September 2004

Revised

Environmental Technology Verification Report

SIEMENS Laser Analytics AB

LDS 3000

CONTINUOUS EMISSION MONITOR FOR AMMONIA

Prepared by
Battelle

Under a cooperative agreement with

U.S. Environmental Protection Agency

September 2004

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Siemens Laser Analytics AB
LDS 3000 Continuous Emission Monitor for Ammonia

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. Environmental Protection Agency (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 verification 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.

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List of Abbreviations

AEP	American Electric Power
AMS	Advanced Monitoring Systems
ASTM	American Society of Testing and Materials
CEM	continuous emission monitor
cm	centimeter
CTM	conditional test method
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
ft^3	cubic foot
H_2O	water
I/O	input/output
IC	ion chromatography
ISE	ion selective electrode
L	liter
lb	pound
m	meter
mg	milligram
min	minute
NH_3	ammonia
NH_4^+	ammonium
NIST	National Institute of Standards and Technology
NO_x	nitrogen oxide
PE	performance evaluation
ppmv	parts per million volume
ppmwv	parts per million, wet volume basis
QA	quality assurance
QC	quality control
QMP	quality management plan
RSD	relative standard deviation
SCR	selective catalytic reduction
TSA	technical systems audit

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 (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of a continuous emission monitor (CEM) for ammonia (NH_3), the Siemens Laser Analytics AB LDS 3000 (LDS 3000).

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the LDS 3000. The following is a description of the LDS 3000, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The LDS 3000 is designed to measure gases in situ and in real time in harsh environments and to provide dynamic dust load compensation, interference-free operation, and minimized maintenance by means of a patented built-in calibration system.

The operation of the LDS 3000 is based on Beer-Lambert’s law: light propagating through a gas mixture will be absorbed by the presence of gas molecules. Second derivative spectroscopy is used to enhance resolution and immunity against hostile environments (flames, etc.) and minimize zero and span drift. The LDS 3000 uses the light emitted from a semiconductor laser tuned over a single absorption line of the gas to be measured. The light is split into five paths using a passive optical splitter. One, two, or three paths are used for the measurement channels. Two internal paths are used for internal checks of the laser: one is used to monitor the laser power, and one is used in an internal measurement path. This latter path is resident inside the central unit of the LDS 3000 (Figure 2-1) and uses a glass reference cell.

Figure 2-1. Siemens Laser Analytics AB LDS 3000 Ammonia CEM

A complete LDS 3000 system consists of the central unit, the standard sensor, and the hybrid cable connecting them. The central unit contains the critical components and is placed in a control room or similar environment. It incorporates a control panel with display, built-in keyboard, control computer, laser, reference cell, control electronics for the laser, and slots for up to three receiver channels. The central unit also handles a large number of input/output (I/O) units for 4 to 20 milliampere I/O and relay output. The standard sensor consists of a transmitter and a receiver intended to be positioned on opposite sides of the duct. The transmitter contains provisions for a fiber-optic connector; the receiver contains a photo detector and some minor electronics. Normally, the sensor optics are protected from the measurement environment by use of pressurized instrument air or air blower fans. The hybrid cable is composed of two optical fibers and two electrical wires for 24 volts direct current. (The loop cable interconnecting the sensor pair does not contain the single-mode fiber.)

The central unit weighs 66 pounds (lb) and measures 16 inches x 19 inches x 15 inches. Its power consumption is 150 Watts, and it runs on 85 to 264 volts alternating current, 50/60 hertz, 200 volt-amperes. The standard sensor weighs 22 lb and measures 18 inches x 8 inches x 6 inches.

In this verification test, the LDS 3000 was set up to provide a reading of NH_3 concentration every 15 seconds, by means of a data smoothing algorithm implemented in the LDS 3000 software, as described in Section 3.2.

Chapter 3
Test Design and Procedures

3.1 Introduction

The objective of this verification test of the LDS 3000 was to evaluate its ability to determine gaseous ammonia in flue gas under normal operating conditions in a full-scale coal-fired power plant equipped with selective catalytic reduction (SCR) nitrogen oxide (NO_x) control technology.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Continuous Emission Monitors for Ammonia at a Coal-Fired Facility*(1) at American Electric Power's (AEP's) Mountaineer Plant in New Haven, West Virginia, from July 15 to August 15, 2003.

