summarizes the PE audits that will be done. These audits will be the responsibility of Battelle staff and will be carried out with the cooperation of host facility staff.

These PE audits will be carried out once during the period of operation at the host facility. Battelle will supply the equipment or standards needed to make the independent PE measurements. If agreement outside the indicated tolerance is found, the PE audit will be repeated. Further failure to achieve agreement will result in recalibrating the independent measurement device. Continued lack of agreement will result in all relevant data being flagged.

Table 2. Summary of PE Audits

Parameter	Audit Procedure	Expected Tolerance
Temperature	Compare to independent temperature measurement	±2% absolute temperature
Barometric Pressure	Compare to independent pressure measurement	±0.5 inch of H_2O
Flue Gas Differential Pressure	Compare to independent pressure measurement	±0.5 inch of H_2O
Mass (H_2O)	Check balance with calibrated weights	±1% or 0.5 g, whichever is larger
Ammonia (overall measurement)	Spike reference method trains	± 20% bias in spike recovery
Ammonia (ISE analysis)	Blind audit sample	± 10% of standard concentration
Ammonia (IC analysis)	Blind audit sample	± 10% of standard concentration

The PE audit shall include spiking reference method sampling trains with known amounts of ammonia and conducting sample analysis on the train without sampling the combustion gas. An NIST-traceable ammonium standard solution will be used for that purpose. During each week of sampling, three blank trains shall be spiked with a known amount of an ammonia standard solution, such that the ammonia concentration in the sample solution is approximately equal to the concentration expected from the collection of a 5 ft^3 sample of flue gas with 2 ppmv ammonia. The spiked trains shall be transported to the sampling location but shall not be used to collect a sample of flue gas. The trains shall then be disassembled, and the spiked samples shall be analyzed on-site by ISE, and the percent recovery will be calculated. Agreement of ammonia determined in sample analysis with that spiked into the sample train is expected to be within 20%. If the recovery of the field spikes is not >80% and <120%, no additional reference sampling will be conducted until the cause of the discrepancy is investigated and rectified if possible. Because reference sample analysis is performed on-site by ISE, PE audit results for the

overall ammonia measurement will be available during the test and will be used to improve reference method procedures, if necessary.

The performance of the ISE and the IC used to analyze the reference samples shall be audited by analyzing an ammonium standard that is independent of those used for the calibration. This sample will be provided as a blind audit sample, and the operator of the ISE and the IC should not be aware of the concentration of the sample. If agreement between the measured concentration and the standard concentration is not within ±10%, the cause of the discrepancy will be investigated and rectified if possible.

5.3.3 Data Quality Audit

Battelle's Quality Manager shall audit at least 10% of the verification data acquired in the verification test. The Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing audit will be checked.

5.3.4 Assessment Reports

Each assessment and audit will be documented in accordance with Section 3.3.4 of the QMP for the AMS Center.[1] Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Space for response to adverse findings or potential problems
- Possible recommendations for resolving problems
- Citation of any noteworthy practices that may be of use to others
- Confirmation that corrective actions have been implemented and are effective.

5.3.5 Corrective Action

The Battelle Quality Manager, during the course of any assessment or audit, shall identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator shall ensure that a response is provided for each adverse finding or potential problem and implement any necessary followup corrective action. The Battelle Quality Manager shall ensure that follow-up corrective action has been taken.

6 DATA ANALYSIS AND REPORTING

6.1 Data Acquisition

Data acquisition in the verification test includes recording the data from the CEMs undergoing testing, documenting sampling conditions and analytical results from the reference method, and recording operational data such as combustion source conditions, test temperatures, and the times of test activities.

Data storage for the commercial CEMs undergoing verification shall be the responsibility of the CEM vendors. Each CEM must have some form of data acquisition device, such as a digital display whose readings can be recorded manually, a printout of analyzer response, or an electronic data recorder that stores individual analyzer readings. The vendor shall be responsible for reporting the response of the CEM for the entire test period. The CEM data are to be provided to Battelle regularly and must include all individual readings of the CEM listed by time of day. Averaged results, e.g., ammonia data averaged over the period of a reference method sampling run, may also be provided, if available. If not provided, averaging will be performed by Battelle in data processing.

Other data shall be recorded in laboratory record books. These records will be reviewed by Battelle to identify and resolve any inconsistencies. All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, and dated by the person making the correction.

