

# Battelle

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**Environmental Technology  
Verification Program**  
Advanced Monitoring  
Systems Center

Test/QA Plan for Verification  
of Cavity Ringdown Spectroscopy  
Systems for Ammonia Monitoring  
in Stack Gas

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# **TEST/QA PLAN**

**for**

## **Verification of Cavity Ringdown Spectroscopy Systems For Ammonia Monitoring in Stack Gas**

**Version 1.0**

**June 24, 2009**

**Prepared by**

**Battelle  
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**SECTION A**  
**PROJECT MANAGEMENT**

**A1    VENDOR APPROVAL PAGE**

ETV Advanced Monitoring Systems Center

Test/QA Plan for Verification of  
Cavity Ringdown Spectroscopy Systems  
For Ammonia Monitoring in Stack Gas

Version 1.0

June 24, 2009  
APPROVAL:

Name \_\_\_\_\_

Company \_\_\_\_\_

Date \_\_\_\_\_

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## **A4 VERIFICATION TEST ORGANIZATION**

The verification test described in this document will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil.

This verification test will be coordinated and directed by Battelle in cooperation with the EPA, with the support of the Instrumentation and Control (I&C) Center located at the Tennessee Valley Authority's (TVA) Kingston Fossil Plant. The performance of this test is being funded in part by the Electric Power Research Institute. A 90-day period of field testing will be conducted at the plant and will involve the evaluation of commercial cavity ringdown spectroscopy (CRDS) monitoring systems specifically for the measurement of ammonia in stack gas. I&C Center staff will provide on-site support during the verification test. A commercial stack-testing company will provide ammonia reference method sampling under subcontract to Battelle.

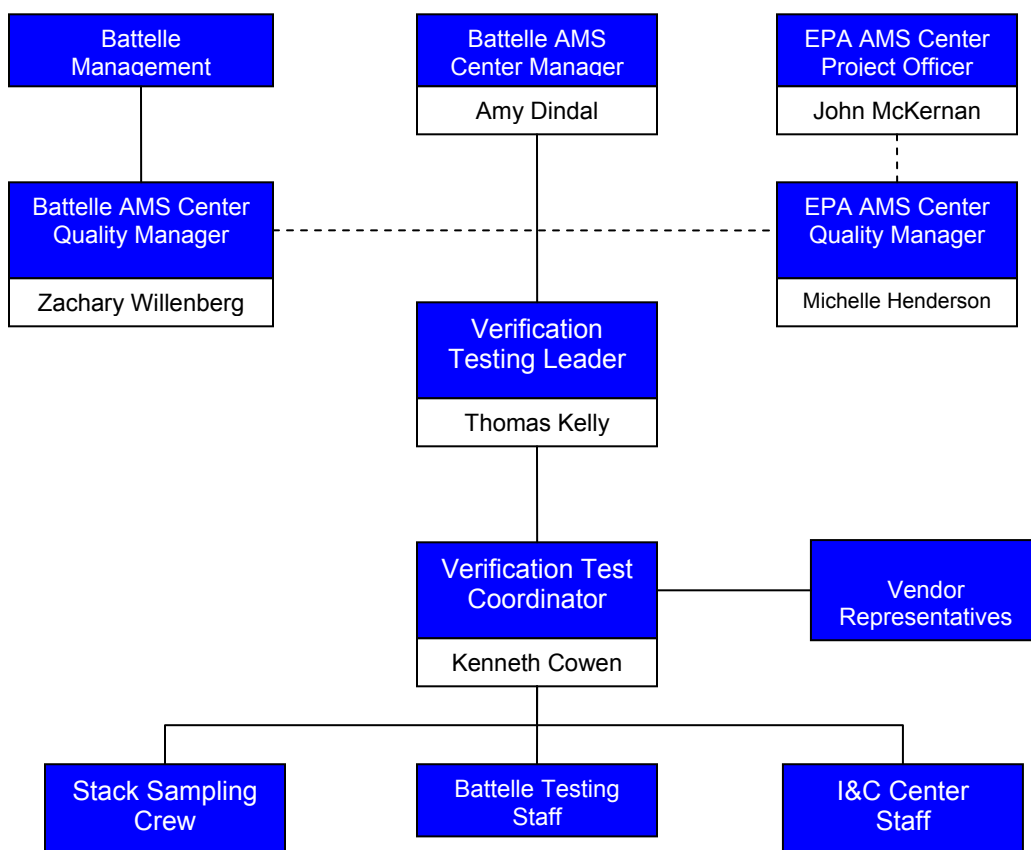
The vendors of the CRDS systems being tested will install, operate, and repair or maintain one of their systems during the verification test.

Quality assurance (QA) oversight will be provided by the Battelle AMS Center Quality Manager, and by the EPA AMS Center Quality Manager at her discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below.

### **A4.1 Battelle**

Dr. Kenneth Cowen is the AMS Center Verification Test Coordinator for this test. In this role, Dr. Cowen will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, he will:

- Assemble a team of qualified technical staff to conduct the verification test.
- Direct the team (Battelle, vendor, I&C Center staff, and subcontractor) in performing the verification test in accordance with this test/QA plan.



**Figure 1. Organizational Chart**

- Ensure that all quality procedures specified in the test/QA plan and in the AMS Center Quality Management Plan<sup>1</sup> (QMP) are followed.
- Prepare the draft and final test/QA plan, verification report(s), and verification statement(s).
- Revise the draft test/QA plan, verification report(s), and verification statement(s) in response to reviewers' comments.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Serve as the primary point of contact for vendor representatives and collaborators.

- Coordinate distribution of the final test/QA plan, verification report(s), and statement(s).
- Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.

Dr. Thomas Kelly is Battelle's Verification Testing Leader for the AMS Center. Dr. Kelly will:

- Support Dr. Cowen in preparing the test/QA plan and organizing the test.
- Review the draft and final test/QA plan.
- Review the draft verification report(s) and statement(s).
- Support Dr. Cowen in responding to any issues raised in assessment reports and audits.

Ms. Amy Dindal is Battelle's manager for the AMS Center. Ms. Dindal will:

- Review the draft and final test/QA plan.
- Review the draft and final verification report(s) and verification statement(s).
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- Ensure that confidentiality of sensitive vendor information is maintained.
- Maintain communication with EPA's AMS Center Project Officer and Quality Manager.
- Facilitate a stop work order if Battelle or EPA QA staff discover adverse findings that will compromise data quality or test results.

Battelle Field Testing Staff will oversee portions of the testing of the CRDS systems.

Specifically, Battelle staff will be on-site during the first and last week of the verification test, and will be in weekly communication with the I&C Center staff during the other portions of the verification testing, and with technology vendors as needed. The responsibilities of the field testing staff will be to:



- Perform the verification test as described in the test/QA plan.
- Communicate with the I&C Center testing staff on the planning, performance, and reporting of the reference sampling and analysis.
- Record qualitative observations about the maintenance and operation of the CRDS systems during testing.
- Perform on-site analysis of aliquots of the collected reference samples to provide preliminary indications of flue gas ammonia concentrations.
- Assure that the data from the CRDS systems are compiled, recorded, and transmitted to the Verification Test Coordinator on at least a weekly basis.
- Perform analysis of the collected data to carry out the statistical evaluations in Section B1.2.
- Provide input on test procedures, technology operation and maintenance, and field conditions for the draft verification reports.

Mr. Zachary Willenberg is Battelle's Quality Manager for the AMS Center. Mr. Willenberg will:

- Review the draft and final test/QA plan.
- Conduct a technical systems audit at least once near the beginning of the verification test, or designate other QA staff to conduct the audit.
- Audit at least 10% of the verification data.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.
- Notify Battelle's AMS Center Manager to issue a stop work order if audits indicate that data quality is being compromised.
- Provide a summary of the QA/QC activities and results for the verification reports.
- Review the draft and final verification report(s) and verification statement(s).
- Assume overall responsibility for documenting adherence to the test/QA plan.

#### **A4.2 Vendors**

The responsibilities of the CRDS system vendors are as follows:

- Review and provide comments on the draft test/QA plan.
- Approve the final test/QA plan prior to test initiation.
- Provide a complete monitoring system for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their monitoring system for the duration of the verification test.
- Supply a representative to install, operate, and maintain their technologies during the verification test.
- Provide the data from the monitoring system to the Battelle field testing staff within one week of collection.
- Provide training to site operator(s) and others associated with supervising and/or maintaining system operation including during the verification testing period.
- Provide written instructions for routine operation of their technologies, including a daily checklist of diagnostic and/or maintenance activities.
- Review and provide comments on the draft verification report and statement for their monitoring system.

#### **A4.3 EPA**

EPA's responsibilities are based on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan"<sup>2</sup> (ETV QMP). The roles of specific EPA testing staff are as follows:

Ms. Michelle Henderson is EPA's AMS Center Quality Manager. Ms. Henderson will:

- Review the draft test/QA plan.
- Perform at her option one external technical systems audit during the verification test.
- Notify the EPA AMS Center Manager of the need for a stop work order if the external audit indicates that data quality is being compromised.
- Prepare and distribute an assessment report summarizing results of the external audit.
- Review the draft verification report(s) and statement(s).

Dr. John McKernan is EPA's Project Officer for the AMS Center. Dr. McKernan will:

- Review the draft test/QA plan.
- Approve the final test/QA plan.
- Review and approve deviations to the approved final test/QA plan.
- Appoint a delegate to review and approve deviations to the approved final test/QA plan in his absence, so that testing progress will not be delayed.
- Review the draft verification report(s) and statement(s).
- Oversee the EPA review process for the verification report(s) and statement(s).
- Coordinate the submission of verification report(s) and statement(s) for final EPA approval.

#### **A4.4 I&C Center**

I&C Center personnel are responsible for providing on-site support during testing, and will:

- Ensure that Battelle testing staff, vendors, and subcontractors have appropriate access to the test site.
- Ensure suitable space and electrical power to perform the necessary testing activities at the test site.
- 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.

Mr. Rabon Johnson is the I&C Center Technical Lead for this verification test. Mr. Johnson will:

- Review the draft test/QA plan.

- Be the primary I&C contact for Battelle's Verification Test Coordinator.
- Ensure that designated I&C staff are available for the verification test.
- Coordinate distribution of the test/QA plan to I&C staff.
- Ensure that I&C Center staff conduct test procedures according to the test/QA plan.
- Review and approve all data and records related to I&C operation.

