July 2011

Environmental Technology Verification Report

PICARRO
MODEL G1103-C AMMONIA ANALYZER

Prepared by
Battelle

Battelle
The Business of Innovation

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U.S. Environmental Protection Agency

July 2011

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

PICARRO, INC. MODEL G1103-C AMMONIA ANALYZER

by
Brad Goodwin, Ken Cowen, Thomas Kelly, Amy Dindal, Battelle
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Notice

FOREWORD

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. We acknowledge the financial support of the Electrical Power Research Institute (EPRI). Quality assurance oversight was provided by Michelle Henderson, U.S. EPA, and Zachary Willenberg, Battelle. We would also like to thank the Tennessee Valley Authority and the staff at the host facilities for their support and for providing a venue for the performance of this verification test. Finally, the authors thank Dr. Will Ollison of the American Petroleum Institute, Mr. Chuck Dene of EPRI, and Mr. Dennis Mikel of U.S. EPA’s Office of Air Quality Planning and Standards for their review of the test/QA plan and this verification report.

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List of Abbreviations

AMS	Advanced Monitoring Center
APH	air preheater
ºC	Degrees Celsius (or Centigrade)
CRDS	cavity ring-down spectroscopy
CTM	Conditional Test Method
DFB	distributed feedback laser
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
ETV	Environmental Technology Verification
IC	ion chromatography
NIST	National Institute of Standards and Technology
NO_x	nitrogen oxides
PE	performance evaluation
QA	quality assurance
QC	quality control
QMP	quality management plan
ppm	parts per million
RPD	relative percent difference
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
TQAP	test/QA plan
TSA	technical systems audit
TVA	Tennessee Valley Authority
µsec	microseconds

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance and quality control (QA/QC) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Risk Management Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. Real-time ammonia monitoring systems for the measurement of excess ammonia (ammonia slip) were identified as a priority technology category for verification through the AMS Center stakeholder process. The AMS Center recently evaluated the performance of the Picarro, Inc., Model G1103-c ammonia analyzer for analysis of ammonia in flue gas at a coal fired power plant.

Chapter 2
Technology Description

This report provides results for the verification testing of the Picarro, Inc., Model G1103-c. The following is a description of the Model G1103-c, based on information provided by the vendor. The information provided below was not verified in this test.

The Model G1103-c, shown in Figure 2-1, is an analyzer designed to measure ammonia at the parts-per-billion level in the presence of carbon dioxide, water vapor, and other gas species present in flue gas streams. This analyzer is based on cavity ring-down spectroscopy (CRDS), which is a technique in which a gas sample is introduced into a high-finesse optical cavity and the optical absorbance of the sample is determined, thus providing concentration or isotopic ratio measurements of a particular gas species of interest.[1,2]

Figure 2-1. The Picarro Model G1103-c ammonia analyzer.

Figure 2-2 shows a block diagram of the Picarro CRDS analyzer. The components which make up a basic CRDS instrument are a laser, a high-finesse optical cavity consisting of two or more mirrors, and a photo-detector, where finesse is ratio of the free spectral range of the optical cavity divided by the full width at half maximum of the transmission bands. Operationally, light from a laser is injected into the cavity through one partially reflecting mirror. The light intensity inside the cavity then builds up over time and is monitored through a second partially reflecting mirror using a photo-detector located outside the cavity. The "ring-down" measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially with a time constant, τ, that depends on the losses due to the cavity mirrors and the absorption and scattering of the sample being measured. Measurement of gas concentration is based on the fact that the decay time constant is shorter when an absorbing gas is present in the cavity than when no absorbing gas is present. After shutting off the laser, most of the light remains trapped within the cavity for a relatively long period of time (i.e., microseconds [μsec]), producing an effective path length of tens of kilometers through the sample.

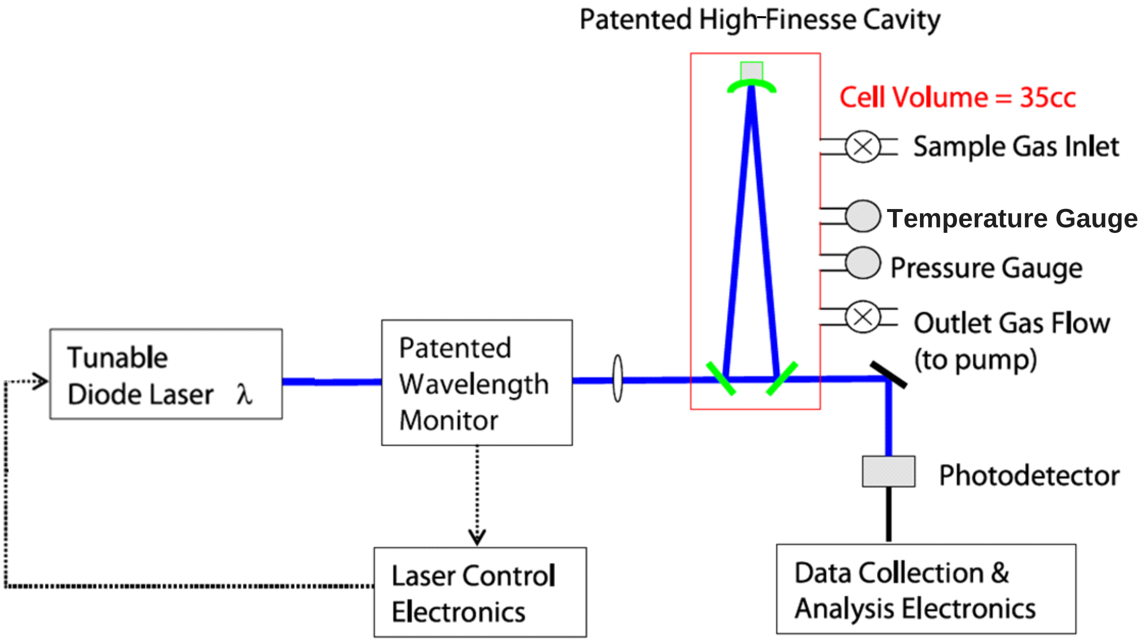

Figure 2-2. Block diagram of the Picarro Model G1103-c ammonia analyzer.

The Model G1103-c utilizes a telecom-grade distributed feedback (DFB) laser. Light from the DFB laser is transported to a wavelength monitor via a polarization-maintaining optical fiber. The analyzer is designed to simultaneously measure optical absorption using a proprietary traveling wave cavity and the optical frequency at which the absorption occurs using a proprietary wavelength monitor. The temperature and pressure of the ambient air sample continuously flowing through the optical cavity are regulated at all times to 45 ºC and 140 Torr, respectively. A typical empty cavity decay constant, τ, is 40 μsec for this instrument. The normalized reproducibility of the measured ring-down time constant ($\Delta\tau/\tau$) is better than 0.02%. With a ring-down acquisition rate of 100 Hz, the typical sensitivity (1 sigma) of the instrument is $1.6\times10^{-11}\text{cm}^{-1}/\text{Hz}^{1/2}$ which corresponds to approximately 0.3 ppb of ammonia in one second, or about 0.025 ppb with five of minutes of averaging. The Model G1103-c has an operational range of 0-10 ppm NH_3, with an optional extended range up to 50 ppm.

The analyzer continuously scans the laser over individual ammonia spectral features and records the absorption loss and wavelength at each spectral point. Each spectrum is comprised of absorption loss as a function of optical frequency. The concentration is proportional to the area under each measured spectral feature. Concentration measurements are provided approximately every second, corresponding to a total of 100 ring-down and wavelength monitor measurements. The wavelength monitor used in the analyzer is solid-state in design and has no moving parts. It is designed to provide wavelength measurements over a frequency range corresponding to greater than 100 nm. The wavelength precision (defined as the repeatability of the wavelength measurement at a single spectral point) is approximately 1MHz (1σ) or approximately 3 x 10^{-5} cm^{-1}. The relative accuracy, defined as the repeatability of the difference of the wavelength measurement between two spectral points separated by approximately 1 GHz or approximately 0.03 cm^{-1} (the width of a typical absorption line at a typical operating pressure of 140 Torr) during a spectral scan is approximately 0.3MHz (approximately 1 x 10^{-5} cm^{-1}). The size and shape of the ammonia spectral line at 6,548 cm^{-1} is a sensitive function of the temperature and pressure of the sample. Therefore, the analyzer is designed to control the sample gas temperature to a precision of a few hundredths of a degree (1σ) over ambient temperatures ranging from 10 to 35ºC and the sample pressure to a precision of 0.05 Torr (1σ). In the analyzer, a combination of proportional valves (for flow control) is used to maintain the cavity at a known constant pressure. Ammonia is a toxic, reactive, and corrosive compound that is soluble in water. These characteristics are known to prolong the transport time, thereby slowing gas monitor response times in a closed-path system that may contain water. Care has been taken to use Teflon for all wetted materials to keep this effect to a minimum.

The Model G1103-c has dimensions of 43 x 25 x 59 cm (17” x 9.75” x 23”) including the base, and can be rack mounted or operated on a bench top. The approximate purchase price of the Model G1103-c is $55,000.