The performance parameters addressed by the test/QA plan included:

- Agreement with standards
- Relative accuracy
- Linearity
- Precision
- Calibration and zero drift
- Response time
- Ease of use
- Data completeness.

Agreement with standards was assessed for the LDS 3000 based on the differences between LDS 3000 readings and known concentrations of ammonia prepared from ammonia compressed gas standards. Relative accuracy refers to the degree of agreement of LDS 3000 readings with flue gas ammonia measurements made by a reference method. Precision was assessed in terms of the repeatability of the LDS 3000 ammonia measurements with stable ammonia concentrations. Linearity, calibration drift, zero drift, and response time were assessed using commercial compressed gas standards of ammonia and high purity nitrogen zero gas. The effort spent in installing and maintaining the LDS 3000 was documented and used to assess ease of use. The amount of time the LDS 3000 was operational was recorded to assess data completeness.

3.2 Test Design

The LDS 3000 was installed at AEP's Mountaineer Plant approximately two weeks prior to testing, and a shakedown run was conducted before verification testing began. The LDS 3000 was installed between the exit of the SCR and the inlet of the air heater. Upstream of this location the gas flow exiting upward from the SCR catalyst beds underwent a 180° turn, to flow downward through the duct where the CEM was installed. A port for reference method sampling was located in the same duct with the LDS 3000. The sampling ports were assigned so that the LDS 3000 was unaffected by the operation of any other CEM or by the reference method sampling. The LDS 3000 was equipped with an in-line gas cell (the wedge module) that was used during dynamic spiking, and an external 1-meter path length gas cell that was used for calibration. The LDS 3000 operated in a dual light path configuration, with one path passing through the external gas cell and the other passing through the wedge cell and the flue gas duct. The external gas cell allowed zero or calibration gas to be supplied to the LDS 3000 light path without the complication of variability in the flue gas. This type of cell is not designed to be used by customers in normal operation. The wedge cell is recommended for such use, and was used for dynamic spiking experiments because it allowed a known standard addition of zero or calibration gas into the light path passing through the flue gas duct. Because of its smaller volume, the wedge cell was also used in tests of LDS 3000 response time.

Testing began on July 15, 2003, and continued until August 15, 2003. The boiler and SCR operated continuously during the test period. During verification testing, the LDS 3000 continuously monitored ammonia over the entire five-week test period. The LDS 3000 provided integrated average ammonia readings at 15-second intervals. The 15-second readings provided by the LDS 3000 were actually exponential moving averages calculated by the following equation:

$$y(i) = (y(i-1)*(\exp(-1/tc) + x(i)*(1-\exp(-1/tc))$$

where y is the LDS 3000 reading, x is the current raw 15-second measurement, tc is the LDS 3000 time constant, and i is the data index. Therefore, at any moment, each "15-second reading" is a function of the raw data at that moment and the previous reading, with the exponential moving average equation applied to both. Hereafter, the term "15-second reading" will refer to the smoothed data output to the data acquisition system after the exponential moving average equation was applied by the LDS 3000 software. These smoothed 15-second readings were used directly or averaged over longer time periods to address the target performance parameters.

Reference method sampling (see Section 3.4.1) was conducted on each weekday during the first and fifth weeks. On each day of reference method sampling, duplicate reference method samples were collected simultaneously using parallel sampling trains over each of three different sampling periods. The 15-second LDS 3000 readings during these periods were used to calculate one-hour averages with the intent to compare them with the ammonia concentrations measured by the reference method.

The rectangular duct at the test location was 20 feet 8 inches by 32 feet in cross section. Figure 3-1 shows a schematic of the test configuration in the duct. The LDS 3000 light path traversed the duct approximately 10 feet from the duct wall parallel to the 20-foot side and covered approximately 5.5 meters (18 linear feet). The reference method port was located in a corner of the duct, approximately eight feet from the 20-foot side. External access to the reference method port was severely restricted. Consequently, it was not possible to use a probe long enough to penetrate well into the duct. In fact, reference method samples could be collected only at a depth of less than one foot inside the inner wall of the duct. Because of concern about the representativeness of the reference measurements, the ammonia concentrations across the duct were mapped after the conclusion of the test period, to assess ammonia uniformity in the duct. The results of that effort, and the limitations of the reference measurements, are reported in Section 3.4.1.