#### **A4.5. Reference Method Stack Sampling Subcontractors**

Reference method sampling for ammonia will be conducted by one or more subcontractors to Battelle. Analysis of the collected samples will be conducted by Battelle or one or more subcontractors to Battelle. Such subcontractors may include organizations responsible for operation of the host facility. The responsibilities of such subcontractors are:

- Assemble trained technical staff to conduct reference method sampling for the verification test.
- Perform the reference method sampling in adherence to the quality requirements in this test/QA plan and the requirements of the EPA Conditional Test Method – (CTM-027) Procedure for Collection and Analysis of Ammonia in Stationary Sources.<sup>3</sup>
- 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 Dr. Cowen in responding to any issues raised in assessment reports and audits related to reference method sampling and analysis.

## **A5 BACKGROUND**

### **A5.1 Technology Need**

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Among the

technology categories recommended for testing are CRDS systems. In particular, the use of CRDS systems for the measurement of ammonia in flue gas at a coal fired power plant was identified as an area of interest for technology verification.

Selective catalytic reduction (SCR) technologies are commonly used on coal-fired power plants to reduce nitrogen oxides ( $\text{NO}_x$ ) emissions through a chemical reaction with ammonia ( $\text{NH}_3$ ). These technologies require the introduction of large quantities of  $\text{NH}_3$  to reduce the  $\text{NO}_x$  emissions in a stoichiometric fashion. However, frequently a small amount of excess  $\text{NH}_3$  is introduced which subsequently is emitted in the flue gas. This excess ammonia, called slip, is frequently difficult to measure because of its relatively low concentration. CRDS systems have been proposed as a potentially viable means of monitoring ammonia slip because of the highly sensitive nature of the CRDS technique.

#### **A.5.2 Technology Description**

CRDS systems are spectrometers that enhance sensitivity to target analytes through the use of multi-pass optical cells that vastly increase the effective pathlength of the absorbing radiation over typical absorption techniques.<sup>4,5</sup> In CRDS, the beam from a laser enters a cavity defined by two or more highly reflective mirrors. As the light in the cavity reflects back and forth between the mirrors, a small portion of the light exits the cavity since the mirrors are not completely reflective. The amount of light exiting the cavity is directly proportional to the intensity in the cavity. Thus, by monitoring the intensity of light exiting the cavity, the intensity of the light in the chamber can be deduced.

In the absence of an absorbing species in the cavity, once the laser is turned off the light intensity inside the cavity will steadily leak out and decay (or “ring down”) to zero in an exponential fashion. If a gas species that absorbs the laser light is introduced into the cavity, a portion of the light will be absorbed and the ring-down time will shorten compared to that in a cavity without any additional absorption due to a targeted gas species. Measurement of the respective ring-down times thus allows for an accurate determination of the concentration of the absorbing gas in the cavity.

## **A6 VERIFICATION TEST DESCRIPTION AND SCHEDULE**

The purpose of this verification test is to generate performance data on CRDS monitoring technologies with a particular focus on monitoring of ammonia under normal operating conditions in a full-scale coal-fired power plant utilizing an SCR NO<sub>x</sub> control technology. The data generated from this verification test are intended to provide organizations and users interested in installing and operating these systems with information on their potential reliability.

### **A6.1 Verification Test Description**

The test will be conducted over a period of approximately 90 days and will involve the continuous operation of CRDS monitoring systems at an operational coal-fired power plant. During testing, the CRDS systems will continuously monitor ammonia slip concentration in the flue gas downstream of the SCR. If feasible within plant operating requirements, the host facility will intentionally introduce upset conditions to change the ammonia slip at various times during the verification test.

The CRDS systems will be evaluated on the following performance parameters:

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

Accuracy will be assessed for the CRDS systems being verified by determining the degree of agreement with known concentrations of ammonia compressed gas standards. During the first and last full weeks of testing, duplicate reference method samples will be collected to assess the comparability of the CRDS measurements with the standard reference method results. Precision will be assessed in terms of the repeatability of the ammonia measurements under stable test conditions using ammonia compressed gas standards. Calibration drift, zero drift, linearity, and

response time will also be assessed using commercial compressed gas standards of ammonia and zero air. Data completeness will be determined from a review of the valid data collected during the verification testing period. Operational performance parameters such as maintenance requirements, ease of use, and costs will be determined from observations by the Battelle field testing staff and from on-site I&C Center staff. This test is not intended to simulate long-term performance of these technologies at a monitoring site.

Subsequent to the verification test, a verification report will be drafted for the monitoring system tested. This report will be reviewed by the vendor and by peer reviewers, revised, and submitted to EPA for final approval. In performing the verification test, Battelle will follow the technical and QA procedures specified in this test/QA plan and will comply with the data quality requirements in the AMS Center QMP.<sup>1</sup>

## **A6.2 Proposed Testing Schedule**

Table 1 shows the planned schedule of testing and data analysis/reporting activities to be conducted in this verification. The verification process is planned to begin in June 2009 and be completed in November 2009. The period of operation of the monitoring systems at the Kingston Fossil Plant will be approximately 90 days, with routine operation expected to begin on June 29 and continue until September 17, 2009, or until all testing activities are completed. During testing, duplicate reference samples will be collected thrice each day during two separate five day periods. One of these five day periods will occur within the first three weeks of the verification test (i.e., June 29-July 17,) and the second will occur within the last three weeks of the verification test (i.e., August 31-September 17). The actual reference method sampling periods will be determined based on the availability of the stack testing crew. Additionally, dynamic spiking test runs will be conducted within the first three weeks and the last three weeks of the verification test period to challenge the CRDS systems with ammonia compressed gas standards in a repeatable fashion to assess system accuracy and precision. Also, zero and calibration drift measurements will be made by means of ammonia standard challenges conducted weekly throughout the verification test.

**Table 1. Planned Verification Test Schedule**

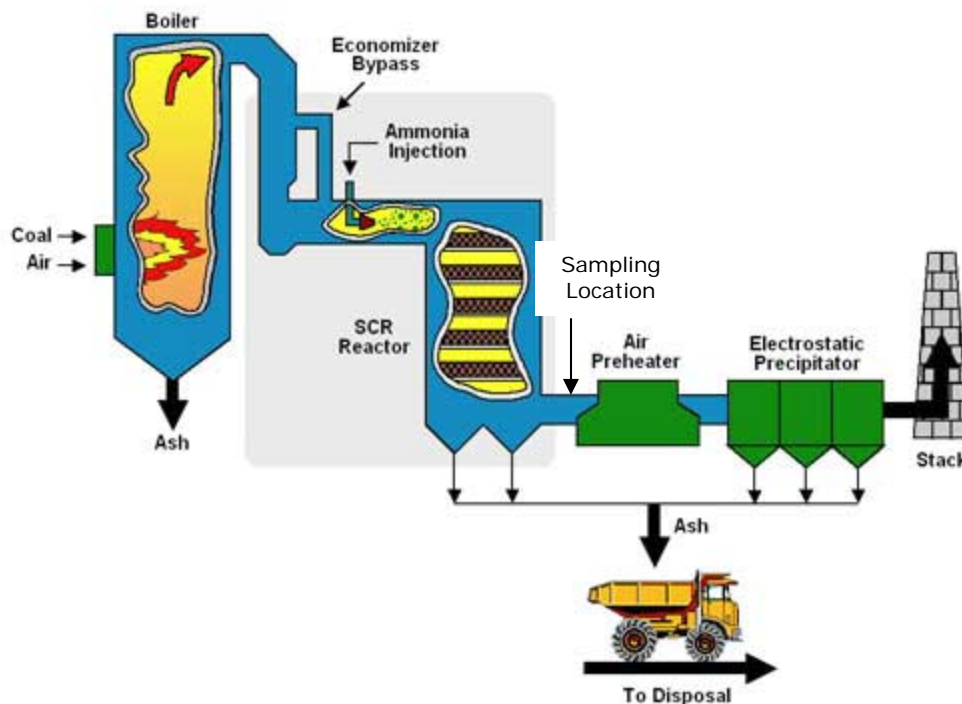
Date(s)	Testing Activities	Data Analysis and Reporting
June 25-26	Installation/shakedown	Prepare report template Review and summarize field testing staff observations Compile data from CRDS systems Compile reference method results Begin draft report(s) Perform data analysis
June 29- September 17	Verification testing period	
June 29-July 17	Dynamic spiking test runs	
June 29-July 17	Reference sampling period	
June 29-September 17	Weekly zero/calibration checks	Complete draft report(s) Begin draft report(s) Perform data analysis
August 31- September 17	Reference sampling period	
September 14-17	Dynamic spiking test runs	
September 18	Remove CRDS systems from test site	
October 16		Complete draft report(s)
November 13		Complete peer review of draft report(s)
November 30		Revise draft report(s) Submit final report(s) for EPA approval

### A6.3 Test Facility

TVA's Kingston Fossil Plant is a 1.7 gigawatt (GW) coal fired power plant located on Watts Bar Reservoir on the Tennessee River near Kingston, Tennessee. The plant has nine generating units: units 1–4, rated at 175 megawatt (MW) each, and units 5–9, rated at 200 MW each. Each of the nine power generating units operates in steady state and is equipped with a cold-side SCR system to reduce nitrogen oxide emissions. Figure 2 shows a schematic illustration of a typical SCR installation at a coal fired power plant. The CRDS systems will be installed on a section of duct work downstream of the SCR and upstream of the air preheater (APH) and electrostatic precipitator (ESP), which are separated by approximately 75 meters at the Kingston Fossil Plant. Collocated sampling ports will be used for reference method sampling. In general, there are multiple ports within several feet of the probe providing sample to the CRDS systems. Traverse sampling will be conducted once to assess stratification in the duct. However, the probe used for providing sample gas to the CRDS systems is fixed and will not vary. Reference method sampling will be performed at the same depth in the duct as the CRDS sampling. A schematic of the actual set up will be included in the verification report.

The I&C Center is a 4,500 ft<sup>2</sup> facility adjacent to the Kingston Fossil Plant in Harriman, TN. I&C Center staff will provide on-site support during the verification test.





**Figure 2. Schematic illustration of typical SCR installation at a coal fired power plant.**  
(Source <http://www.netl.doe.gov/technologies/coalpower/cctc/index.html>).

#### **A7 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA**

The objective of this verification test is to evaluate the performance of the CRDS systems under realistic operating conditions at an operational coal fired power plant. This evaluation will in part assess the capabilities of the CRDS systems for determining the ammonia concentration in the flue gas through comparisons to collocated reference samples collected during the verification test period. Additionally, this verification test will include instrument challenges using ammonia gas standards to assess performance under controlled and repeatable test conditions. The verification test will also rely upon operator observations to assess other performance characteristics of the CRDS systems being tested including data completeness, ease of use, and maintenance requirements.