Chapter 3
Test Design and Procedures

3.1 Introduction

Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) technologies are commonly used on coal-fired power plants to reduce nitrogen oxides (NO_x) emissions through chemical reaction with ammonia (NH_3). These technologies require the introduction of large quantities of NH_3 to reduce the NO_x emissions in a stoichiometric fashion. However, frequently a small amount of excess NH_3 is introduced that 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 high sensitivity of the technique.

The purpose of this verification test was 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 SCR or SNCR NO_x control technology. The test was conducted over a period of approximately 90 days and involved the continuous operation of the Picarro Model G1103-c at an operational coal-fired power plant. During testing, the Model G1103-c continuously monitored ammonia slip concentration in the flue gas downstream of NO_x control technology.

This verification test was conducted according to procedures specified in *Test/QA Plan for Verification of Cavity Ring-down Spectroscopy Systems For Ammonia Monitoring in Stack Gas* [4] (TQAP) and adhered to the quality system defined in the ETV AMS Center Quality Management Plan (QMP)[5]. The testing conducted satisfied EPA QA Category III requirements. The TQAP and/or this verification report were reviewed by:

- Charles Dene, Electric Power Research Institute (TQAP only)
- William Ollison, American Petroleum Institute
- Dennis Mikel, U.S. EPA
- Kristen Benedict, U.S. EPA (report only)

The Picarro Model G1103-c was evaluated in the field test on the following performance parameters:

- Accuracy
- Data completeness
- Operational factors including ease of use, maintenance requirements, and consumables used/waste generated.

An attempt was made to evaluate precision, calibration/zero drift, linearity, and response time in the field test through dynamic spiking with compressed standard gases. However, because of complications associated with delivering the compressed gases to the analyzer in the field (e.g., long equilibration times), these parameters were evaluated in laboratory testing subsequent to the field study. Duplicate reference method samples collected during the last week of field testing were used to assess the comparability of the CRDS measurements with the standard reference method results. Data completeness was determined from a review of the valid data collected during the verification testing period. Operational performance parameters such as ease of use, maintenance requirements, and consumables used/waste generated were determined from observations by the Battelle field testing staff and from on-site staff. This test was not intended to simulate long-term performance of the Model G1103-c at a monitoring site.

3.2 Field Site

Testing was performed at a full-scale coal fired power plant owned and operated by the Tennessee Valley Authority (TVA). Initially, the Model G1103-c was installed at a unit of the Kingston Fossil Plant in Kingston, TN on June 25, 2009, at a location downstream of the SCR and upstream of the air preheater (APH). However, because of low power demand, the unit on which the Model G1103-c was installed was not in use for several consecutive weeks. This prompted a move of the Model G1103-c to a different unit at the plant on July 20, 2009. After that installation, reference method sampling was performed on July 20-21, 2009, using a modified version of EPA CTM-027[3] to assess the ammonia concentration in the flue gas. The results of those reference measurements indicated that there was no detectable ammonia slip in the sample stream. Consequently, the decision was made to relocate the testing to a facility where appreciable ammonia slip levels were likely to be present.

An alternative test facility was identified and the Model G1103-c was moved and installed at the alternate power plant on July 24, 2009. Testing was conducted through the end of October. The power plant where testing was performed included multiple 200 megawatt boilers, each configured with SNCR NO_x reduction capabilities that involved the injection of an aqueous urea solution into each boiler. During testing, the Picarro Model G1103-c system was installed in an environmentally controlled instrument shelter to maintain temperature stability of the analyzer. The Model G1103-c was installed along with other continuous emission monitors (CEMs) and supplied with flue gas that was sampled from the superheated section of one boiler. The flue gas was drawn from the duct using a dilution probe (100:1 dilution) incorporating a particulate filter, and was delivered to the Model G1103-c through approximately 150-200 feet of heated (100 ºC) Teflon tubing. Dilution of the flue gas was deemed necessary to condition the sample and minimize potential condensation processes in the sample line.

3.3 Test Procedures

The flue gas delivered to the Model 1103-c was drawn from a section of duct work upstream of the APH and electrostatic precipitator (ESP). The ports for the reference method sampling were located directly in-line with the dilution probe delivering the flue gas to the Model G1103-c. Figure 3-1 shows the locations of the dilution probe and reference method sampling trains at the test facility. The dilution probe extended inward from the blue box mounted on the wall of the duct as shown in this figure. The diluted flue gas was delivered to the instrument trailer through the heated umbilical cord protruding from the box. The port used for the collection of the reference method samples was directly below the dilution sampling point, and is shown in Figure 3-1 with a sampling probe installed.

3.3.1 Reference Method Sampling

Reference sampling was performed according to CTM-027[3], with the following modifications:

- Sampling was not conducted isokinetically since only gaseous ammonia was measured by the Model G1103-c.
- Sampling was conducted with a nozzle since isokinetic sampling was not necessary.

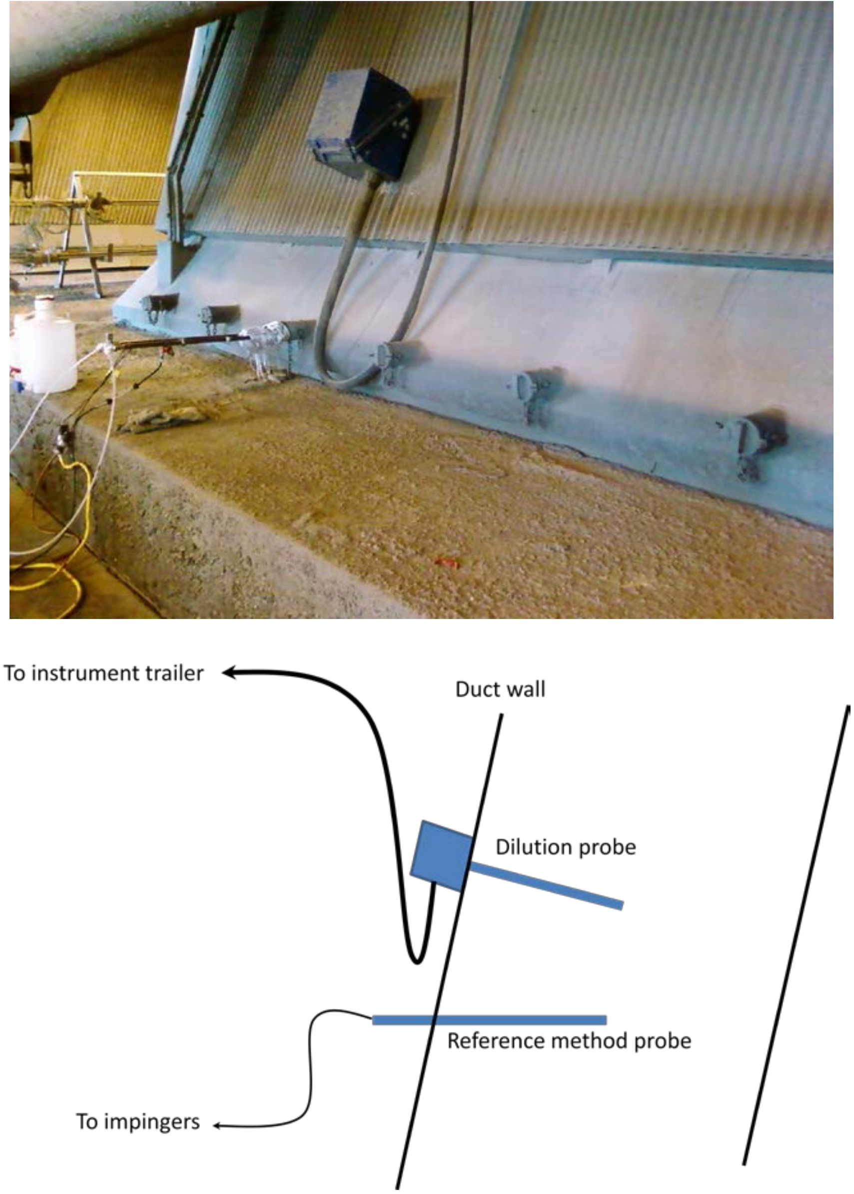

Figure 3-1. Dilution probe installation and reference method sampling ports.

Each reference method test run involved the simultaneous collection of samples from two collocated trains. Thus each reference method test run provided two reference ammonia samples for comparison to the Model G1103-c data. The sampling duration for each run was typically between 20 and 30 minutes. Each collected sample was analyzed on-site by ion chromatography (IC) for ammonia as ammonium ion (NH_4^+). For each test run the Model G1103-c results and the analytical results of the individual reference method measurements were normalized to 7% O_2. The reference method sampling schedule was compressed to three days to allow for set-up and tear-down activities for the test crew.

In addition to the reference method samples, field blank samples and field spike samples were recovered from separate sampling trains on each day that reference method samples were collected. Each field blank and spike train was transported to the sampling location and then recovered without sampling the flue gas. The samples were analyzed by the same procedures as normal samples.