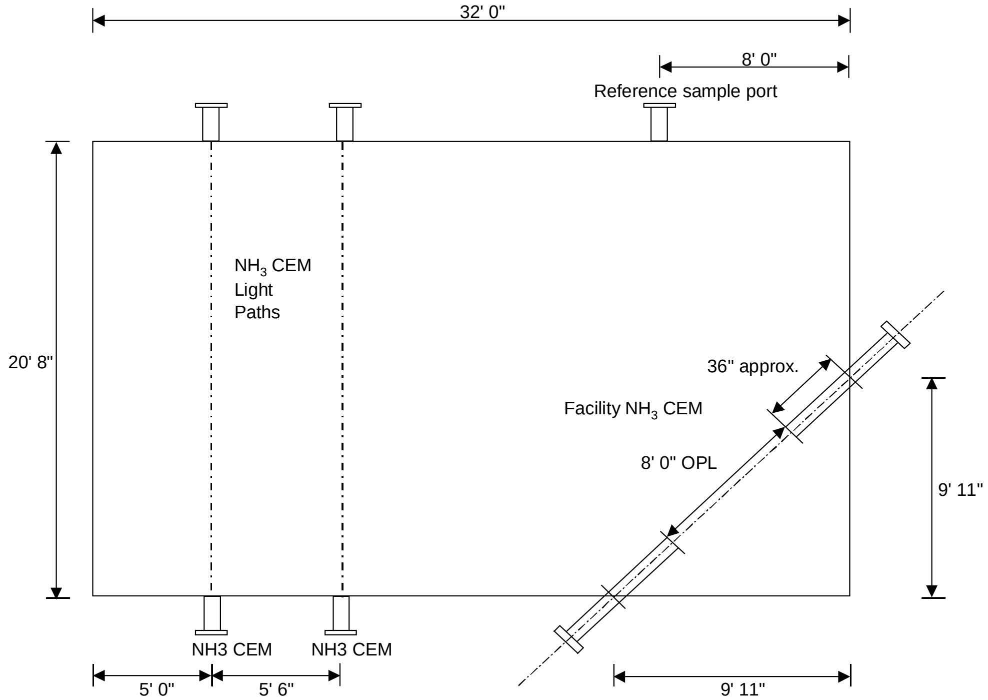

Figure 3-1. Schematic of CEM Locations in Ammonia CEM Verification

During the third week of the test, dynamic spiking was attempted using the external gas cell. However, this approach proved unsatisfactory because of the relatively large size of that cell, and consequently an alternative approach was adopted. During the fifth week of testing, the LDS 3000 was challenged with a series of dynamic spikes of a compressed ammonia gas standard and nitrogen zero gas, using the wedge module in line with the cross-duct light path. The LDS 3000 responses to the ammonia spikes were determined by subtracting the average ammonia concentration observed without spiking from the average ammonia concentration observed during spiking. The results of these runs were used to assess the agreement with standards, linearity, and precision of the LDS 3000. The external gas cell also was found to be too large to adequately assess LDS 3000 response time. As a result, 15-second readings from the dynamic spiking also were used to assess response time of the LDS 3000.

During each day of reference method sampling, zero and span checks were conducted by challenging the LDS 3000 with nitrogen zero gas and with a commercial compressed ammonia gas standard using the LDS 3000's external gas cell. These zero/span checks were used to assess the zero and calibration drift of the LDS 3000 during the test period. During the second, third, and fourth weeks of the test, the LDS 3000 operated continuously without any performance testing.