To ensure that this verification test provides suitable data for a robust evaluation of performance, a variety of data quality objectives (DQOs) have been established for this test. The DQOs indicate the minimum quality of data required to meet the objectives of the verification test and are different than the QA/QC requirements of the reference method. The DQOs for this verification test were established to assess the performance of the CRDS systems relative to

reference measurements and challenges with compressed gas standards. In order to provide a suitable benchmark for comparison, the reference measurements and standard gas challenges must meet the DQOs. The DQOs for this verification test include specific objectives for reference method measurements, dynamic spiking challenges, zero/calibration drift measurements, and data completeness. The DQOs are quantitatively defined in Table 2 in terms of specific data quality indicators (DQIs) and their acceptance criteria.

**Table 2. DQIs and Criteria for Critical Measurements for Reference Methods.**

DQI	Method of Assessment	Frequency	Acceptance Criteria	Corrective Action
Reference method sampling flow rate accuracy	Comparison to independent flow transfer standard	At least once for each reference method meter box	$\pm 10\%$ of target flow rate	Inspect meter box and repeat comparison; replace meter box as needed.
Reference method precision	Comparison of duplicate reference method samples	Each reference method sampling period	$\pm 35\%$ agreement	Investigate discrepancy if possible. Reanalyze samples. Discard if not resolved.
Dilution accuracy	In-probe introduction of challenge gas with CEM measurement	At least once during testing	$\pm 10\%$ of calculated concentration	Investigate discrepancy if possible. Repeat measurement and recalibrate.
Reference method representativeness	Duct traverse measurements	At least once during testing	$\pm 35\%$	Investigate discrepancy if possible. Repeat if possible.
Reference method data completeness	Calculation of percent valid data	After data validation	$\geq 80\%$ valid paired samples	Conduct additional reference method sampling if possible
Dynamic spiking data completeness	Calculation of percent valid data	After data validation	$\geq 90\%$ valid results	Conduct additional dynamic spiking testing if possible
Zero/calibration check data completeness	Calculation of percent valid data	After data validation	$\geq 90\%$ valid results	Conduct additional zero/cal. check testing if possible
Dynamic spiking gas standard flow rate accuracy	Comparison to independent flow transfer standard	Each dynamic spiking run	$\pm 10\%$	Investigate discrepancy. Inspect meter and replace meter box as needed.

The quality of the reference method measurements will be assured by adherence to these DQI criteria and the requirements of the reference methods, including the calibration and QA/QC requirements of those methods, which are discussed in detail in Sections B2-B7 of this test/QA plan. Calibration standards and QC samples must meet National Institute of Standards and Technology (NIST) traceability, when available. The quality of the reference method measurements will be monitored by inclusion of blank samples and performance evaluation (PE)

samples as appropriate. Section C1.1 presents a description of the PE audit samples/measurements to be performed and the acceptance criteria for those measurements.

Additionally, the verification test relies in part on observations of the Battelle field testing staff for assessment of the performance of the CRDS systems being tested. The requirements for these observations are described in the discussion of documentation requirements and data review, verification, and validation requirements for this verification test.

The Battelle Quality Manager or his designee will perform a technical systems audit (TSA) at least once during this verification test to augment these QA/QC requirements. This TSA will be performed within the first week of the verification test. The EPA Quality Manager also may conduct an independent TSA, at her discretion.

#### **A8 SPECIAL TRAINING/CERTIFICATION**

Documentation of training related to technology testing, field testing, data analysis, and reporting is maintained for all Battelle technical staff in training files at their respective locations. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. Battelle technical staff supporting this verification test have a minimum of a bachelor's degree in science/engineering.

The verification test described in this test/QA plan will be performed at the I&C center facility. All participants in this verification test (i.e., Battelle, EPA, subcontractor, and vendor staff) will adhere to the health and safety requirements of the facility. Vendor staff will operate only their CRDS systems during parts of the verification test. They are not responsible for, nor permitted to, operate the combustion source, or perform any other verification activities identified in this test/QA plan.

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

## **A9 DOCUMENTATION AND RECORDS**

The records for this verification test include the test/QA plan, chain-of-custody forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), and the final verification report(s). All of these records will be maintained in the Verification Test Coordinator's office during the test and may be transferred to permanent storage at Battelle's Records Management Office (RMO) at the conclusion of the verification test. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's RMO. EPA will be notified before disposal of any files. For each week of ammonia reference method sampling, the documentation and results of the reference method measurements made by the subcontractor staff will be submitted to Battelle within 10 days after completion of each week of reference method sampling. Section B10 further details the data recording practices and responsibilities.

## **SECTION B**

### **MEASUREMENT AND DATA ACQUISITION**

#### **B1 EXPERIMENTAL DESIGN**

The verification test described in this test/QA plan will specifically address verification of CRDS systems for ammonia monitoring in flue gas by evaluating the following performance factors:

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

The verification test will be conducted over a period of approximately 90 days. A window of approximately one week prior to testing will be available for installing the CRDS systems at the facility, and conducting a shakedown run of the CRDS systems before the verification test begins. The installation/shakedown period is scheduled to begin June 18, 2009. The 90 days of testing will follow immediately after the setup/shakedown period.

The verification testing will involve continuous monitoring of ammonia in the flue gas by the CRDS systems over the entire 90 day test period, with reference method sampling conducted on each day during two separate five day periods. One of these five day periods will occur within the first three weeks of the verification test (i.e., June 22-July 12,) and the second will occur within the last three weeks of the verification test (i.e., August 31-September 17). The actual reference method sampling periods will be determined based on the availability of the stack testing crew. On each day of reference method sampling, duplicate reference method samples will be collected over each of three different sampling periods for a total of 30 pairs of duplicate reference samples in this test. The reference method sampling will be performed based on the

methods described in EPA CTM-027 for time integrated sampling and analysis of ammonia from stationary sources with the following modifications:

- Sampling will not be conducted isokinetically since only gaseous ammonia is measured by the CRDS systems.
- Sampling will not be conducted with a nozzle since isokinetic sampling is not necessary.
- Since sampling will not be performed isokinetically, the sampling flow rate and duration will be determined in a manner that is sufficient to allow the collection of a sample volume that results in an aqueous  $\text{NH}_4^+$  concentration that falls between 10-50% of the calibration range of the ion chromatography (IC) analysis method (e.g., between 1-5  $\mu\text{g/mL}$  solution), assuming an ammonia concentration of 2 ppm in the flue gas.
- Samples collected during the verification will be split into two aliquots with one aliquot submitted for analysis by IC based on the procedures in CTM-027<sup>3</sup>, and the other analyzed immediately in the field by an ion selective electrode (ISE) based on the procedures in South Coast Air Quality Management District, Method 207.1: Determination of Ammonia Emissions from Stationary Sources.<sup>6</sup>

The average CRDS readings during these periods will be compared with the ammonia concentrations determined from the reference method samples. During each day of reference method sampling and at least once per week during the other periods of testing, a zero and span check will be conducted on the CRDS systems by challenging each with zero air and an ammonia gas standard of known concentration at approximately 80% of full scale for the CRDS system. Thus, a total of 21 zero/span checks will be used to assess drift of the CRDS systems during the test period. These data will also be used to assess response time of the CRDS systems.

During the first three and last three weeks of testing, each of the CRDS systems will be challenged independently with a series of runs involving dynamic spiking of compressed ammonia gas standards into the CRDS intake gas flow, with 12 test runs at each of three different nominal concentrations and 36 test runs at the background concentration. The results of these runs will be used to assess accuracy and precision of the CRDS systems as well as the linearity in instrument response of the CRDS systems.

Table 3 presents a summary of the tests to be performed.

**Table 3. Summary of Tests and Testing Frequency**

Performance Parameter	Objective	Comparison Based On	Testing Frequency	Number of Data Points
Accuracy	Determine degree of quantitative agreement with compressed gas standard	Dynamic spiking with NH <sub>3</sub> gas standards	12 runs at each of three nominal concentrations during the first and last week of testing	72
Comparability	Determine degree of quantitative agreement with reference method	Reference method results	Three runs per day during two separate 5-day periods (10 days total)	30 duplicate pairs
Linearity	Determine linearity of response over a range of NH <sub>3</sub> concentrations	Dynamic spiking with gas standards	12 runs at each of three nominal concentrations during both the first and last full weeks of testing	72 above background and 72 background
Precision	Determine repeatability of successive measurements at fixed NH <sub>3</sub> levels	Repetitive measurements under constant facility conditions measured	Each reference method sampling run, and each dynamic spiking run	102
Cal/Zero Drift	Determine stability of zero gas and span gas response over successive days	Zero gas and NH <sub>3</sub> gas standard	Each day during reference sampling and once per week during other testing periods	21
Response Time	Determine rise and fall time	Recording successive readings at start and end of sampling NH <sub>3</sub> gas standard	Once during each day of dynamic spiking testing	2

Throughout the verification test, each CRDS system undergoing testing will be operated by the CRDS vendor's own staff or by on-site I&C Center staff trained by the vendor. However, the intent of the testing is for the CRDS systems to operate continuously in a manner simulating operation at a combustion 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 CRDS systems 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 CRDS system data required for verification.

### **B1.1 Test Procedures**

The CRDS systems undergoing verification will be installed on a section of duct work downstream of the SCR and upstream of the APH and ESP. The ports for the reference method sampling will be located on the same duct with the CRDS systems and as close as possible to the sampling locations of the CRDS systems. The sampling ports will be assigned so that no CRDS system is affected by the operation of any other CRDS system or by the reference method sampling. The CRDS systems will 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 weeks when reference method testing is conducted, the CRDS systems undergoing testing will be supplied (one at a time) with zero gas and then with a commercial compressed gas standard containing ammonia. The order in which the CRDS systems are challenged in this way will be varied from day to day.

#### ***B1.1.1 Reference Method Sampling***

During verification testing, reference sampling will be conducted simultaneously with two trains collocated with the CRDS systems being tested. Thus each of the three reference sampling periods during a test day will provide two reference ammonia samples for comparison to the CRDS data. Reference method sampling will be conducted based on the procedures in CTM-027, with the modifications described above. The sampling duration for each run is expected to be typically between 30 and 60 minutes, although actual times will be based on the actual sampling flow rate and observed flue gas NH<sub>3</sub> levels.

Unique sample identification numbers will be implemented so that final data used for verification can be traced back through the analytical process to the original sample. Field blank samples will also 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 will



be transported to the sampling location. Care will be taken that the blank train is selected at random from the prepared trains, so that different trains are used as the blank on different days.