In all cases, strict confidentiality of data from each vendor's CEM, and strict separation of data from different CEMs, shall be maintained. Separate files (including manual records, printouts, and/or electronic data files) shall be kept for each CEM. At no time during verification testing will Battelle staff engage in any comparison in performance of the participating CEMs.

Table 3 summarizes the types of data to be recorded; how, how often, and by whom the recording is made; and the disposition or subsequent processing of the data. The general approach is to record all test information immediately and in a consistent format throughout all tests. Data recorded by the vendors is to be turned over to Battelle staff immediately upon completion of each test day. Identical file formats will be used to make quantitative evaluations of the data from all CEMs tested, to assure uniformity of data treatment. This process of data recording and compiling will be overseen by the Verification Test Coordinator.

6.2 Data Review

Records generated in the verification test shall be reviewed by a Battelle staff member within two weeks after the completion of the test, before these records are used to calculate, evaluate, or report verification results. These records may include laboratory record books; operating data from the combustion source, data from the CEMs, or reference method analytical results. This review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. The host facility, subcontractor and/or vendor staff will be consulted as needed to clarify any issues about the data records. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed.

Table 3. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[(a)]
Dates, times of test events	Battelle	Laboratory record books	Start/end of test, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Test parameters (temperature, analyte/interferant identities and concentrations, gas flows, etc.)	Battelle Host facility	Laboratory record books	When set or changed, or as needed to document stability.	Used to organize/check test results, manually incorporated in data spreadsheets as necessary.
NH_3 CEM readings	Vendor or designee	Data acquisition system (data logger, PC, laptop, etc.).	Continuously at specified acquisition rate throughout CEM operation.	Electronically transferred to spreadsheets
Reference method sampling data	Battelle Host facility	Laboratory record books or file data sheets as appropriate	At least at start/end of reference sample, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Reference method sample analysis, chain of custody, and results	Battelle Host facility	Laboratory record books, chain of custody forms, data sheets, or data acquisition system, as appropriate.	Throughout sample handling and analysis process	Transferred to spreadsheets

[(a)] All activities subsequent to data recording are carried out by Battelle.

6.3 Reporting

Separate verification reports shall be prepared for each CEM provided by one commercial vendor. The verification report will present the test data, as well as the results of the statistical evaluation of those data.

The verification reports will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. These sections will be common to each verification report resulting from this verification test. The results of the verification test will then be stated quantitatively, without comparison to any other CEM tested or comment on the acceptability of the CEM's performance. The preparation of draft verification reports, the review of reports by vendors and others, the revision of the reports, final approval, and the distribution of the reports will be conducted as stated in the Generic Verification Protocol for the Advanced Monitoring Systems Pilot.[5] Preparation, approval, and use of verification statements summarizing the results of this test will also be subject to the requirements of that same protocol.

7 HEALTH AND SAFETY

The verification test described in this protocol shall be performed at the host facility. All participants in this verification test will adhere to the health and safety requirements of the facility. Vendor staff will operate only their CEMs during the verification test. They are not responsible for, nor permitted to, operate the combustion source or perform any other verification activities identified in this protocol. Operating the CEMs themselves does not pose any known chemical, fire, mechanical, electrical, noise, or other potential hazard.

All visiting staff at the host facility will be given a site-specific safety briefing prior to the installation and operation of the CEMs. This briefing will include a description of emergency operating procedures (i.e., in case of fire, tornado, laboratory accident) and identification and location and operation of safety equipment (e.g., fire alarms, fire extinguishers, eye washes, exits).

8 REFERENCES

1. Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center, U.S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, Version 4.0 December 2002.

2. Procedure for the Collection and Analysis of Ammonia in Stationary Sources, Conditional Test Method 027, U.S. Environmental Protection Agency, Research Triangle Part, North Carolina, August 1997.

3. Standard Specification for Collection and Analysis of Ammonia Nitrogen in Flue Gas Using Wet Chemical Sampling and Specific Ion Analysis, Draft Standard, ASTM, West Conshohocken, Pennsylvania, October, 2000.

4. Field Test of Ammonia Collection/Analysis Method, Draft Report, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1995.

5. Generic Verification Protocol for the Advanced Monitoring Systems Pilot, Battelle, Columbus, Ohio, October 1998.