Throughout the verification test, the LDS 3000 was operated by the vendor's own staff or by Battelle staff trained by the vendor. The intent of the testing was to operate the LDS 3000 continuously in a manner simulating installed operation at a combustion facility. As a result, once the verification test began, no adjustment or recalibration was performed other than that which would be conducted automatically by the LDS 3000 in normal unattended operation. Maintenance procedures were carried out as needed, but testing was not interrupted in such cases. Those maintenance procedures consisted of cleaning the filters on the blowers that kept particulate matter off the optical windows in the duct. This maintenance was conducted every few days during the test. The use of the blowers was necessitated by the lack of an adequate supply of clean facility instrument air. The use of the blowers, and their resulting maintenance, would not be needed in a normal permanent installation.

3.3 Test Conditions

Table 3-1 shows the levels of ammonia and other constituents in the flue gas stream at AEP's Mountaineer Plant. Some of the data in Table 3-1 were obtained during the reference method sampling runs (see Section 3.4.1). Note that the percent moisture values in Table 3-1 vary widely. This variability does not appear realistic, and may result from measurement error in the reference sampling.

Table 3-1. Summary of Flue Gas Parameters or Constituent Concentrations at AEP's Mountaineer Plant

Parameter/Constituent	Typical Concentration or Range
NH_3	0.15 to 1.5 parts per million on a wet volume basis (ppmwv)[a]
NO_x	37 parts per million volume (ppmv)[b]
Sulfur dioxide	540 ppmv[b]
Oxygen	3.1 to 4.28%[c]
Dust loading	4.3 grains/dry standard cubic foot[b]
Moisture	4.4 to 10.8%[c]
Carbon dioxide	14.6 to 15.6%[c]
Temperature	648 to 679ºF[c]

[a] Typical 15-minute ppmwv taken from the LDS 3000.

[b] Typical values supplied by AEP.

[c] As measured during reference method sampling.

3.4 Test Procedures

3.4.1 Reference Method

The test/QA plan(1) called for comparing the LD500 results with those from a time-integrated measurement of ammonia in flue gas obtained using a modified EPA Conditional Test Method (CTM027).(2) That conditional test method is similar to a draft American Society for Testing and Materials (ASTM) method(3) for measuring ammonia. However, the draft ASTM method calls for analysis by ion selective electrode (ISE) whereas EPA CTM027 calls for analysis by ion chromatography (IC). The draft ASTM method also calls for a smaller volume of a more dilute acid solution in the sampling impingers than does EPA CTM027. Since the dilute acid is more appropriate for measuring low levels of ammonia, EPA CTM027 was modified to use the ASTM acid volumes and concentrations for this verification test.

During verification testing, reference sampling was conducted simultaneously with two collocated trains, with each sampling run lasting 60 minutes. Thus, each of the three reference sampling periods during a test day provided two reference ammonia samples for comparison with the LD500 data. Field blank samples also were recovered from one blank sampling train on each of three days during each week that reference method samples were collected. Additionally, on each of three days during each week of reference sampling, one sample train was spiked with ammonia solution to serve as a field spike sample. The spike was added as an aqueous standard directly to the front impinger in the train.

Four reference method samples (two from each week of reference method sampling) were also spiked with additional ammonium after analysis and then reanalyzed to establish the spike recoveries. A performance evaluation audit of the reference method using National Institute of Standards and Technology (NIST)-traceable ammonia standards was also conducted.

The reference method blank, spike, and audit sample results met all applicable criteria stated in the test/QA plan,(1) indicating that the reference method sampling was properly carried out. Blank sample concentrations were less than 10% of any duct sample ammonia concentration, and laboratory spike recovery was always within 10% of the expected value (and usually within 5%). Field spike recoveries were well within the 20% acceptance criterion, and the audit sample results agreed within about 5%. However, due to the inability to extend the reference method probe across the duct (see Section 3.2), concern arose that the reference samples might not adequately represent the duct ammonia concentrations, for comparison with data from the CEMs undergoing verification.

To address this concern, after the verification test was concluded, an ammonia mapping study was conducted to assess the representativeness of the reference method sampling location relative to the light path of the LDS 3000. In this mapping study, reference method samples were collected simultaneously at the reference method port and at three locations along the LDS 3000 monitoring path (50, 68, and 86 inches inside the inner duct wall) on August 20 and again on August 21. The results of the ammonia mapping study showed that ammonia concentrations at the reference sampling point were typically two to five times lower than those at points along the LDS 3000 light path. The difference between the reference point results and those from points along the light path was generally greatest for the points on the light path that were farthest into the duct. Based on these observations, the reference data were judged to be not representative of the flue gas sampled by the LDS 3000. Consequently, no quantitative assessment of the relative accuracy of the LDS 3000 and reference method results is made in this report.