Results of the individual reference method measurements will be normalized to 7% O<sub>2</sub>. It is expected from previous results that the precision of duplicate reference method results will be within about 35 percent relative percent difference (RPD), determined as

$$RPD = \frac{R_1 - R_2}{(R_1 + R_2)/2} \times 100$$

where  $R_1$  and  $R_2$  are the reference method results for the duplicate trains.

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  $\pm 35\%$  throughout each week of testing. As a result, the entire set of reference method results, not merely those from a single test day, will be considered in screening for reference data quality. The reference method results will be reviewed before verification comparisons are made, to identify individual 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 co-located sampling trains
- Consistency of results with previous and later results at the respective sampling location

The ammonia concentration values and the associated RPD values for each test run will be plotted as a function of test number to graphically illustrate any trends in ammonia concentrations and identify potential outliers in the RPD values. Reference method pairs that exhibit an RPD that exceeds 35% will be flagged, and effort will be made to find an assignable cause for the divergent result. Reference method results which are flagged as outliers will be reported, but will not be used for verification unless appropriately documented. 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 methods.

### ***B1.1.2 Dynamic Spiking***

During the first three weeks and last three weeks of testing, each of the CRDS systems will be challenged with a series of dynamic spiking runs. The dynamic spiking will be conducted by injecting ammonia gas into the probe tip upstream of the particulate filter such that the ammonia spike passes through as much of the sampling system as possible. The ammonia gas standard will be mixed with the flue gas at a ratio of  $\leq 1$  part spike gas to 9 parts flue gas. The flow rate of the compressed gas and the dilution ratio of the spike gas will be used to calculate the expected increase in ammonia concentration introduced during the spiking. An Environics Model 6100 dilution system will be used to deliver the appropriate spike gas concentration to CRDS system.

During these runs the ammonia concentrations will be increased by approximately 2, 5, and 8 ppmv above the native flue gas concentration. At each spike concentration, a series of CRDS challenge runs will be conducted including 12 spiked and 12 unspiked sample measurements. These measurements will be performed by sampling pairs of spiked samples, followed by sampling pairs of unspiked samples. Prior to measurement, each CRDS will be readied by purging the gas cell with at least 10 volumes of flue gas spiked with zero air. After this purging is completed, a standard ammonia gas mixture will be introduced, at a measured flow rate, to the sampling probe. The CRDS readings of the spiked sample will be recorded after at least 10 volumes of gas have passed through the CRDS gas cell. A second such spiked sample will be measured after at least five volumes of gas have passed through the CRDS gas cell after the measurement of the first spiked sample. After the second spiked sample is measured, a pair of unspiked samples will 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 will be conducted a total of six times at each of the spike concentrations to obtain 12 spiked and 12 unspiked samples at each concentration. The procedures will be once each during the first three weeks and last three weeks of the verification test (June 29 - July 17 and August 31- September 17).

### ***B1.1.3 Zero/Calibration Checks***

During each day of reference method sampling and at least once during each other week of verification testing the CRDS systems being evaluated will be independently supplied with zero

air and a compressed gas standard to assess zero and calibration drift of the systems. The same compressed gas standard will be used in all such checks, to assess drift in CRDS response.

## **B1.2 Statistical Evaluation**

Prior to any statistical evaluations, all results from the reference method sampling and the CRDS systems being evaluated will be normalized to 7% O<sub>2</sub> using the results from the facility CEMs operating during the verification test.

### **B1.2.1 Accuracy**

The relative accuracy (RA) of the CRDS systems will be assessed from the dynamic spiking results using Equation 1:

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

where  $d$  refers to the difference between the calculated ammonia concentration from the dynamic spiking and the average of the CRDS 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  $t_{n-1}^{\alpha}$  is the t value for the  $100(1 - \alpha)^{\text{th}}$  percentile of the distribution with  $n-1$  degrees of freedom. The relative accuracy will be determined for an  $\alpha$  value of 0.025 (i.e., 97.5 percent confidence level, one-tailed). The RA calculated in this way

can be interpreted as an upper confidence bound for the relative bias of the analyzer, i.e.,  $\frac{|\bar{d}|}{\bar{x}}$ ,

where the superscript bar indicates the average value of the differences or of the reference values. Relative accuracy will be calculated separately at each of the spiking levels, and separately for each CRDS system undergoing verification.

### **B1.2.2 Comparability**

Comparability between the CRDS results and the Method 207.1 reference method results will be assessed using Equation 1, but with  $d$  representing the difference between the average of paired reference method results and the average of the CRDS results from the period during which the paired reference method samples were collected, and  $x$  corresponding to the average of the

paired reference method results. Comparability will be calculated using all reference method sample results (assuming all reference method samples can be treated as independent results), and separately for each CRDS system undergoing verification.

#### ***B1.2.3 Precision***

Precision will be calculated in terms of the percent relative standard deviation (RSD) of the CRDS measurements made during the dynamic spiking test runs and reference method sampling periods. During each such run, all the readings from each CRDS system undergoing testing will be recorded, and the mean will be calculated. The precision will be calculated as the standard deviation of the mean values divided by the mean. Precision will be calculated for each dynamic spiking target concentration level. Precision in dynamic spiking response will be reported separately from precision in flue gas monitoring.

#### ***B1.2.4 Linearity***

Linearity will be assessed by a linear regression analysis of the dynamic spiking data using the calculated ammonia concentrations as the independent variable and the CRDS results as the dependent variable. The “known” ammonia concentrations will be subject to uncertainty from variable flue gas ammonia background concentrations. The results of the dynamic spiking test will be plotted and linearity will be expressed in terms of slope, intercept, and coefficient of determination ( $r^2$ ).

#### ***B1.2.5 Zero/Calibration Drift***

Calibration and zero drift will be reported in terms of the mean, relative standard deviation, and range (maximum and minimum) of the readings obtained from the CRDS in the routine weekly sampling of the same ammonia standard gas, and of zero gas. These results, along with the range of the data, will indicate the week-to-week variation in zero and standard readings.

#### ***B1.2.6 Response Time***

Response time will be assessed in terms of both the rise and fall times of each CRDS when sampling the ammonia gas standard. Rise time (i.e., 0% - 95% response time) will be determined by recording all CRDS readings as the gas supplied to the CRDS 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 CRDS readings as the gas supplied is switched from the ammonia standard back

to zero gas. For CRDS systems which provide periodic rather than continuous readings, determination of rise and fall times may involve interpolation between readings.

Rise and fall times will each be determined once during dynamic spiking testing performed in each of the first and last weeks of testing for each CRDS. Rise and fall times will be reported in units of seconds.

#### ***B1.2.7 Data Completeness***

Data completeness will be assessed based on the overall data return achieved by each CRDS system during the testing period. For each of the CRDS systems, this calculation will use the total number of apparently valid data points reported by the monitoring systems divided by the total number of data points potential available in the entire field period. The causes of any incompleteness of data return will be established from operator observations or vendor records, and noted in the discussion of data completeness results.

#### ***B1.2.8 Operational Factors***

Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, etc., will be evaluated based on observations recorded by Battelle and I&C Center staff, and explained by the vendor as needed. Battelle or I&C Center staff will be at the Kingston plant whenever the vendor is present and will record all activities performed on the monitoring systems. A laboratory record book will be maintained at the test site, and will be used to enter daily observations on these factors. Examples of information to be recorded in the record books include the daily status of diagnostic indicators for the CRDS systems; use or replacement of any consumables; the effort or cost associated with maintenance or repair; vendor effort (e.g., time on site) for repair or maintenance; the duration and causes of any down time or data acquisition failure; and observations about ease of use of the CRDS systems. These observations will be summarized to aid in describing CRDS system performance in the verification report.

### **B1.3 Reporting**

The statistical comparisons described above will be conducted separately for each CRDS system being tested, and information on the operational performance will be compiled and reported. A

verification report will be prepared for each CRDS system tested, that presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the monitoring systems will be recorded by Battelle testing staff at the time of observation during the field test, and summarized in the verification report. For example, descriptions of the data acquisition procedures, use of vendor-supplied proprietary software, consumables used, repairs and maintenance needed, and the nature of any problems will be presented in the report. The verification report will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. The results of the verification test regarding CRDS system performance will be stated quantitatively. Each draft verification report will be subjected to review by the vendor, EPA, and other peer reviewers. The resulting review comments will be addressed in a subsequent revision of the report, and the peer review comments and responses will be tabulated to document the peer review process and submitted to EPA. The reporting and review process will be conducted according to the requirements of the ETV/AMS Center QMP.<sup>1</sup>

## **B2 SAMPLING METHOD REQUIREMENTS**

Reference method sampling will be conducted based on the procedures described in EPA CTM-027,<sup>3</sup> with the exception of the modifications described in Section B1 of this test/QA plan. This method uses an EPA Method 17<sup>7</sup> sampling train that consists of a borosilicate or quartz probe liner, borosilicate or quartz nozzle, Pitot tube, differential pressure gauge, in-stack filter holder and filter, ice-cooled Greenberg-Smith impingers for sample collection, and metering system. For this verification test, isokinetic sampling will not be conducted, so no nozzle is necessary. The sampling will be conducted at a selected sampling rate until an appropriate volume has been collected that is sufficient to provide samples with  $\text{NH}_4^+$  concentrations in solution of between 1-5  $\mu\text{g/mL}$ , based on an assumed flue gas concentration of 2 ppmv  $\text{NH}_3$ . The sampling rate and or sampling time may be adjusted if on-site analysis of previous reference method samples indicates adjustments should be made.

## **B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS**

Samples will be recovered from the reference method trains within two hours of sample collection according to the procedures described in Section 4.1 of CTM-027. Each of the

reference samples will be split into two aliquots, with one aliquot preserved as described in Section 4.1 of CTM-027 and the other aliquot analyzed on-site by the SCAQMD Method 207.1 using an ISE. The analyses performed by ISE are meant to serve as an on-site indication of the reference method sampling results and are not anticipated to be used for verification purposes. The on-site analysis will be conducted within two hours of sample recovery by Battelle, using available on-site facilities. The front and back impingers will be analyzed separately on-site by ISE. Samples will be warmed as needed to within  $\pm 2^{\circ}\text{C}$  of the temperature of the standards used for calibration of the ISE. Although filter samples will be collected, they will not be analyzed for this verification test.

The aliquots to be analyzed by IC according to CTM-027 will be stored and transported to the analytical laboratory under refrigerated conditions at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until analysis. Prior to analysis, the samples will be allowed to warm slowly to room temperature, and will be analyzed within 4 hours of removal from the refrigerated conditions.