3.3.2 Dynamic Spiking

The Picarro Model G1103-c was challenged in the field with ammonia compressed gas standards. Initially, the ammonia gas standard was supplied directly to the Model G1103-c (i.e., disconnected from the dilution probe) after off-line dynamic dilution with zero air using an Environics Model 6100 mass flow dilution system. However, this method was found impractical for routine testing activities because of the time required for equilibration of the dilution system and an apparent effect from residual ammonia gas in the sample delivery system.

Additionally, on-line dynamic spiking was attempted in the field by introducing the ammonia gas standard into the probe tip upstream of the particulate filter such that the ammonia spike passed through the dilution probe where it was mixed with diluent gas at a ratio of 1:100. However, because of the length of tubing required to deliver the compressed gas standard from the gas cylinder to the probe tip and then back to the analyzer, and the “sticky” nature of the ammonia gas, the time required for the ammonia concentration to equilibrate also made this method of dynamic spiking impractical. Furthermore, since several process-control continuous emission monitors (CEMs) sampled from the same gas stream, through the probe spiking required that these CEMs remain off-line during the dynamic spiking procedure. Extended periods of off-line operation was not acceptable to the plant operator. Consequently dynamic spiking was not performed in the field during this verification test. Instead, laboratory testing was conducted as described in Section 3.3.3 to assess precision, linearity, zero/calibration drift, and response time.

3.3.3 Laboratory Testing

After completion of the field testing, the Picarro Model G1103-c was challenged under laboratory conditions by supplying zero air and an ammonia reference standard diluted over a range of target concentrations. During this laboratory testing, ammonia was delivered to the Picarro Model G1103-c using a permeation oven (Vici Metronics, Dynacalibrator Model 340) operated at 30 ± 1 ºC with a certified ammonia permeation tube (Vici Metronics, Part Number 181-055-0140-F56-C30, certified rate 1,351 ng/min ± 0.15%). Dilution air was supplied using a zero air generator (Aadco, Model 737). Separate lines were used to deliver the ammonia and zero air to the Model G1103-c, to avoid delays due to equilibration of the delivery lines. Ammonia from the permeation oven was continuously flowed through the ammonia delivery line, even when not connected to the Model G1103-c, to prevent potential variations in ammonia concentrations caused by adsorption and desorption in the line. At each concentration level, the air flow rate through the permeation oven was measured using a calibrated flow meter (Bios, DryCal DC-2).

Reference ammonia concentrations [or C, in ng/L (or equivalently μg/m^3)] were calculated according to:

$$C = \frac{K \times P}{F} \tag{1}$$

where *K* is equal to 1.439 and is determined from the ideal gas constant and the molecular weight of ammonia, *P* is the permeation rate of the ammonia permeation tube (ng/min), and *F* is the dilution gas flow rate (L/min).

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures and all verification testing were performed in accordance with the test/QA plan for this verification test[4] and the quality management plan (QMP) for the AMS Center.[5] QA/QC procedures and results are described below.

4.1 Reference Method QA/QC

The following sections describe the QA/QC procedures employed in the collection and analysis of reference samples.

4.1.1 Precision

The precision of duplicate reference method results was calculated for each test run as

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

where R_1 and R_2 are the reference method results for the duplicate trains. Table 4-1 presents the results of the reference method analyses. Note that the two separate train results presented are each the average of duplicate analyses for each sample (see Section 4.1.2).

Because the boiler load varied throughout the testing period as the demand changed, the ammonia levels in the facility also varied. Consequently, during the reference testing the ammonia levels are likely to have varied considerably more than the anticipated ± 35% prescribed in the test/QA plan.[4] As a result, the reference data were not screened to identify outliers relative to the mean of the reference method data, but were screened to identify those paired samples that exceeded 35% RPD.

Of the 24 reference method sampling runs, 10 exhibited RPDs that exceeded 35% (Table 4-1). Of the test runs that exceeded 35% RPD, the RPD values ranged from 38 to 83% and had an average of 53%. No assignable cause was identified for the observed differences between the duplicate trains. These results are in contrast to previous reference method sampling at this facility during July 24 -25 that showed no significant differences between duplicate trains. Battelle's Quality Manager was on-site during the collection of several of the reference method samples to conduct a technical systems audit and observed nothing in the sample collection or analytical procedures to account for the observed differences. Each reference method sample was analyzed on-site by duplicate IC instruments (see Section 4.1.2) and showed good precision between the duplicate analyses. Previous spot checks of the ammonia concentration from different ports suggested a gradient across the width of the duct. However, since the duplicate probes were sampling from the same port, the proximity of the probes to one another during the sample collection (approximately 2-3 inches) was likely not sufficient to account for the observed differences. In three test runs, it appeared that one of the duplicate trains experienced a leak which resulted in measured ammonia concentrations near zero. Therefore, these test runs were flagged as outliers in Table 4-1 and were not used in data comparisons to the Model G1103-c. Thus, 21 sets of duplicate reference method results were compared to the results generated by the Model G1103-c.

Table 4-1. Summary of Reference Method Results

Date	Run	Ammonia Slip (ppm @ 7% O_2)		RPD
		Train 1	Train 2	
10/27/2009	1	11.7	28.4	83.1%
	2	17.8	36.0	67.7%
	3	22.1	27.1	20.2%
	4	19.3	20.5	6.1%
	5	15.8	13.5	16.0%
10/28/2009	6	1.5*	19.1	*
	7	2.2*	16.6	*
	8	16.4	17.7	7.6%
	9	19.0	15.3	21.6%
	10	21.2	11.7	57.9%
	11	17.1	10.0	52.6%
	12	18.6	19.2	3.0%
10/29/2009	13	16.4	12.9	24.0%
	14	14.1	18.6	27.7%
	15	13.4	9.9	30.6%
	16	13.6	13.9	2.7%
	17	9.0	0.2*	*
	18	9.5	15.6	48.8%
	19	13.9	21.6	43.4%
	20	15.9	24.7	43.4%
	21	14.1	20.6	37.6%
	22	13.1	15.0	13.9%
	23	10.0	16.5	49.6%
	24	9.1	14.5	46.1%

* Leak suspected in sampling train during sample collection. No RPD calculated.

4.1.2 Duplicate Analysis

Each reference method sample collected was analyzed on-site on duplicate, collocated IC instruments. To assess the analytical precision of the reference method, the RPD of the duplicate analyses for each sample were calculated and are presented in Table 4-2. On average, the results of the duplicate analyses from the collocated IC instruments were within 5%. In all but three instances among the 48 RPD values in Table 4-2, the calculated RPD was within 10%.

4.1.3 Field Blanks

Field blank samples were collected each day during reference method testing and analyzed to assess the level of potential contamination in the preparation, handling, and analysis of the reference method trains. For these field blanks, reference method trains were prepared and transported to the duct for sampling but were not used for sampling. The trains were recovered and analyzed on-site as normal samples using duplicate IC instruments. The results of the analysis of these samples are presented in Table 4-3 in terms of the equivalent flue gas ammonia concentration based on typical reference method sampling conditions. In all cases, the measured ammonia in the blank samples was below 1% of the calibration range and far below the expected concentration in the reference samples (typically 10 to 20 ppm).

Table 4-2. Summary of RPD in Duplicate Analyses for Reference Method Samples

Date	Run	RPD	
		Train 1	Train 2
10/27/2009	1	3.0%	5.0%
	2	1.2%	2.6%
	3	3.9%	0.3%
	4	3.4%	1.0%
	5	6.7%	1.6%
10/28/2009	6	8.5%	6.6%
	7	5.0%	1.5%
	8	0.6%	13.9%
	9	1.8%	2.4%
	10	5.1%	1.2%
	11	4.1%	2.3%
	12	2.2%	2.3%
10/29/2009	13	5.4%	1.1%
	14	5.5%	8.8%
	15	10.0%	0.1%
	16	7.1%	4.0%
	17	7.9%	31.9%
	18	5.8%	0.2%
	19	4.7%	2.2%
	20	4.3%	4.3%
	21	3.8%	0.8%
	22	4.7%	3.1%
	23	5.2%	1.7%
	24	3.5%	5.4%
Average		4.7%	4.3%
Standard Deviation		2.3%	6.6%
Maximum		10.0%	31.9%

Table 4-3. Results of Field Blank Analyses

Date	Ammonia (ppm)	
	IC 1	IC 2
10/27/2009	0.007	0
10/28/2009	0.011	0
10/29/2009	0.028	0.025

4.1.4 Spiked Trains

On each day of reference method sampling, a spiked reference method train was prepared using a National Institute of Standards and Technology (NIST)-traceable ammonia standard. These trains were prepared and transported to the sampling duct but were not used for sampling. The trains were recovered and analyzed on-site as normal samples using duplicate IC instruments. The results of the analysis of these samples are presented in Table 4-4 in terms of equivalent flue gas ammonia concentration. All spike recoveries were within 10% of the target NH_3 spikes.

Table 4-4. Results of Spiked Train Analyses

Date	Spike Target, (ppm)	NH_3 Analysis, (ppm)		Percent Difference	
		IC 1	IC 2	IC 1	IC 2
10/27/2009	1.66	1.50	1.53	-9.6%	-8.1%
10/28/2009	1.67	1.65	1.55	-1.5%	-7.7%
10/29/2009	1.45	1.38	1.43	-5.1%	-1.5%

4.2 Audits

4.2.1 Performance Evaluation Audit

Performance evaluation (PE) audits were made to ensure the quality of the critical measurements. The thermocouples used for the stack temperature measurements were audited by making collocated measurements using an independent thermocouple with a NIST-traceable calibration. The results of these audits showed agreement within 2% in absolute temperature between the test and audit thermocouples.