3.4.2 Dynamic Spiking

During the fifth week of testing, the LDS 3000 was challenged with a series of dynamic spiking runs using the wedge cell in line with the cross-duct light path. This approach was an improvement over the dynamic spiking attempted with the external gas cell in the third week of testing. During these runs, the effective ammonia concentrations in the light path were increased by 3.78, 9.20, and 14.4 ppmwv above the flue gas concentration. At each of these spike concentrations, a series of runs was conducted that produced 12 spiked and 12 unspiked sample measurements. The path length of the flue gas duct was 5.5 meters (m), whereas the path length of the wedge cell was 7.1 centimeters (cm; i.e., 0.071 m). The internal volume of this cell was 0.216 liters (L). To perform a dynamic spike, this cell was purged with either a standard ammonia gas mixture or nitrogen zero gas. The purge flow rate to the cell was 1 L/minute (min), which produced approximately 4.6 cell volume changes per minute. A five-minute purge was adequate to obtain a stable reading.

To obtain a dynamic spike observation, a standard ammonia gas mixture was introduced to the wedge cell until a stable reading was observed. A two-minute period of readings was then obtained and the cell was allowed to purge for an additional three minutes before another two-minute period of readings was obtained, thus providing two spiked measurements. The cell purge gas was then changed to zero nitrogen, and the cycle was repeated to obtain two periods of unspiked ammonia readings. In summary, the following procedure was used to obtain dynamic spiking data:

1. Allow the wedge cell to purge for approximately five minutes with the ammonia standard (this yields 23 cell volume changes).

2. Select the next two minutes of 15-second LDS 3000 readings and calculate a two-minute average value. This value is the first spiked sample measurement.

3. Allow the wedge cell to purge with the ammonia standard for an additional three minutes (this yields 13.8 cell volume changes).

4. Select the next two minutes of 15-second LDS 3000 readings and calculate a two-minute average value. This value is the second spiked sample measurement.

5. Repeat steps 1 through 4 using zero nitrogen to purge the cell, to obtain two unspiked sample measurements.

This procedure for collecting the spiked and unspiked measurements was conducted a total of six times at each of the three spike concentrations to obtain 12 spiked and 12 unspiked measurements at each concentration (36 total spiked observations and 36 unspiked). Linearity was evaluated using all 36 two-minute average spiked observations.

The expected LDS 3000 response was calculated based on the concentration of the ammonia standard gas and a 0.071-m/5.5-m factor to correct for the difference between the 7.1-cm light path in the wedge cell and the 5.5-m light path in the flue gas duct. A temperature compensation factor of 2.399 also was applied to correct the expected LDS 3000 response for the difference between the wedge cell temperature (ambient) and the flue gas temperature (350ºC). The actual LDS 3000 spike response was calculated by subtracting the average reading when zero gas passed through the cell from the measurements when spike gas passed through the cell.

A single average unspiked reading was determined from all of the unspiked LDS 3000 readings, and that unspiked average was subtracted from each spiked measurement before comparisons were made to the gas standard spike concentration.

3.5 Quality Assurance Procedures

QA/quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(4) and the test/QA plan for this verification test.(1) These procedures are briefly described in this section. Results of the QA/QC procedures are presented in Section 4.

3.5.1 Performance Evaluation Audit

A performance evaluation (PE) audit was conducted to assess the quality of the measurements made in this verification test. This audit addressed only measurements that factor into the data used for verification, i.e., the LDS 3000 and the staff operating the LDS 3000 were not the subject of the PE audit. This audit was performed once during the verification test by analyzing a standard or comparing a reading with one that was independent of standards used during the testing. Table 3-2 summarizes the approach and equipment used for the PE audits, and shows the expected agreement of audit results. These audits were the responsibility of Battelle staff and were carried out with the cooperation of facility staff. Results of the PE audit are summarized in Sections 3.4.1 and 4.2.1.