#### **B4 ANALYTICAL METHOD REQUIREMENTS**

The samples analyzed on-site will be analyzed using a calibrated ISE as described in the SCAQMD Method 207.1. The ISE will be calibrated using at least four  $\text{NH}_4^{+}$  standard solutions bracketing the concentration range of interest (e.g., 0.1-10  $\mu\text{g/mL}$ ). The samples and the standard solutions will be analyzed at the same temperature, preferably about  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

The samples analyzed by IC will be analyzed according to the procedures described in CTM-027. Calibration of the IC will be performed according to the procedures in Section 4.2 of CTM-027 and include six standard solutions that bracket the concentration range of interest (e.g., 0.1-10  $\mu\text{g/mL}$ ).

#### **B5 QUALITY CONTROL REQUIREMENTS**

Table 4 summarizes the QC requirements of the reference method sampling and analysis, including frequency of the QC activities, the acceptance criteria, and corrective actions. QC requirements for the ISE analysis have also been included although it is not expected that the ISE analysis will be used for any statistical comparisons to the CRDS systems being tested.

**Table 4. Quality Control Requirements for Reference Method Sampling and Analysis**

QC Activity	Frequency	Acceptance Criterion	Corrective Action
Field blank train	1 per day of reference method sampling	< 10% of expected ammonia concentration	Clean sampling train components; obtain new solvents/solutions
Pre-test leak check	Each sampling run	< 4% of average flow rate	Check sampling train, reseed connections, and replace components, as necessary.
Post-test leak check	Each sampling run	< 4% of average flow rate	Inspect sampling train, Flag data
Meter box calibration	Each sampling run	< 5% difference in DGM calibration factor	Check sampling train, reseed connections, and replace components as necessary. Recalibrate
ISE calibration	Each day of analysis	$-54 \geq \text{Slope} \geq -60$ $r^2 \geq 0.997$	Check the electrode, prepare fresh standards, troubleshoot the instrument, or perform routine instrument maintenance
ISE blank solution check	Beginning of each batch	<10% of expected ammonia concentration	Recalibrate ISE, prepare new calibration standards, as needed
Duplicate sample analysis	Each sample	Relative percent difference (RPD) < 5%	Recalibrate ISE, prepare new samples as needed
Calibration verification solution check	After every fifth duplicate sample and at the end of sample batch	Relative percent accuracy (RPA) < 10%	Recalibrate ISE, prepare new calibration standards, as needed
Matrix spike check	Once per batch	None established	Although there are no criteria for acceptability of percent recovery, the data are useful for identifying possible errors in the analysis
Temperature stability check	Each standard solution and sample	$\pm 2^\circ \text{C}$	Recalibrate, reanalyze samples
IC calibration	Each day of analysis	$\text{Slope} = 1.0 \pm 10\%$ $r^2 \geq 0.99$	Recalibrate IC, prepare new calibration standards, as needed
IC blank solution check	Beginning of each batch	<10% of expected ammonia concentration	Recalibrate IC, prepare new calibration standards, as needed
IC duplicate sample analysis	After every tenth sample	Relative percent difference (RPD) < 5%	Recalibrate IC, prepare new samples as needed
Calibration verification solution check	After every tenth sample	Relative percent accuracy (RPA) < 10%	Recalibrate IC, prepare new calibration standards, as needed

During each week of reference method sampling, a total of five sampling trains (one per day) will 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 blank trains will then



be disassembled and the field blank solutions will be analyzed on-site by ISE to ensure that the background concentration due to on-site handling and exposure is  $< 10\%$  of the expected ammonia content of the samples. If background ammonia levels are greater than  $10\%$  of the expected sample ammonia concentrations, the cause of the contamination will be investigated and rectified, if possible.

Laboratory blank solutions will be prepared from  $0.04\text{ N H}_2\text{SO}_4$  for ISE analysis, and analyzed prior to analysis of the reference samples. A laboratory blank solution will also be analyzed after every  $10^{\text{th}}$  reference method sample to ensure no drift in the ISE calibration. If the blank levels are greater than  $10\%$  of the expected sample concentrations, the cause of the contamination will be investigated and rectified, and all analyses performed after the most recent acceptable blank will be invalidated and analysis of those samples will be repeated (if possible).

Laboratory spike solutions will be prepared in  $0.04\text{ N H}_2\text{SO}_4$  with concentrations approximately equal to ammonia concentrations expected from the collection of a sample of flue gas containing  $2\text{ ppmv}$  ammonia. These solutions will be prepared for ISE and IC analysis using a NIST traceable ammonia solutions different than those used for the calibration of the ISE and IC. The solutions will be analyzed prior to analysis of the reference samples. A laboratory spike solution will also be analyzed after every  $10^{\text{th}}$  reference method sample to ensure no drift in the ISE or IC instrumentation. If the measured concentrations are not within  $\pm 10\%$  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).

## **B6 INSTRUMENT/ EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE**

The glassware, filters, and associated equipment for performance of the reference method sampling will be supplied by the subcontractor and will meet the requirements of the CTM-027 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 five blank trains and five spiked trains per week. Preparation, sampling, sample recovery, and

cleaning of used trains will be the responsibility of the stack sampling subcontractor in this verification test.

## **B7 INSTRUMENT CALIBRATION AND FREQUENCY**

### **B7.1 Sampling Meter Box**

The sampling metering instrumentation used for the reference sample collection will be calibrated based on the requirements of EPA Method 5,<sup>8</sup> and references therein. These requirements include those for the dry gas meter, temperature, and pressure sensors, but will exclude those of the nozzle calibrations which are not required since sampling will not be performed isokinetically.

Additionally, Class 1 glassware will be used for preparation of calibration and audit solutions. The balance used to measure impinger solution masses will be calibrated using NIST-traceable weights that bracket the expected range of masses to be measured. Agreement between measured and actual weights will be within the greater of 1% or 0.5 g.

### **B7.2 Ion Selective Electrode**

The ISE will be calibrated according to the manufacturer's recommendations using at least three different solutions, prepared from NIST traceable ammonium standards that bracket the  $\text{NH}_4^+$  concentration range of interest (e.g., 0.1-10  $\mu\text{g/mL}$ ). Immediately after calibration, at least four standard solutions will be reanalyzed using the ISE. If the ISE reading does not agree within 10% of the standard concentrations the calibration will be repeated. The calibration will be conducted on-site daily during each week of reference sampling.

### **B7.2 Ion Chromatograph**

The IC used for analysis of the reference method samples will be calibrated according to manufacturer's recommendations using at least six different solutions, prepared from NIST traceable ammonium standards, that bracket the  $\text{NH}_4^+$  concentration range of interest (e.g., 0.1-10  $\mu\text{g/mL}$ ). Immediately after calibration, at least three standard solutions will be reanalyzed using the IC. If the IC readings do not agree within 10% of the standard concentrations the calibration will be repeated. The calibration will be conducted daily during each day of analysis.

### **B7.3 Facility CEMs**

This verification will make use of monitoring equipment already integrated into the Kingston facility. This equipment includes monitors for major flue gas constituents ( $O_2$ ,  $CO_2$ ) and for chemical contaminants ( $CO$ ,  $NO_x$ ,  $SO_2$ ), as well as sensors for temperature and pressure installed at the facility. These devices are considered part of the host facility for purposes of this test, and will be operated and calibrated by the host facility during this verification according to normal facility procedures. All calibration results must be documented for inclusion in the verification test data files and verification report.

### **B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES**

Upon receipt of any supplies or consumables used for the dynamic spiking testing and for the reference method sampling and analysis, Battelle or subcontractor staff will visually inspect and ensure that the materials received are those that were ordered and that there are no visual signs of damage that could compromise the suitability of the materials. If damaged or inappropriate goods are received they will be returned or disposed of and arrangements will be made to receive replacement materials. Certificates of analysis (COA) or other documentation of analytical purity will be checked for all gases, reagents, and standards to ensure suitability for this verification test. Unsuitable materials will be returned or disposed of and arrangements for the receipt of replacement materials will be made.

The high purity gases used for zeroing of the CRDS systems will be commercial ultra-high purity (UHP, i.e., minimum 99.999% purity) air or nitrogen. Compressed gas standards containing ammonia will be obtained for use in the calibration checks and the dynamic spiking activities of the CRDS systems. 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 testing. Multiple cylinders of uniform concentration will be obtained, if required to meet the gas consumption rates during the test. All cylinders will include a COA specifying analytical purity and the cylinder calibration expiration date.

### **B9 NON-DIRECT MEASUREMENTS**

No non-direct measurements will be used during this verification test.

## **B10 DATA MANAGEMENT**

Various types of data will be acquired and recorded electronically or manually by Battelle, vendor, and I&C Center staff during this verification test. All data will be recorded in permanent ink. Corrections to records will be made by drawing a single line through the entry to be corrected and providing a simple explanation for the correction, along with a date and the initials of the person making the correction. Table 5 summarizes the types of data to be recorded. All maintenance activities, repairs, calibrations, and operator observations relevant to the operation of the monitoring systems being tested will be documented by Battelle or vendor staff in the laboratory record book (LRB). Measurements taken during the collection of the reference method samples will be compiled by subcontractor staff in hard copy or electronic format, and submitted to Battelle in the form of an analytical report at the conclusion of reference sampling periods. Figure 3 shows an example field data sheet that will be used by the stack sampling crew. Report formats will include all necessary data to allow traceability from the raw data to final results.

Records received by or generated by any Battelle, subcontractor, or I&C Center staff during the verification test will be reviewed by a Battelle staff member within two weeks of receipt or generation, respectively, before the records are used to calculate, evaluate, or report verification results. If a Battelle staff member generated the record, this review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, any calculations performed by Battelle, subcontractor, or I&C Center staff will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this test/QA plan.