Two balances were used during the preparation and analysis of the reference method samples, one for measurements of large masses (e.g., > 100 g) and the other for more precise measurements of smaller weights (e.g., < 50 g). Both balances were audited using a set of NIST-traceable weights. The results of the PE audit showed differences between the measured and actual weights of less than 1%.

PE audit samples were prepared from an independent ammonium standard solution and were analyzed by the duplicate IC instruments used for the analysis of the reference method samples. Table 4-5 summarizes the results of those analyses. In all cases, the results of the PE audit showed differences between the measured and nominal concentrations of less than 10%.

Table 4-5. Performance Evaluation Audit Results of Ammonia Analysis by Ion Chromatography

Date	Nominal Concentration	Measured Concentration	
		IC 1 (% Diff)	IC 2 (% Diff)
10/26/2009	2.86 ppm	2.88 (0.5%)	3.13 (9.4%)
10/27/2009	2.86 ppm	2.89 (0.8%)	2.95 (3.1%)

4.2.2 Technical Systems Audit

A technical systems audit (TSA) was performed on October 28, 2009 by the Battelle Quality Manager, Mr. Zachary Willenberg. Because of difficulties in implementation of the field testing portion of this verification test and scheduling of the stack testing crew, the TSA was conducted near the end of the verification test rather than near the beginning of the test as called for in the TQAP. A checklist was prepared by Battelle QA Manager, and approved by the EPA QA Manager and used for performance of the audit. Minor discrepancies were noted between the actual procedures and those specified in CTM-027.[3] In particular, isokinetic sampling was not performed, the recovery of the sample train occurred at the collection point not at a different laboratory, and a single sample bottle was used for the collection of all sections of the sample train, as opposed to the use of separate bottles for the different sections. Also, a duct transverse was not conducted prior to collection of the reference samples. Rather, the sampling probes were inserted to the same depth as the dilution probe to allow for sampling under similar conditions. None of the items noted had any apparent bearing on the sampling or analytical results. An audit report was prepared and provided to the Verification Test Coordinator for review of any findings.

4.2.3 Data Quality Audit

Records generated in the verification test received a one-to-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed. At least 10% of the data generated were reviewed along with the laboratory record book. Data were reviewed from initial acquisition through final reporting. An audit report was prepared and provided to the Verification Test Coordinator for review of any findings.

4.3 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[5] The results of the TSA and ADQ were submitted to the EPA.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.1 are presented in this chapter. Qualitative observations were also used to evaluate verification test data.

5.1 Accuracy

The accuracy of Model G1103-c readings was evaluated in two ways. Firstly, the RPD of the Model G1103-c readings relative to the field reference results and the laboratory calibration check results was calculated to assess accuracy. The RPD was calculated by adapting Equation 2 in Section 4.1.1 (i.e., by using the field reference method results or the laboratory calibration check results and Model G1103-c results, instead of the duplicate reference results in the RPD calculation.)

Additionally, the relative accuracy (RA) of the Picarro Model G1103-c readings was also assessed by comparison to the reference method results from the field test and the laboratory calibration check results based on Equation 3:

$$RA = \frac{\left|\bar{d}\right| + t_{n-1}^{\alpha}\frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\% \qquad \textbf{\textit{(3)}}$$

where *d* refers to the difference between the calculated ammonia concentration from the reference method or calibration check and the average of the CRDS measurements recorded during the respective measurement periods, and $\bar{x}$ corresponds to the mean of the measured reference method results or calibration check concentration. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the $100(1 - \alpha)^{th}$ percentile of the distribution with n-1 degrees of freedom. The relative accuracy was determined for a α 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., $\frac{\left|\bar{d}\right|}{\bar{x}}$, where the superscript bar indicates the mean value of the differences, or of the reference values.

5.2 Linearity

Linearity was assessed from a linear regression analysis of the multipoint calibration data collected during the laboratory testing. The analysis used the theoretical ammonia concentrations delivered to the Picarro Model G1103-c as the independent variable and the measured results from the Model G1103-c as the dependent variable. The theoretical ammonia concentrations were based on delivery of a certified ammonia mass emission rate in a calibrated dilution flow rate. The results of the multipoint calibration were plotted and linearity was expressed in terms of slope, intercept, and coefficient of determination (r^2).

5.3 Precision

Since dynamic spiking was not performed in the field, precision was calculated in a different fashion than described in the TQAP. For this verification test, precision was calculated in terms of the percent relative standard deviation (RSD) of the CRDS measurements made during the zero/span checks conducted during the laboratory testing. During each zero/span check, the mean and standard deviation of the readings recorded for each check were calculated during the last five minutes of the check. The RSD was calculated as the standard deviation of the mean multiplied by 100 and divided by the mean, for each check. This measure of precision differs from the originally planned measure of precision in that the Model G1103-c was not measuring flue gas during the addition of the gas standard. Thus, precision measured here is a more direct measure of the instrument precision as it does not include variability in ammonia concentrations from the flue gas.

5.4 Zero/Calibration Drift

Calibration and zero drift were reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the Model G1103-c daily measurement of the same ammonia standard gas, and of zero gas. These results, along with the range of the data, indicate the daily variation in zero and standard readings over the two week period of laboratory zero/calibration drift measurements.

5.5 Response Time

Response time was assessed in terms of both the rise and fall times of the Model G1103-c when sampling the ammonia gas standard delivered during the zero/calibration drift checks. Rise time (i.e., 0% - 95% response time) was determined from the response when the gas delivered to the Model G1103-c was switched from zero gas to the ammonia standard. After a stable reading had been achieved, the fall time (i.e., the 100% to 5% response time) was determined from the response when the gas delivered to the Model G1103-c was switched from the ammonia standard back to zero gas.

5.6 Data Completeness

Data completeness was assessed based on the overall data return achieved by the Model G1103-c during the testing period. This calculation determined the total number of apparently valid data points reported by the monitoring system divided by the total number of data points potentially available in the entire field period. The causes of any incompleteness of data return were investigated based on operator observations or vendor records, and were noted in the discussion of data completeness results.

5.7 Operational Factors

Operational factors regarding ease of use, data output, maintenance needs, consumables used, etc., were evaluated based on observations recorded by Battelle and on-site support staff, and were explained by the vendor as needed. Battelle or testing staff recorded all activities performed on the monitoring systems in a laboratory record book maintained at the test site, including observations on the performance factors given above. Examples of information recorded in the record books include the use or replacement of any consumables; 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 Model G1103-c. These observations are summarized in this report to aid in describing the performance of the Model G1103-c.

Chapter 6
Test Results

Figure 6-1 shows the ammonia concentrations measured by the Model G1103-c along with the relative boiler load and urea injection rates at the host facility during the period from July 24-September 10, 2009. During this period the Model G1103-c sampled from the reheat side of Unit 2 at the host facility. The ammonia readings shown represent approximately 10-minute averages of the data from the Model G1103-c and are corrected for the 100-fold dilution introduced by the sampling probe. The boiler output and urea injection rate values are presented in arbitrary units. The periodic spikes in the Model G1103-c readings coincide with periods when the daily zero/span calibration checks were performed. During the morning of August 27, operation of the boiler was stopped because of low demand and the unit remained out of operation until September 11, when the Model G1103-c was moved to a different boiler.

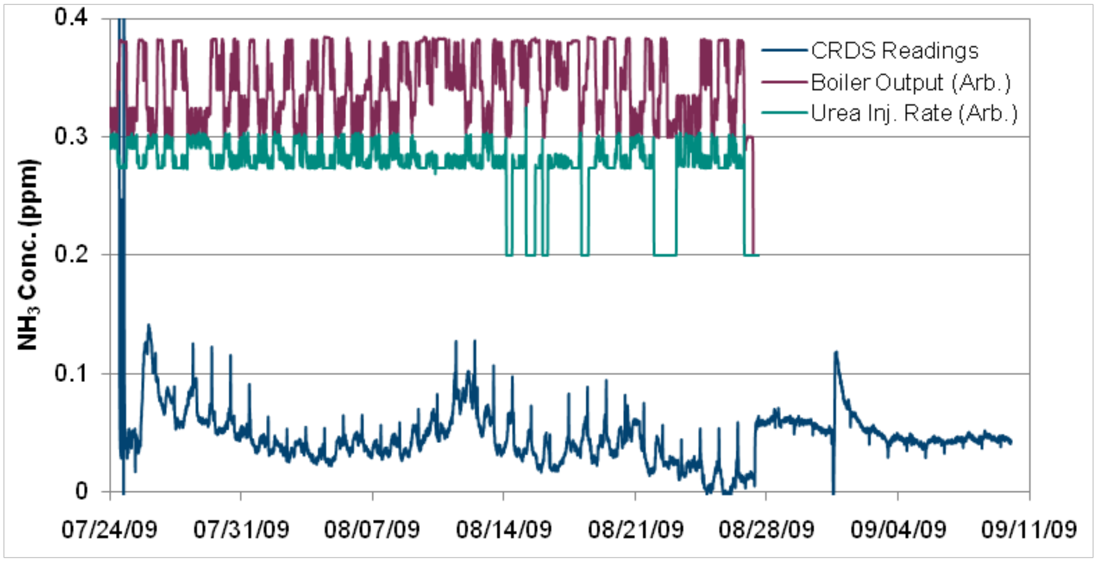

Figure 6-1. Comparison of Model G1103-c readings to the boiler output and urea injection rate between July 24 and September 11, 2009.