**Table 5. Summary of Data Recording Process**

<b>Data to Be Recorded</b>	<b>Where Recorded</b>	<b>How Often Recorded</b>	<b>By Whom</b>	<b>Disposition of Data</b>
Dates, times, and details of test events	ETV LRBs, field sampling records	Start/end of test event	Battelle, I&C Staff, and subcontractor staff	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
CRDS system calibration information, maintenance, down time, etc.	ETV LRBs, or electronically	When performed	Vendor, Battelle, I&C Center staff	Incorporated in verification report as necessary
CRDS system readings	Recorded electronically by each monitor and then downloaded to computer daily	Recorded continuously by each monitoring system	Vendor or I&C Center staff for transfer to Battelle	Converted to spreadsheet for statistical analysis and comparisons
Host facility CEM measurement results	Electronically from continuous gas analyzers	Recorded continuously by analyzers	I&C Center for transfer to Battelle	Converted to spreadsheets for calculation of flue gas concentrations, and statistical analysis and comparisons
Reference method procedures, calibrations, QA, etc.	ETV LRBs, or data recording forms	Throughout sampling and analysis processes	Subcontractor or Battelle	Retained as documentation of reference method performance
Reference method analysis results	ETV LRBs, or data recording forms or electronically from analytical method	Every sample analysis	Subcontractor or Battelle	Converted to spreadsheets for calculation of flue gas concentrations, and statistical analysis and comparisons

Among the QA activities conducted by Battelle QA staff will be an audit of data quality. This audit will consist of a review by the Battelle Quality Manager of at least 10% of the test data. During the course of any such audit, the Battelle Quality Manager will inform the technical staff of any findings and any immediate corrective action that should be taken. If serious data quality problems exist, the Battelle Quality Manager will inform the AMS Center Manager who is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

Entered Data	symbol	units
General Information		
<b>EPA Method 2</b> Barometric Pressure	Pb	in Hg
<b>EPA Method 3</b> O <sub>2</sub> Concentration CO <sub>2</sub> Concentration	O <sub>2</sub> CO <sub>2</sub>	%vd %vd
<b>EPA Method 4</b> Meter Factor Meter Volume Average Meter Temperature Average dH Condensate Catch	Ym Vm Tm dH Vlc	 ft3 °F in H <sub>2</sub> O ml
<b>EPA Method 027</b> IC analysis-1st Impinger IC analysis-2nd Impinger IC analysis-3rd Impinger	Mp1 Mp2 Mp3	mg/l mg/l mg/l
Calculated Data		
<b>EPA Method 2, 3, and 4</b> Standard Dry Volume $Vm * Ym * 17.04 * ((dH + Pb) / (13.6) / (460 + Tm))$ Equivalent Vapor Volume $Vlc * 0.04707$ Moisture $(Vvstd / (Vwstd + Vmstd)) * 100$	Vmstd Vwstd Bws	dscf scf %v
<b>EPA Method 027</b> Ammonia Concentration - 1st Impinger Ammonia Concentration - 2nd Impinger Ammonia Concentration - 3rd Impinger Total Ammonia Concentration	Mc1 Mc2 Mc3 Mctotal	ppmvd ppmvd ppmvd ppmvd

**JOHN SEVIER FOSSIL PLANT UNIT 1**  
**NH3 Sample Train**

Point No	Grid No	date	1st Impinger	100 ml 0.1N H2SO4	pretest weight	posttest weight
Test No		start time	2nd Impinger	100 ml 0.1N H2SO4		
Run No		end time	3rd Impinger	empty		
meter no		baro press. in Hg	4th Impinger	300 g Silica Gel		
mtf factor		static press. in H2O				
OH @						
nozzle dia						

data taken by	sample leak chk	pretest	posttest	sample leak check	pretest	posttest	K Factor	Flue Gas O2	Flue Gas CO2

Test Point	Sample Time min	meter vol ft <sup>3</sup>	vel head in H <sub>2</sub> O	delta h in H <sub>2</sub> O	vacuum in Hg	meter temp deg F	meter temp out deg F	filter temp deg F	stack temp deg F	exit gas temp deg F
Start			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
			n/a						n/a	
end			n/a						n/a	

**Figure 3. Example field data form.**

## **SECTION C**

### **ASSESSMENT AND OVERSIGHT**

#### **C1 ASSESSMENTS AND RESPONSE ACTIONS**

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of this test/QA plan is to establish mechanisms necessary to ensure this. Internal quality control measures described in this test/QA plan, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator. Technical staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work with the Battelle Quality Manager to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

Changes to requirements in the approved test/QA plan will be documented on the appropriate form in the AMS QMP and be brought to the attention of the EPA AMS Center Project Officer (PO) and EPA AMS Center QA Manager. If approval by the EPA PO or his designee is not received within 24 hours of notification testing will be halted until a suitable resolution has been achieved.

##### **C1.1 Performance Evaluation Audit**

A PE audit will be conducted within the first two weeks of testing to assess the quality of the critical measurements associated with the dynamic spiking procedures and the reference sampling and analysis methods. Table 6 shows the critical measurements to be audited, with the audit procedures and acceptance criteria for the audit comparisons. If the PE audit results do not meet the acceptance criteria shown, they will be repeated. If the outlying results persist, a

change in reference method instrument and a repeat of the PE audit may be considered, and data will be flagged until the PE audit results are acceptable. This audit will be performed once during the verification test, and will be the responsibility of the Verification Test Coordinator or designee.

The PE audit of the dynamic spiking flow rate will be conducted using an independent NIST-traceable flow transfer standard (e.g., Bios, Model DC-2, or comparable). The target criterion for this audit is agreement between the measured and nominal flow rate within  $\pm 10\%$ . If this criterion is not met, the cause of the problem will be investigated and corrected if possible. Components of the sampling train will be replaced as necessary until the flow rate criterion is met.

**Table 6. Methods and Acceptance Criteria for PE Audit Measurements**

Critical Measurement	PE Audit Method	Acceptance Criteria
Dynamic spiking flow rate	Compare to independent flow transfer standard	$\pm 10\%$ actual flow rate
Stack Temperature	Compare to independent temperature measurement	$\pm 2\%$ absolute temperature
Barometric Pressure	Compare to independent pressure measurement	$\pm 0.5$ inch of H <sub>2</sub> O
Flue Gas Differential Pressure	Compare to independent pressure measurement	$\pm 0.5$ inch of H <sub>2</sub> O
Mass (H <sub>2</sub> O)	Check balance with calibrated weights	$\pm 1\%$ or 0.5 g, whichever is larger
Ammonia (overall measurement)	Spike reference method trains	$\pm 20\%$ bias in spike recovery
Ammonia (ISE analysis)	Blind audit sample	$\pm 10\%$ of standard concentration
Ammonia (IC analysis)	Blind audit sample	$\pm 10\%$ of standard concentration

The PE audit will include spiking reference method sampling trains with known amounts of ammonia, and conducting sample analysis on the train without sampling the combustion gas. A NIST-traceable ammonium standard solution will be used for that purpose. During each week of sampling, five blank trains will be prepared spiked with a known amount of an ammonia standard solution, such that the ammonium concentration in the sample solution is within 10-50% of the calibration range of the IC (e.g., 1-5  $\mu\text{g/mL}$ ). The spiked trains will be 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 spiked samples will be analyzed both on-site by ISE and in the laboratory by IC, 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 percent. 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 PE audit of the analytical methods will be performed by supplying audit samples prepared from independent NIST-traceable standard solutions. These audit samples will be analyzed and compared to the known sample concentrations. The acceptance criterion for this audit is for agreement between the measured and actual concentrations within  $\pm 10\%$ .

### **C1.2 Technical Systems Audits**

The Battelle Quality Manager will perform a TSA at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP,<sup>1</sup> this test/QA plan, published reference methods, and any SOPs used by the test facility. In this TSA, the Battelle Quality Manager, or designee, may review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. In the TSA, the Battelle Quality Manager will tour the test site; observe the reference method sampling and sample recovery; inspect documentation of reference sample chain of custody; and review laboratory record books. He will also check gas standard certifications and data acquisition procedures, and may confer with the vendor, I&C Center, and subcontractor staff. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA AMS Center Project Officer and Quality Manager will receive a copy of Battelle's TSA report. 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 technical staff at the time of the audit and documented in a TSA report.

### **C1.3 Data Quality Audits**

The Battelle Quality Manager, or designee, will audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager, or designee, will trace the data from initial acquisition (as received from the ISE, I&C, and vendors), through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked. Data must undergo a 100% validation and verification by technical staff (i.e. Verification Test Coordinator, or designee) before it will be assessed as part of the data quality audit.

### **C1.4 QA/QC Reporting**

Each assessment and audit will be documented in accordance with Section 3.3.4 of the AMS Center QMP.<sup>1</sup> The results of the TSA will be submitted to EPA. Assessment reports will include the following:

- X Identification of any adverse findings or potential problems
- X Response to adverse findings or potential problems
- X Recommendations for resolving problems
- X Confirmation that solutions have been implemented and are effective
- X Citation of any noteworthy practices that may be of use to others.

## **C2 REPORTS TO MANAGEMENT**

The Battelle Quality Manager, during the course of any assessment or audit, will 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 will notify the AMS Center Manager, who is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The test/QA plan and final report are reviewed by EPA AMS Center QA staff and the EPA AMS Center program

management staff. Upon final review and approval, both documents will then be posted on the ETV website ([www.epa.gov/etv](http://www.epa.gov/etv)).

## **SECTION D**

### **DATA VALIDATION AND USABILITY**

#### **D1 DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS**

The key data review and data verification requirements for this test are stated in Section B10 of this test/QA plan. In general, the data review requirements specify that data generated during this test will be reviewed by a Battelle technical staff member within two weeks of generation of the data. The reviewer will be familiar with the technical aspects of the verification test but will not be the person who generated the data. This process will serve both as the data review and the data verification, and will ensure that the data have been recorded, transmitted and processed properly. Furthermore, this process will ensure that the monitoring systems data and reference method data were collected under appropriate testing conditions and that the reference sample data meet the specifications of analytical methods.

The data validation requirements for this test involve an assessment of the quality of the data relative to the DQIs, reference method QC requirements, and audit acceptance criteria specified for this test in Tables 2, 4, and 6, respectively. The results of the reference method QC activities and the PE audit results will be compared with the appropriate acceptance criteria in Tables 4 and 6, respectively, to ensure that the reference method measurements were properly performed. Furthermore, the results of the reference method measurements and dynamic spiking measurements will be compared with the appropriate DQIs listed in Table 2 to validate the quality of the data. Any deficiencies in these data will be flagged and excluded from any statistical comparisons to the CRDS systems being tested, unless these deviations are accompanied by descriptions of their potential impacts on the data quality.

#### **D2 VERIFICATION AND VALIDATION METHODS**

Data verification is conducted as part of the data review as described in Section B10 of this test/QA plan. A visual inspection of handwritten data will be conducted to ensure that all entries were properly recorded or transcribed, and that any erroneous entries were properly noted (i.e.,

single line through the entry, with an error code and the initials of the recorder and date of entry).

Electronic data from the CRDS systems, continuous gas analyzers, and analytical equipment used during the test will be inspected to ensure proper transfer from the datalogging system. All calculations used to transform the data will be reviewed to ensure the accuracy and the appropriateness of the calculations. Calculations performed manually will be reviewed and repeated using a handheld calculator or commercial software (e.g., Excel). Calculations performed using standard commercial office software (e.g., Excel) will be reviewed by inspection of the equations used for the calculations and verification of selected calculations by handheld calculator. Calculations performed using specialized commercial software (i.e., for analytical instrumentation) will be reviewed by inspection and, when feasible, verified by handheld calculator, or standard commercial office software.

To ensure that the data generated from this test meet the goals of the test, a number of data validation procedures will be performed. Sections B and C of this test/QA plan provide a description of the validation safeguards employed for this verification test. Data validation efforts include the completion of QC activities, and the performance of TSA and PE audits as described in Section C. The data from this test will be evaluated relative to the measurement DQIs described in Section A7, and the PE audit acceptance criteria given in Section C1.1 of this test/QA plan. Data failing to meet these criteria will be flagged in the data set and not used for evaluation of the monitoring systems, unless these deviations are accompanied by descriptions of their potential impacts on the data quality.

An audit of data quality will be conducted by the Battelle Quality Manager to ensure that data review, verification, and validation procedures were completed, and to assure the overall quality of the data.

### **D3 RECONCILIATION WITH USER REQUIREMENTS**

This purpose of this verification test is to evaluate the performance of CRDS systems. In part, this evaluation will include comparisons of results from the monitoring systems to the results from reference method samples generated from the SCAQMD Method 207.1. To meet the requirements of the user community, the reference data collected during this verification test will

meet the QA requirements of the reference method. Additional performance data regarding operational characteristics of the monitoring systems will be collected by verification test personnel. To meet the requirements of the user community, these data will include thorough documentation of the performance of the monitoring systems during the verification test. The data review, verification, and validation procedures described above will assure that data meeting these requirements are accurately presented in the verification reports generated from this test, and will assure that data not meeting these requirements will be appropriately flagged and discussed in the verification reports.

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the vendor, EPA, and expert peer reviewers. The reviews of this test/QA plan will help to improve the design of the verification test and the resulting report(s) such that they better meet the needs of potential users of these monitoring systems.

## **SECTION E**

### **REFERENCES**

1. Battelle, Quality Management Plan for the ETV Advanced Monitoring Systems Center, Version 7.0, U.S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, November 2008.
2. U.S. EPA, Environmental Technology Verification Program Quality Management Plan, EPA Report No: 600/R-08/009 EPA/600/R-03/021, U.S. Environmental Protection Agency, Cincinnati, Ohio, January 2008.
3. U.S. EPA, Conditional Test Method (CTM-027) Procedure for Collection and Analysis of Ammonia in Stationary Sources, August 1997. Available at: <http://www.epa.gov/ttn/emc/ctm.html>
4. Busch KW, Busch MA, Cavity Ringdown Spectroscopy: An Ultratrace Absorption Measurement Technique. ACS Symposium Series 720, Oxford (1997).
5. Atkinson, D. B., "Solving chemical problems of environmental importance using cavity ring-down spectroscopy," The Analyst 128, 117-125 (2003).
6. SCAQMD, Method 207.1: Determination of Ammonia Emissions from Stationary Sources, South Coast Air Quality Management District, Source Test Engineering/Laboratory Services, April 2006.
7. U.S. EPA, Method 17 – Determination of Particulate Matter Emissions from Stationary Sources, Available at: <http://www.epa.gov/ttn/emc/promgate.html>
8. U.S. EPA, Method 5 – Determination of Particulate Matter Emissions from Stationary Sources, Available at: <http://www.epa.gov/ttn/emc/promgate.html>

## **APPENDIX A**

### **Conditional Test Method (CTM-027)**

#### **Procedure for Collection and Analysis of Ammonia in Stationary Sources**

PROCEDURE FOR COLLECTION AND ANALYSIS OF AMMONIA  
IN STATIONARY SOURCES

Conditional Test Method (CTM-027)

This method has been validated at a coal-fired boiler at a power plant (call Rima Howell at (919) 541-0443 if you'd like a copy of the validation report) using the procedures in Test Method 301 (40 CFR Part 63, Appendix A). Use of this method at other sources is not recommended without proper validation.

1.0 SAMPLING EQUIPMENT AND SUPPLIES

1.1 Sampling Train

A Method 17 sampling train is required to collect the ammonia samples. This system is described in 40 CFR Part 60, Appendix A, and in the EPA *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III - Stationary Source Specific Methods*, Section 3.11, January, 1982 (EPA-600/4-77-027b). Figure 17-3 of 40 CFR 60, Appendix A, may be modified for use as a data sheet. Method 17 train components specified for collection and measurement of ammonia are as follows:

1.1.1 Probe Liner - Use borosilicate or quartz glass tubing, enclosed in a stainless steel sheath.

1.1.2 Probe Nozzle - Use a borosilicate or quartz glass nozzle. The design should have a sharp, tapered edge, and be formed in a button-hook or elbow configuration. Since isokinetic sampling is required, a range of interior diameter nozzles should be available to accommodate various stack flows.

1.1.3 Pitot Tube - Use a type S design, meeting the requirements of EPA Method 2 (40 CFR Part 60, Appendix A).

1.1.4 Differential Pressure Gauge - Use an inclined manometer or an equivalent device. Two are required, one to monitor stack pressure, and the other to monitor the orifice pressure differential.

1.1.5 In-Stack Filter Holder and Filter - A filter holder made of borosilicate glass or Teflon, a filter support (with a selection of gaskets such as silicone rubber, Teflon, or Viton, each capable of withstanding stack gas temperature), and a glass fiber filter are



required.

1.1.7 Impingers - Two Greenburg-Smith (G-S) impingers and two impingers with the tips removed are required. They are connected in series and all are immersed in an ice bath. The first G-S impinger assembly downstream of the filter holder is charged with 100 mL of 0.1N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution; the second G-S assembly also contains 100 mL of 0.1N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution; the third impinger has the tip removed and the container is either empty or contains 100 mL 0.1N  $\text{H}_2\text{SO}_4$  (depending on the need to prevent breakthrough due to high ammonia concentrations and/or high flowrate requirement); and the fourth assembly, also with the impinger tip cut off, contains a pre-weighed amount (200 to 300 g) of indicating silica gel.

1.1.8 Metering System - The metering system is composed of a vacuum gauge, vacuum pump, thermometers accurate to  $\pm 3^\circ\text{C}$  from 0 to  $90^\circ\text{C}$  ( $\pm 6^\circ\text{F}$  from 32 to  $194^\circ\text{F}$ ) to measure gas temperatures entering and exiting the dry gas meter, a dry gas meter (accurate to 2 percent), and related tubing, fittings, and gauges. When used with a pitot tube, the metering system should allow verification that sampling is isokinetic and be adjustable to maintain isokinetic conditions.

## 1.2 Sample Recovery Apparatus

1.2.1 Wash Bottles - Two polyethylene wash bottles are needed. One contains deionized water for rinsing out droplets of impinger solution that adhere to impinger vessels and their connecting glassware after the solution has been poured into sample bottles. It is also used to rinse the interiors of the probe and the filter holder at the end of a sampling session. The second bottle contains reagent-grade acetone to rinse and speed the air drying of the water-rinsed components. NOTE: Do not add the acetone to the water rinses. Do not store acetone in plastic bottles; keep it in a glass container and transfer it to the plastic wash bottle when needed.

1.2.2 Graduated Cylinders - Glass or high-density polyethylene (HDPE) graduated cylinders to measure the volumes of the impinger solutions after a run to determine moisture content of stack or vent.

1.2.3 Sample Storage Containers - Clean HDPE bottles of 250 or 500-mL capacity are used to store the 0.1N  $\text{H}_2\text{SO}_4$  impinger solutions and rinses for later ion chromatographic analysis. The spent silica gel is also stored in bottles for weighing. These bottles should have wide mouths and provide airtight seals.

### 1.3 Reagents and Other Supplies

1.3.1 Filters - Glass fiber filters without organic binders must be used. They should have a collection efficiency of at least 99.95 percent for 0.3- $\mu$ m-diameter particles.

1.3.2 Silica Gel - Indicator type, mesh size 6-16.

1.3.3 Water - Deionized water that has been blank-checked for ammonium ion and other constituents of interest. The conductivity should be 5  $\mu$ S/cm or lower.

1.3.4 0.1N Sulfuric Acid Solution - Obtain by purchase of reagent grade 0.1N acid or by volumetric dilution of higher concentrations of reagent grade acid by pouring the acid into deionized water.

1.3.5 Other Supplies - Stopwatch, pocket barometer, plastic cooler to store sample bottles, polyethylene bags and labels for storage and labeling of sample bottles, and crushed ice are needed. Plastic gloves and/or plastic forceps are needed to handle the filters.

## 2.0 ASSEMBLY OF EQUIPMENT FOR SOURCE SAMPLING

### 2.1 Sample Train Assembly

Figure 17-1 (40 CFR Part 60, Appendix A) illustrates the arrangement of equipment at the source location. The calibration of the heater settings and the sample metering system should be completed in the laboratory before transferring the equipment to the field.

2.1.1 Filter Holder and Probe - Place a glass fiber filter on the filter support of the filter holder. Use plastic gloves or plastic forceps to handle the filter. Avoid contact with the hands. Assemble the filter holder and attach it to the end of the probe. Attach the probe nozzle to the entrance of the filter holder. Insert the probe, with nozzle attached, into a port of the source vent or stack.

2.1.2 Impinger Train - Prepare the four impingers as follows. First G-S impinger: 100 mL of 0.1N sulfuric acid. Second G-S impinger: 100 mL of 0.1N sulfuric acid. Third impinger: empty or contains 100 mL 0.1N H<sub>2</sub>SO<sub>4</sub> (depending on the need to prevent

breakthrough due to high ammonia concentrations and/or high flowrate requirement). Fourth impinger: a known, preweighed amount (200-300 g) of indicating silica gel, 6-16 mesh. Connect the first impinger to the exit of the glassware union joined to the probe liner exit. Connect the four impingers to each other. Connect the fourth impinger to the inlet of the sample meter system. Add crushed ice and cold water to the container that holds all impingers. Immerse the impingers to a point at least 10 cm above the level of the impinger liquid level. Allow the impingers to cool for 10 minutes before beginning to sample.

### 3.0 OPERATION OF AMMONIA SAMPLING TRAIN

#### 3.1 Sampling Procedure

Follow the isokinetic sampling procedure outlined in Section 4.1, Method 17.