In general, the ammonia concentrations measured by the Model G1103-c during the July 24-September 11 period were substantially below the concentrations expected based on IC reference method sampling/analysis performed on Unit 2 to spot-check ammonia concentrations during instrument installation and shakedown on July 24-25. During that period, results from the reference method sampling indicated ammonia concentrations of approximately 1 to 5 ppm, whereas the Model G1103-c measurements of the flue gas during this period showed ammonia concentrations of approximately 0.020 to 0.060 ppm. The cause for the discrepancy could not be determined. To assess whether this was the result of delivering sample through the relatively long sampling line, the Model G1103-c was moved from the instrument trailer to the duct and several attempts were made to deliver conditioned flue gas to the Model G1103-c without the use of long sampling lines. In one instance, the flue gas was sampled through the reference method probe and conditioned using a Baldwin Environmental Model 10410 electronic water condenser prior to delivery to the Model G1103-c. Also, flue gas was collected directly into a Tedlar sampling bag and delivered to the Model G1103-c, both with and without dilution with nitrogen. However, in all instances upon cooling the vapor phase ammonia appeared to co-condense with the water vapor in the flue gas. Analysis of the condensate indicated ammonia concentrations consistent with the reference method measurements, indicating the presence of ammonia in the flue gas. No attempt was made to collect an impinger sample of the diluted gas (similar to the reference method collection) since the 100-fold dilution of the flue gas would have resulted in a sampling time of approximately 2,000 minutes. Thus, during the time when the Model G-1103c was installed on Unit 2, there was no clear evidence that ammonia concentrations measured by the Model G-1103c in the dilution probe were representative of the actual concentrations in the duct.

On September 11, the sampling point was switched such that the Model G1103-c sampled from the superheat side of Unit 1 rather than the reheat side of Unit 2 at the host facility. Prior to routine sampling from Unit 1, several dynamic spiking tests were performed using compressed gas standards to confirm proper operation of the Model G1103-c. Off-line dynamic spiking was performed by disconnecting the Model G1103-c from the dilution probe and delivering known concentrations of ammonia to the Model G1103-c using an off-line dynamic dilution system (Environics, Model 6100) with zero air as the ammonia diluent. The results of those tests indicated that although the Model G1103-c responded to the ammonia gas standards that were supplied at the expected concentrations, there were several drawbacks to the sample delivery that precluded routine use of this testing method for challenging the Model G1103-c. In particular, a substantial equilibration time was associated with delivery of either ammonia or zero air, and successive delivery of a target ammonia concentration separated by delivery of zero air suggested a potential “memory effect”. Subsequent laboratory testing used separate sample lines for the NH_3 standard and the zero air with a continuous flow through the NH_3 line to prevent the need for equilibration within the calibration system.

In addition to the off-line dynamic spiking tests, on-line dynamic spiking was performed using through-the-probe delivery of the compressed ammonia gas standard. The calibration compressed gas (100 ppm NH_3 in N_2) was introduced to the calibration line at the instrument shelter and sent through the calibration line to the probe where it was subsequently diluted (100:1) and travelled in dilute form back through the sampling line to the analyzer. Both the calibration line and sampling lines were heated Teflon tubing approximately 150 feet in length. Figure 6-2 shows the response of the Model G1103-c to the ammonia standard during the through-the-probe spiking.

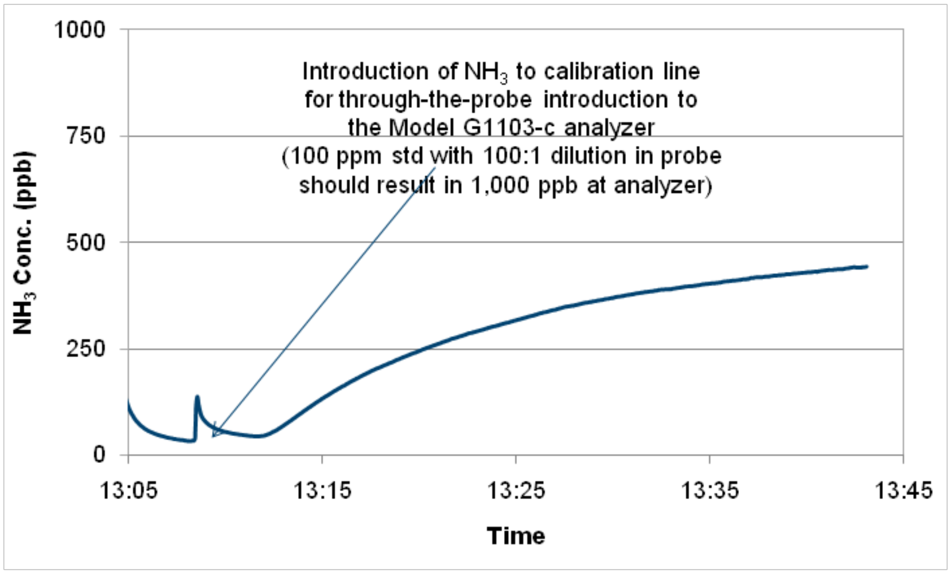

Figure 6-2. Results of through-the-probe dynamic spiking.

Figure 6-2 illustrates a gradual increase in the measured ammonia beginning several minutes after initial introduction of the standard gas. The relatively long period (approximately 30 minutes) required for the ammonia signal to equilibrate is likely the result of equilibration of the calibration and sampling lines. Although the ammonia signal did not reach equilibrium during the spiking, it does not appear that the signal would have reached the expected 1,000 ppb level. It is not clear whether the apparent low response is attributable to the Model G1103-c or to sample loss in the calibration or sampling lines. However, subsequent laboratory testing using short sampling lines indicated response times on the order of 2-5 minutes rather than the much longer response time observed here. Continued through-the-probe dynamic spiking was not practical because of the large volume of gas consumed during this procedure, due to the required over-pressurization of the probe to prevent entrainment of flue gas. Furthermore, through-the-probe spiking required that the several process control CEMs remained off-line during the dynamic spiking procedure, which was not acceptable to the plant operator.

Figure 6-3 shows the ammonia concentrations measured by the Model G1103-c along with the relative boiler load and urea injection rates during the period from September 11- October 29, 2009. During this period the Model G1103-c was sampling from the superheat side of Unit 1 at the host facility. The ammonia readings shown in Figure 6-3 represent approximately 10-minute averages of the data from the Model G1103-c and are corrected for the 100-fold dilution introduced by the sampling probe. The boiler output and urea injection rate values are presented in arbitrary units. Although less obvious than in Figure 6-1, there are periodic spikes in the Model G1103-c readings which coincide with periods when the daily zero/span calibration checks were performed. Operation of the boiler was stopped because of low demand on the evening of October 22 and remained off until the evening of October 25. During this period, the readings from the Model G1103-c showed a gradual decay to a concentration corresponding to approximately 0.9 ppm. Since there was no urea injection during this period, these readings may indicate the release of adsorbed ammonia from the walls of the sampling lines, or from the internal surfaces of the facility duct work.

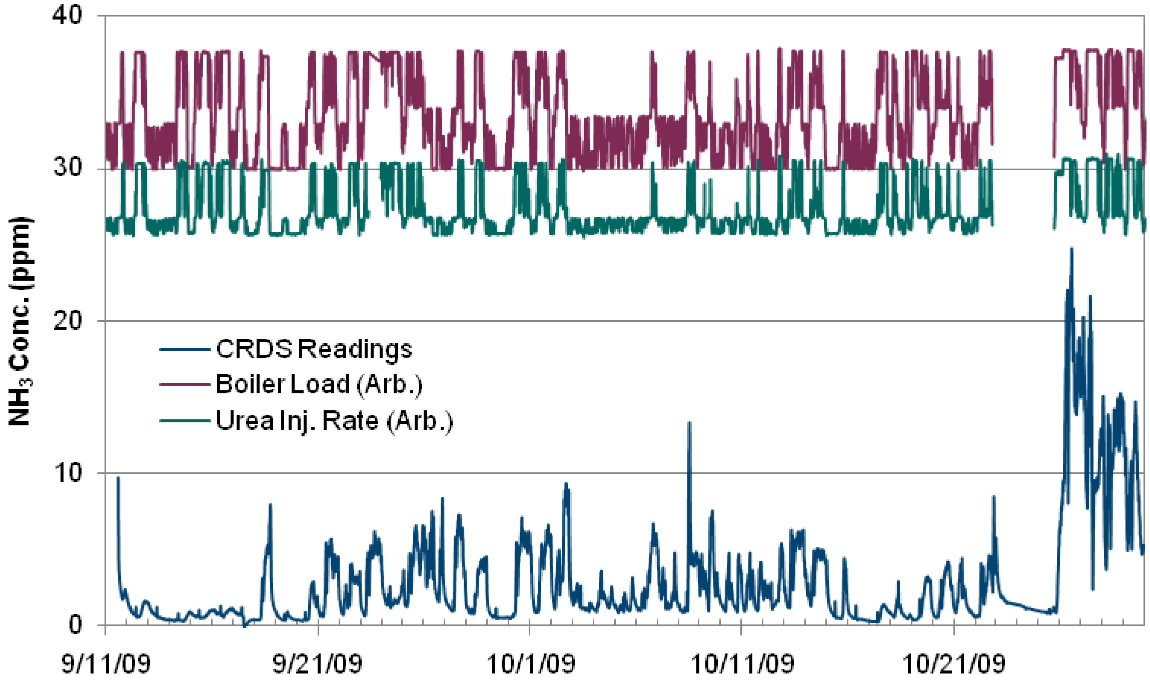

Figure 6-3. Comparison of CRDS readings to the boiler output and urea injection rate between September 11 - October 29, 2009.

6.1 Accuracy

Reference method sampling was performed from October 27 to October 29, 2009 and included a total of 24 sampling runs. Note that although some reference method samples were collected on July 24-25th, because various manipulations to the Model G1103-c analyzer were performed during the collection of those samples, they are not included in the evaluation of accuracy. These manipulations included attempts to bypass the dilution probe and sampling line and deliver conditioned flue gas directly to the Model 1103-c from the reference method probe. During the majority of the reference sampling periods the Model 1103-c was not installed and sampling from the dilution probe system.

Figures 6-4 to 6-6 show the results from the duplicate reference method trains, along with the Model G1103-c measurements for each day of sampling presented as 2-minute rolling averages. From these figures, the significant disparity between the duplicate reference method sampling trains for some of the test runs is evident; those differences were noted in Section 4.1.1 and Table 4-1. For example the first two test runs on both October 27 and 28 (Figures 6-6 and 6-7) show substantial differences between the duplicate trains.

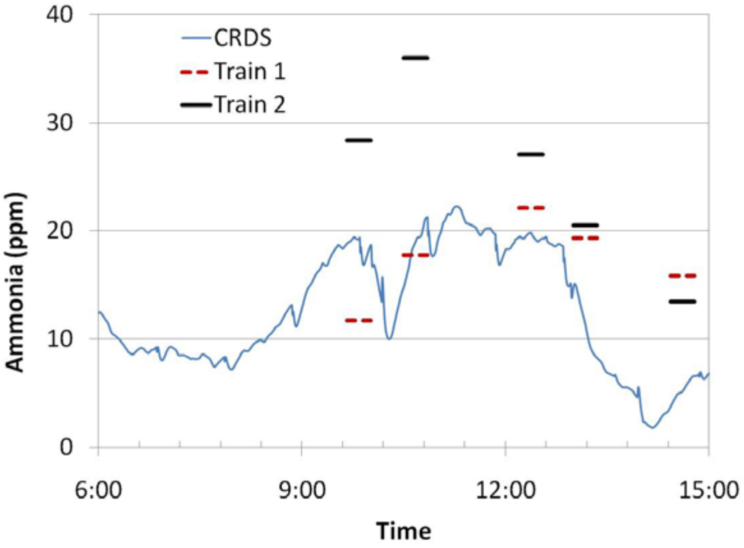

Figure 6-4. Comparison of reference method results and Model G1103-c measurements from October 27, 2009.

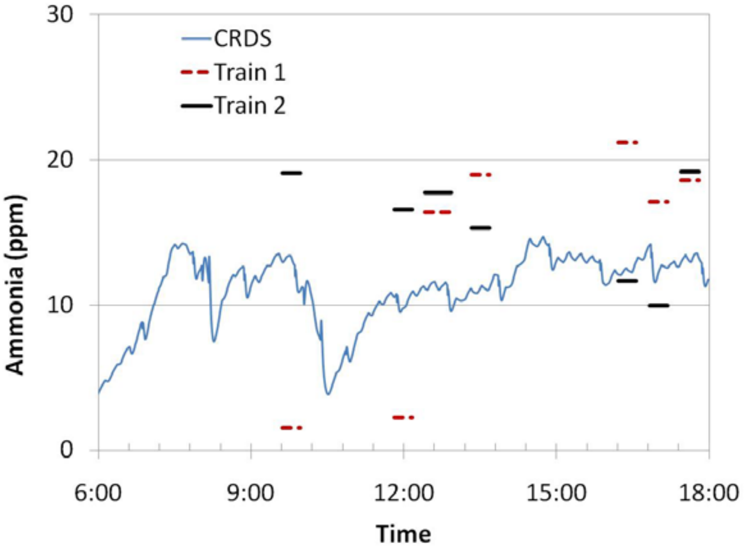

Figure 6-5. Comparison of reference method results and Model G1103-c measurements from October 28, 2009.

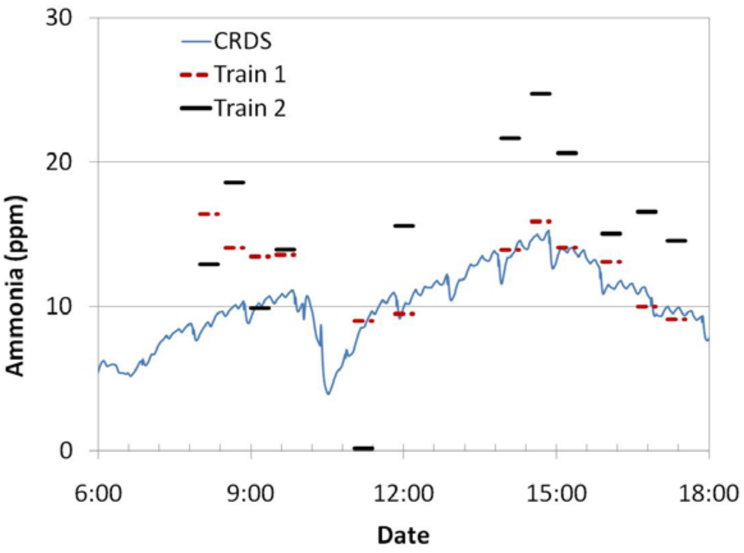

Figure 6-6. Comparison of reference method results and Model G1103-c measurements from October 29, 2009.

Table 6-1 presents a comparison of the reference method results from the field testing portion of this verification test and the dilution corrected average of the 2-minute rolling average of the measurements recorded by the Model G1103-c during each of the reference method test runs. The results in this table have all been normalized to a 7% O_2 concentration in the flue gas. The relative percent difference between the Model G1103-c average and the average of the duplicate reference method trains is also presented for each test run. For each test run, the average of the readings from the Model G1103-c was less than the average of the duplicate reference method results. (Note: For three test runs, one of the duplicate reference method trains was identified as an outlier and is not included in the calculations.) These results indicate that the Model G1103-c readings were, on average, 25% lower than the corresponding reference method results during this verification test. However, it should be noted that reference method samples were collected directly at the duct, whereas the sample analyzed by the Model G1103-c was sampled from the duct through the dilution probe where the flue gas was diluted by a factor of 100 and delivered through approximately 150 ft of heated Teflon tubing to the Model G1103-c. The Model G1103-c system was installed in an environmentally controlled instrument shelter installed along with other CEMs to maintain temperature stability of the analyzer. The RA was calculated from these results according to Equation 1 in Section 5.1 and is shown in Table 6-2 to be 31.9%, and represents the RA of the complete sampling system, including the dilution probe, the transfer line, and the G1103-c itself.

Table 6-2 presents a comparison of the calibration check results from the laboratory testing portion of this verification test and the 2-minute rolling average of the measurements recorded by the Model G1103-c during each calibration check. These results indicate that the Model G1103-c readings were on average 4.3% higher than the corresponding reference gas standard concentration delivered during the calibration checks. The relative accuracy of the Model G1103-c was calculated from these results according to Equation 1 in Section 5.1 and is shown in Table 6-2 to be 4.6%.