#### 3.2 Set Temperatures

Determine the temperature of the stack gas. Preheat the in-stack filter, the probe and the heated area just prior to the entrance to the first impinger to a temperature at or slightly above the stack gas temperature.

#### 3.3 Activate the Sample Train

Leak-check the sample train following the procedures in Section 4.1.4 of Method 17. Record the start point reading of the dry gas meter.

During the sampling period, make several readings of the thermometers at the inlet and outlet wells of the dry gas meter. Record and average these readings. Periodically check the volume of liquid in the first impinger. Very moist stack gas samples could cause the impinger to overflow. If this is about to happen, discontinue sampling and record the time and volume sampled.

At the end of the sampling period, turn off the sampling system. Record the final volume indicated by the dry gas meter. Calculate the total volume sampled.

#### 3.4 Remove and Package Samples

Remove the glass fiber filter and store it in a labeled and pre-weighed petri dish; put the dish in a plastic bag. Save the filter should it be needed for later extraction and analysis. NOTE: Analysis of filter catch is not required for the purposes of this

method. After cleaning and drying the filter holder, install a new filter.

Determine the volume of liquid in each of impingers 1, 2, and 3 by pouring their contents into individual clean graduated cylinders. Record the volume on the data sheet. Pour the contents of each graduated cylinder into individual 250- or 500-mL HDPE bottle. Next, use the deionized water wash bottle to rinse out all interior surfaces of impingers 1, 2, and 3 and the corresponding graduated cylinders. Add the rinse water to the respective bottles for impingers 1, 2, and 3. Rinse the glassware between the filter holder and the first impinger. This rinse may be stored in a small HDPE bottle for separate analysis or it may be combined with the liquid from impinger 1. Limit the volume of rinse water so that the total volume of each impinger plus its rinses is no more than 230 mL. This will allow 20 mL of rinse water to be used in the laboratory to transfer the sample to a 250-mL volumetric flask. In general, do not rinse glassware with acetone to dry it. If acetone must be used to dry the glassware, do not combine the acetone rinse with any sample. Discard the acetone rinses in a proper manner.

Tighten the cap securely and place each bottle in a plastic bag and record a sample number and identifying information on the bag with an indelible marker or securely affix a prepared label. Labels can be made up in advance. Place the sample bottles in an ice cooler. Once in the laboratory, store the bottles in a refrigerator at 4°C (39°F) and analyze the samples by ion chromatography within 2 weeks after collection. Store the filters, in their petri dishes, in a cool, dry location. A summary of the workup and packaging procedures suggested for the method is given in Table A-1.

### 3.5 Conduct Additional Runs

Conduct 2 additional runs in order to complete 3 runs for each test site. Follow the procedures described in Sections 3.1, 3.2, 3.3 and 3.4.

When a sampling session at a testing location is complete, disassemble and clean the interiors of the nozzle, the probe liner, the filter holder, the filter support, the impingers, and all supporting glassware.

### 3.6 Quality Control and Quality Assurance

Designate a sample of the 0.1N sulfuric acid impinger solution as the field blank by placing it in an impinger vessel for an hour but collect no sample. Package the field blank as described for samples. Analyze the collection solution for ammonium to ensure that the background due to onsite handling and exposure is negligible

compared to the ammonium content of samples.

#### 4.0 ANALYSIS OF AMMONIA, AS AMMONIUM ION, BY ION CHROMATOGRAPHY

##### 4.1 Sample Preparation

Analyze samples within 2 weeks after their collection in the field. Keep samples refrigerated (not frozen) at 4°C (39°F) and allowed them to slowly warm to laboratory temperature before analysis.

Table A-1. List of Samples from Method 17 Train for Ammonia

Component	Workup Procedure	Packaging
In-stack filter (47 mm glass fiber) (Optional)	Remove filter from holder with tweezers; place in pre-labeled pre-weighed plastic Petri dish (Optional)	50 mm plastic Petri dish.
In-stack filter housing (front half) (Optional)	Brush adhering particles into Petri dish with artist's brush. Clean with water; wipe dry with lab tissue.	Same as above.
In-stack filter housing (back half) and union connecting it to probe liner	Visually examine for particles. There should be none. Note this. Rinse with three, 10-mL portions of 0.1N H <sub>2</sub> SO <sub>4</sub> from squeeze bottle; rinse into plastic funnel atop 250 mL poly. bottle. Rinse filter housing, union, and funnel 3 times with water; discard rinses. Dry housing and funnel with lab tissue.	250 mL poly. bottle.
Glass probe liner and glassware connecting it to Impinger # 1.	Visually examine for particles. There should be none. Note this. Rinse interiors with three, 10-mL portions of 0.1N H <sub>2</sub> SO <sub>4</sub> into plastic funnel atop same 250 mL poly. bottle used above. Rinse probe liner and glassware 3 times with water; discard rinses.	Same bottle as above.

Impinger # 1 (stem and body). Impinger liquid.  Repeat this procedure for Impinger # 2 and Impinger # 3.	Pour impinger solution into clean, dry graduated poly. cylinder and record volume. Then pour solution into a 250 mL poly. bottle. Rinse each impinger stem, impinger body, and graduated cylinder with three, 5-mL portions of water and transfer these rinses to the 250 mL bottle. Drain water from each impinger stem and body. Shake graduated cylinder and plastic funnel until near dryness.	Use a separate 250 mL poly. bottle for each impinger.
Impinger # 4. Silica gel.	Weigh tared impinger body plus used silica gel to determine weight gain. Transfer silica gel to a 250 mL poly. bottle via funnel. Scrape out any remaining particles with a metal spatula. Remove dust from ground glass surfaces with lab tissue.	250 mL poly. bottle.

4.1.1 Impinger Solutions - Pour the solutions from impingers 1 and 2 (and possibly 3) from their HDPE sampling bottles into separate 250-mL volumetric flasks. Rinse out the interior walls of the bottles several times with approximately 10-mL portions of deionized water. Add each rinse to the applicable 250-mL volumetric flask until the total volume reaches the mark. Do not prepare the solution in impinger 3 for analysis unless analysis of the contents of impingers 1 and 2 indicates breakthrough of ammonia has occurred (the general rule for whether breakthrough has occurred is when the concentration of impinger 2 is greater than 10 percent of the concentration of impinger 1). This process of rinsing and diluting takes the 0.1N H<sub>2</sub>SO<sub>4</sub> impinger solution to an approximately 0.04N H<sub>2</sub>SO<sub>4</sub> solution, making it compatible with the 0.04N H<sub>2</sub>SO<sub>4</sub> solutions used for setup and calibration of the ion chromatograph.

4.1.2 Silica Gel - Determine the weight of the used silica gel and compare this to its initial, unexposed weight. Record the net weight of water absorbed by the silica gel.

#### 4.2 Sample Analysis

An ion chromatograph equipped with a conductivity detector is used for ammonium ion separation and quantitation.

4.2.1 Ion Chromatography Conditions - The conditions found to be suitable for analysis of a sample containing 1 ppmV ammonium in 0.4N sulfuric acid collection media are (Mention of trade names in this case does not constitute endorsement by the Agency; model names and numbers are mentioned in order to provide guidance to the user):

Instrument:

Dionex Model 2120i

Separator Column:

Dionex HPIC-CS1

Suppressor Column:

Dionex Cation Micromembrane

Eluent:

0.005 N hydrochloric acid

Eluent flow rate:

2.3 mL/min

Regenerant:

0.1 M tetrabutylammonium  
hydroxide

Sample loop volume:

100 :L.

4.2.2 Calibration - Prepare a calibration curve each analysis day using at least six standards that bracket the expected range of sample concentrations. This is usually from 0.1 to 10.0 :g of  $\text{NH}_4^+$  per mL of sample. If an electronic integrator is available, use the signal's peak area for calibration and data reduction rather than the peak height. Calibration standards are prepared in 0.04N  $\text{H}_2\text{SO}_4$ , the same concentration of acid as in the diluted samples.

4.2.3 Quality Control and Quality Assurance - Aqueous samples containing known amounts of ammonium ion are available from the U.S. Environmental Protection Agency (EPA), National Institute of Standards and Technology (NIST), and other sources. Use these for quality assurance audits of the analytical process. Conduct quality control checks by periodically analyzing a solution that has an ammonium ion concentration in the range of the calibration standards but that has been prepared independently using a different bottle of ammonium salt than that used to prepare the calibration standards. Make periodic blank checks of reagents.

#### 4.3 Calculations

4.3.1 Determine the total volume of dry gas sampled by subtracting the initial reading of the dry gas meter (DGM) from its final reading. Correct this sample volume to standard conditions (20 °C,

760 mm Hg or 68 °F, 29.92 in. Hg) using the following equation.

$$V_{m(std)} = V_m Y \left( \frac{T_{std}}{T_m} \right) \left[ \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] \quad (1)$$

where

$V_{m(std)}$	=	Volume of gas sample measured by the DGM, corrected to standard conditions
$V_m$	=	Volume of gas sample as measured by DGM
$Y$	=	DGM calibration factor
$T_{std}$	=	Standard absolute temperature, 293 K
$T_m$	=	Absolute average DGM temperature, K
$P_{bar}$	=	Barometric pressure at the sampling site, mm Hg
$P_{std}$	=	Standard absolute pressure, 760 mm Hg
$\Delta H$	=	Average pressure differential across the orifice meter, mm H <sub>2</sub> O
13.6	=	Specific gravity of mercury.

Express  $V_{m(std)}$  in liters. One cubic ft. = 28.316 L.

4.3.2 Determine the concentration of ammonium ion (NH<sub>4</sub><sup>+</sup>) in the diluted impinger solution by application of the ion chromatography (IC) calibration equation. Express this in milligrams NH<sub>4</sub><sup>+</sup> per liter of solution.

4.3.3 Calculate the volume of ammonia gas present in the sample.

$$V_a = \frac{(N) (0.25) (24.04)}{(1000) (18)} \quad (2)$$

where

$V_a$	=	Volume of ammonia gas in the sample of gas taken from the source
$N$	=	Sum of concentrations of ammonium ion, mg/L, in all impinger solutions (and in the probe rinse, if applicable)



0.25	=	Conversion factor, assuming sample in impinger was diluted to 0.25 L (250 mL)
24.04	=	Liters of ideal gas per mole of substance
1/1000	=	Factor to convert mg/L to g/L
18	=	Formula weight of ammonium ion.

4.3.4 Calculate the ppmV of ammonia present in the stack gas sample:

$$C_{\text{NH}_3} = \frac{V_{\text{A}}, \text{ L}}{V_{\text{A(Std)}}, \text{ L}} \times 10^6. \quad (3)$$