Table 6-1. Comparison of Field Test Reference Method Results and Average Model G1103-c Measurements

Date	Run	Ammonia Concentration (ppm)		RPD
		Ave. CRDS	Ave. Ref. (Train 1, Train 2)	
10/27/2009	1	18.8	20.0 (11.7, 28.4)	-6.3%
	2	19.2	26.9 (17.8, 36.0)	-28.6%
	3	19.7	24.6 (22.1, 27.1)	-19.9%
	4	11.7	19.9 (19.3, 20.5)	-41.4%
	5	5.40	14.7 (15.8, 13.5)	-63.0%
10/28/2009	6	12.9	19.1 (*, 19.1)	-
	7	10.5	16.6 (*, 16.6)	-
	8	11.5	17.1 (16.4, 17.7)	-32.5%
	9	11.5	17.2 (19.0, 15.3)	-33.2%
	10	13.0	16.4 (21.2, 11.7)	-20.9%
	11	12.8	13.6 (17.1, 10.0)	-5.6%
	12	13.6	18.9 (18.6, 19.2)	-28.1%
10/29/2009	13	9.20	14.6 (16.4. 12.9)	-37.5%
	14	10.1	16.3 (14.1, 18.6)	-38.3%
	15	10.3	11.7 (13.4, 9.90)	-11.3%
	16	11.0	13.8 (13.6, 13.9)	-19.8%
	17	8.90	9.00 (9.00, *)	-
	18	10.2	12.5 (9.50, 15.6)	-18.9%
	19	13.6	17.8 (13.9, 21.6)	-23.7%
	20	15.3	20.3 (15.9, 24.7)	-24.6%
	21	14.5	17.3 (14.1, 20.6)	-16.6%
	22	11.2	14.1 (13.1, 15.0)	-20.1%
	23	10.6	13.3 (10.0, 16.5)	-19.8%
	24	9.50	11.8 (9.10, 14.5)	-19.5%
	Ave.	12.3	16.8	-25.2%
	Max.	19.7	26.9	-63.0%
	Min.	5.40	11.7	-5.6%
			RA	31.9%

* Outlier. Leak in sampling train suspected but not confirmed.
RA = Relative accuracy (Section 5.1)

Table 6-2. Comparison of Laboratory Calibration Check Results and Average Model G1103-c Measurements

Date	Theoretical Concentration (ppb)	Measured Span Concentration (ppb)	% Difference from Theoretical
8/6/10	1,530	1,598	4.4%
8/9/10	1,520	1,589	4.5%
8/10/10	1,502	1,585	5.5%
	1,521	1,586	4.3%
8/11/10	1,518	1,581	4.1%
8/12/10	1,521	1,586	4.3%
	1,515	1,587	4.8%
8/13/10	1,518	1,585	4.4%
	1,523	1,582	3.9%
8/16/10	1,521	1,579	3.8%
8/17/10	1,519	1,580	4.0%
8/18/10	1,521	1,579	3.8%
Mean	1,519	1,585	4.3%
Maximum	1,530	1,598	5.5%
Minimum	1,502	1,579	3.8%
RA			4.6%

6.2 Linearity

Figures 6-7 and 6-8 show the linear regression results of the multipoint calibration checks of the Model G1103-c conducted at the beginning and end of the laboratory testing, respectively. In these figures, the measured concentrations are plotted as a function of the theoretical ammonia concentrations delivered to the Model G1103-c based on the measured flow rates from the dilution system. The results of these linear regressions are presented in Table 6-3.

For both the initial and final multipoint calibration of the Model G1103-c, these results show slopes within 4% of unity, with intercepts that are statistically indistinguishable from zero, and r^2 values of greater than 0.995. It should be noted that the accuracy of the output flow rate of the permeation oven used to deliver the ammonia is lowest at the highest ammonia concentration (i.e., lowest dilution flow) and has an expected uncertainty of ~2 to 5% at the highest concentrations.

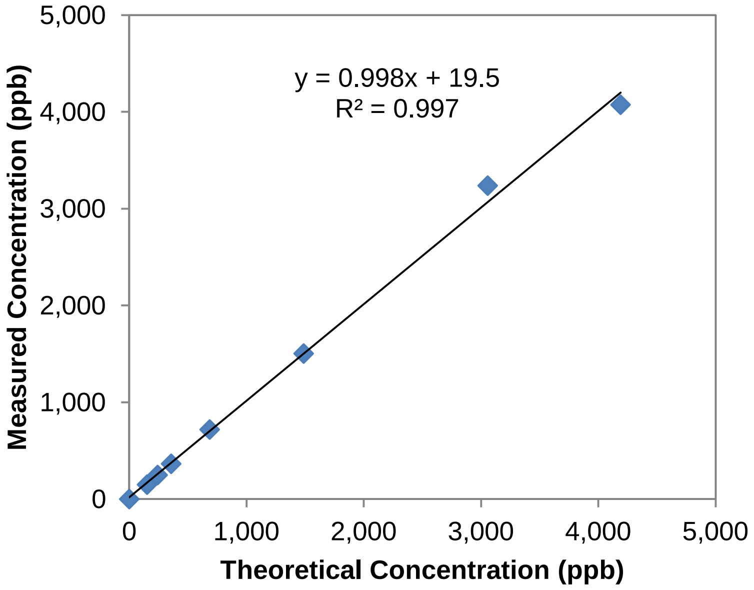

Figure 6-7. Initial multi-point calibration of Picarro Model G1103-c.

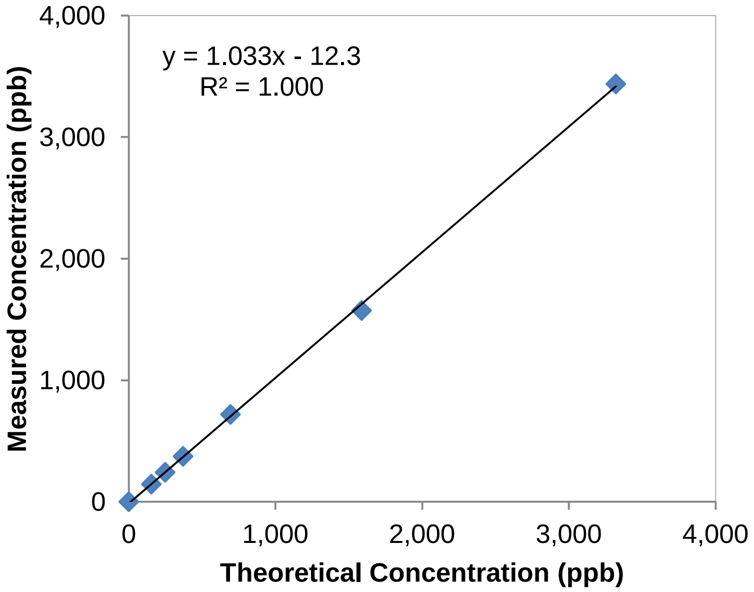

Figure 6-8. Final multi-point calibration of Picarro Model G1103-c.

Table 6-3. Linearity Results for the Model G1103-c

	Slope	Intercept (ppb)	r^2
Initial	0.998 (0.021)	19.5 (41.0)	0.997
Final	1.033 (0.009)	-12.3 (13.3)	1.000

6.3 Precision

Tables 6-4 and 6-5, respectively, shows the results of the zero and span checks of the Model G1103-c conducted during the laboratory testing. The results presented in these tables are calculated from the 2-minute average output values of the Model G1103-c. Included in Table 6-5 are the known ammonia concentrations delivered during the span checks and the calculated difference between the measured and known ammonia concentrations. Each table also presents the mean, standard deviation, and range of the respective zero/span checks.

As shown in Table 6-4 over the course of the two week laboratory testing, the average concentrations reported by the Model G1103-c during the daily zero checks were between 0.21 and 2.19 ppb, with an average value of 1.03 ppb. The standard deviations of the measurements during these zero checks were between 0.04 and 0.11 ppb, with an average value of 0.07 ppb. Although presented, the relative standard deviations have little meaning when assessing precision for zero checks, since as the mean concentration approaches zero the relative standard deviation dramatically increases. The results in Table 6-5 show the average measured concentrations during the span checks were between 1,579 and 1,598 ppb, with an average value of 1,585 ppb. The measured concentrations of the span checks exceeded the theoretical concentrations in all cases. The percent differences between the measured and theoretical values were between 3.8% and 5.5%, with an average value of 4.3%. The standard deviations of the measurements during these zero checks were between 1.1 and 7.5 ppb, with an average value of 2.0 ppb. The calculated relative standard deviations ranged from 0.07% to 0.47%, with an average value of 0.13%.

Table 6-4. Results of Zero Checks of the Model G1103-c

Date	Measured Zero Concentration (ppb)	Standard Deviation (ppb)	RSD (%)
8/6/10	0.770	0.06	8.0%
	2.12	0.06	3.0%
8/9/10	2.08	0.06	2.8%
8/10/10	0.750	0.04	5.7%
	2.19	0.11	4.9%
8/11/10	0.600	0.08	13.1%
8/12/10	0.550	0.07	12.2%
	1.40	0.06	4.2%
8/13/10	0.390	0.05	12.6%
	1.81	0.07	4.1%
8/16/10	0.250	0.04	16.6%
8/17/10	0.210	0.05	24.9%
8/18/10	0.280	0.09	30.9%
Mean	1.03	0.07	11.3%
Maximum	2.19	0.11	30.9%
Minimum	0.210	0.04	2.8%
Standard Deviation	0.770	0.02	9.1%

Table 6-5. Results of Span Checks of the Model G1103-c

Date	Theoretical Concentration (ppb)	Measured Span Concentration (ppb)	% Difference from Theoretical	Standard Deviation (ppb)	RSD
8/6/10	1,530	1,598	4.4%	1.9	0.12%
8/9/10	1,520	1,589	4.5%	1.3	0.08%
8/10/10	1,502	1,585	5.5%	2.1	0.13%
	1,521	1,586	4.3%	2.4	0.15%
8/11/10	1,518	1,581	4.1%	1.2	0.08%
8/12/10	1,521	1,586	4.3%	1.1	0.07%
	1,515	1,587	4.8%	1.4	0.09%
8/13/10	1,518	1,585	4.4%	1.2	0.07%
	1,523	1,582	3.9%	1.1	0.07%
8/16/10	1,521	1,579	3.8%	1.1	0.07%
8/17/10	1,519	1,580	4.0%	7.5	0.47%
8/18/10	1,521	1,579	3.8%	1.8	0.11%
Mean	1,519	1,585	4.3%	2.0	0.13%
Maximum	1,530	1,598	5.5%	7.5	0.47%
Minimum	1,502	1,579	3.8%	1.1	0.07%
St. Dev.	6.5	5.3	0.5%	1.8	0.12%

6.4 Zero/span drift

The results of the zero/span checks were used to assess zero/span drift of the Model G1103-c. Table 6-6 presents the results of the zero/span check measurements along with the calculated differences between successive zero/span checks. These results show no clear trends in drift of either the zero or span readings of the Model G1103-c over the course of the laboratory testing.

Table 6-6. Summary of Zero/Span Drift Checks of the Model G1103-c

Date	Measured Zero Concentration (ppb)	Change from Previous (ppb)	Measured Span Concentration (ppb)	Change from Previous (ppb)
8/6/10	0.770		1,598	
8/9/10	2.08	1.31	1,589	-9
8/10/10	0.750	-1.33	1,585	-4
	2.19	1.44	1,586	1
8/11/10	0.600	-1.59	1,581	-5
8/12/10	0.550	-0.05	1,586	5
	1.40	0.85	1,587	1
8/13/10	0.390	-1.01	1,585	-2
	1.81	1.42	1,582	-3
8/16/10	0.250	-1.56	1,579	-3
8/17/10	0.210	-0.04	1,580	1
8/18/10	0.280	0.07	1,579	-1

6.5 Response Time

Table 6-7 presents the calculated rise and fall times for the Model G1103-c, for the no-average, 30-second average, and 2-minute average output results from the daily zero/span checks.

Table 6-7. Summary of Rise/Fall Times of the Model G1103-c

Date	Rise Time			Fall Time		
	No average	30-sec average	2-min Average	No average	30-sec average	2-min average
8/6/10	03:54	03:59	05:33	00:39	01:04	03:47
8/9/10	01:52	02:06	04:18	01:17	01:42	04:18
8/10/10	02:36	02:46	04:43	00:34	01:03	03:44
	01:57	02:12	04:19	00:39	01:08	03:49
8/11/10	02:37	02:57	04:48	00:44	01:08	03:47
8/12/10	02:31	02:41	04:42	00:39	01:03	03:43
	02:11	02:21	04:27	00:35	01:04	03:40
8/13/10	02:16	02:36	04:38	00:39	01:04	03:44
	02:06	02:16	04:22	00:39	01:03	03:44
8/16/10	02:15	02:35	04:36	00:39	01:04	03:44
8/17/10	02:35	02:55	04:50	00:39	01:03	03:43
8/18/10	02:21	02:41	04:46	00:38	01:03	03:44
Mean	02:26	02:40	04:40	00:42	01:07	02:26
Maximum	03:54	03:59	05:33	01:17	01:42	03:54
Minimum	01:52	02:06	04:18	00:34	01:03	01:52
Std. Deviation	00:32	00:30	00:20	00:11	00:11	00:32

Table 6-6 shows that the fall time of the Model G1103-c was consistently shorter than the rise time, with the mean no-average rise and fall times being 2 min 26 sec and 42 sec, respectively.

6.6 Data Completeness

Throughout the verification test periods including the field and laboratory testing, the Model G1103-c recorded data approximately every three seconds with no gaps in the data. Except for periods when installation, relocation, or maintenance activities were performed, the Model G1103-c exhibited 100% data completeness.

6.7 Operational Factors

6.7.1 Ease of use

Subsequent to the initial installation, the instrument was uninstalled, repackaged, and reinstalled twice during the verification test. These subsequent installations were performed by Battelle and on-site support staff, after receiving training from Picarro representatives during the initial installation. Operation of the Model G1103-c was automated upon instrument startup and required no external intervention. Individual space delimited text data files were automatically generated for each day of testing and saved on an internal hard drive in separate data folders identified with the corresponding date.

6.7.2 *Maintenance*

Table 6-8 presents a summary of the activities performed on the Model G1103-c system during the verification test. The installation of the instrument was initially performed by two representatives of Picarro, who completed the installation in approximately one hour, after which the Picarro representatives performed a variety of diagnostic tests to ensure proper operation and optimize system performance. Those diagnostic tests were performed over the course of approximately two days, although the durations of the individual activities were not recorded. Table 6-8 shows that the Model G1103-c had minimal down time, even with multiple installations in different sampling locations.

Table 6-8. Summary of Maintenance Activities Performed During Verification Testing

Date	Duration	Activity	Down Time
6/25/09	55 minutes	Instrument unpacking, installation	NA
6/25/09 – 6/26/09[1]	Various	Instrument diagnostic checks	NA
7/20/09	~45 minutes	Instrument relocation to operational boiler	~45 minutes
7/22/09	~45 minutes	Tear-down and instrument repacking	~45 minutes
7/24/09	~45 minutes	Instrument installation at new facility	~45 minutes
7/24/09 – 9/11/09	49 days	Routine operation	NA
9/11/09[2]	~5 minutes	Switch sampling line from Unit 2 to Unit 1	~5 minutes
9/11/09	~2.5 hours	Dynamic spiking tests	NA
9/11/09	~45 minutes	Through-the-probe calibration tests	NA
9/11/09 – 10/29/09	48 days	Routine operation	NA
10/26/09 – 10/29/09	Various	Reference method sampling	NA
10/30/09	~60 minutes	Instrument shutdown, removal, and packaging	NA

[1] Although the Model G1103-c was installed and operating, vendor representatives elected to perform a variety of diagnostic checks on June 25 and 26 to ensure proper operation. The durations of the individual diagnostic activities were not recorded separately.

[2] Unit 2 was off-line for two weeks because of low demand. The sampling line was switched to sample from the Superheat side of Unit 1.

6.7.3 *Consumables Used/Waste Generated*

The Model G1103-c uses no compressed gases, reagents, or supplies for normal operation. Thus during routine monitoring activities, no consumables were used and no waste was generated. Compressed gas standards and dilution gas are needed for delivery of calibration standards to the analyzer.

Chapter 7
Performance Summary

Table 7-1 presents a summary of the results of the verification of the Picarro Model G1103-c during this verification test.

Table 7-1. Summary of Selected Verification Test Results for the Picarro Model G1103-c

Performance Parameter	Method of Evaluation	Results						
Linearity	Linear regression of multipoint calibration results		**Slope**	**Intercept**	**r^2**			
		Initial	0.998 (±0.021)	19.5 (±41.0)	0.997			
		Final	1.03 (±0.009)	-12.3 (±13.3)	1.000			
Accuracy	Comparison to reference method results		**Laboratory Testing**	**Field Testing[a]**				
		RSD	4.3%	-25.2%				
		RA	4.6%	31.9%				
Precision	Evaluation of daily zero/span check results		**Zero Check**	**Span Check**				
		Mean	1.03 ppb	1590 ppb				
		St. Dev.	0.77 ppb	5.3 ppb				
		RSD	11.3%	0.13%				
		% Diff. from Theory	N/A	4.3%				
Zero/Span Drift	Evaluation of daily zero/span check results	• No apparent trend in changes between zero and span checks						
Response Time	Calculated from daily zero/span check results		**Rise Time**			**Fall Time**		
		Ave Time	**0 sec**	**30 sec**	**2 min**	**0 sec**	**30 sec**	**2 min**
		Mean	02:26	02:40	04:40	00:42	01:07	02:26
		Std. Dev.	00:32	00:30	00:20	00:11	00:11	00:32
Data Completeness	Ratio of number of data points collected to number of potential data points that could have been collected	• Completeness = 100%						

Ease of use	Operator observations	- Initial installation was completed in ~45 minutes by vendor representatives - Subsequent installations were performed by Battelle and on-site support staff in ~45 minutes - Operation is automated upon powering and requires no external intervention - Operated unattended for duration of testing period - Daily space delimited data files are generated automatically and stored in separate data files on an internal hard drive
Maintenance	Operator observations	- No routine maintenance activities were performed during testing - Non-routine maintenance included diagnostic tests performed after initial installation but prior to routine monitoring periods
Consumables/ waste generated	Operator observations	- No consumables were used and no waste was generated during routine monitoring activities - Compressed gas standards were used for dynamic spiking tests; the waste gas stream from the dynamic spiking was combined with the excess flue gas

[a] These results are based on measurements from the entire field sampling system, including the dilution probe, the transfer line from the duct, and the Model G1103-c, compared with reference method measurements taken directly from the duct.

Chapter 8
References

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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. Battelle, Test/QA Plan for Verification of Cavity Ring-down Spectroscopy Systems For Ammonia Monitoring in Stack Gas, prepared by Battelle, Columbus, Ohio, June 2009.

5. 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.