Table 3-2. Summary of PE Audits

Parameter	Audit Equipment/Approach	Expected Tolerance
Flue Gas Differential Pressure	Independent pressure measurement (Magnehelic gauge, LN342539)	±0.5 inch of H_2O
Mass (H_2O)	Calibrated weights	±1% or 0.5 gram, whichever is larger
Ammonia (overall measurement)	Spike reference method trains	±20% bias in spike recovery
Ammonia (ISE analysis)	Independent audit sample—NIST solution	±10% of standard concentration
Ammonia (IC analysis)	Independent audit sample—NIST solution	±10% of standard concentration

Planned PE audits of flue gas temperature and barometric pressure were not performed. These deviations from the test/QA plan were documented in the program files, but have minimal impact on the results of this verification.

3.5.2 Technical Systems Audit

Battelle's ETV Quality Manager performed a technical systems audit (TSA) on July 16, 2003. The purpose of this TSA was to ensure that the verification test was being performed in accordance with the test/QA plan(1) and that all QA/QC procedures were implemented. As part of the audit, Battelle's ETV Quality Manager reviewed the reference sampling and analysis methods used, compared actual test procedures with those specified in the test/QA plan, and reviewed data acquisition and handling procedures. An independent EPA audit was conducted by the EPA Quality Manager at the same time as the Battelle audit.

3.6 Data Comparisons

Table 3-3 summarizes the data to be used for the verification of the various performance parameters. Chapter 5 presents the statistical procedures used to make these comparisons. Because of the limitations of the reference data (Section 3.4.1), relative accuracy is not listed in Table 3-3 or discussed in the subsequent sections of this report.

The results of the dynamic spiking were used to assess the agreement of the LDS 3000 results with respect to calculated ammonia concentrations determined from the spike gas concentration. For each spiking run, the difference between the ammonia concentration measured by the LDS 3000 and the calculated ammonia concentration from spiking was determined. A total of 36 spike results were obtained. The differences were then used to assess the agreement of the LDS 3000 results with the ammonia standard concentrations as described in Section 5.1.

Linearity of the LDS 3000 response was assessed by linear regression of the two-minute average data from the dynamic spiking runs, as described in Section 5.2. The measured ammonia concentrations and the calculated ammonia concentrations were used to assess linearity over the range from 3.78 to 14.4 ppmwv above background. A total of 36 data points (12 two-minute averages each at 3.78, 9.20, and 14.4 ppmwv above background) was used for this assessment.

Precision of the LDS 3000 was assessed based on the average percent relative standard deviation (% RSD) of the 15-second readings over the duration of each dynamic spiking period, as described in Section 5.3. An average % RSD was determined at each of the three spiking concentrations.

Calibration and zero drift were verified by repeatedly challenging the LDS 3000 with an ammonia compressed gas standard and a nitrogen zero gas, respectively, on each test day during the first and fifth weeks of the test, as described in Section 5.4. Thus, 10 data points were used to assess zero drift, and 10 were used to assess calibration drift.

Table 3-3. Summary of Data Obtained in LDS 3000 Verification Test

Performance Parameter	Objective	Comparison Based On	Total Number of Data Points for Verification
Agreement with Standards	Determine degree of quantitative agreement with compressed gas standard	Dynamic spiking with NH_3 gas standards	36
Linearity	Determine linearity of response over a range of ammonia concentrations	Dynamic spiking with NH_3 gas standards	36
Precision	Determine repeatability of successive measurements at stable ammonia levels	Repetitive measurements during each dynamic spiking run	72
Cal/Zero Drift	Determine stability of zero gas and span gas response over successive days	Zero gas and NH_3 gas standard analyses	20
Response Time	Determine rise and fall times	Recording successive readings in dynamic spiking runs	10

LDS 3000 response time was assessed in the fifth week of the test based on the successive 15-second readings in the dynamic spiking runs, as described in Section 5.5. The data from the dynamic spiking run at the highest concentration (14.4 ppmwv above background) were used to provide the clearest indication of response time. Five measures of rise time and five of fall time were used in the evaluation.

No additional test activities were required to determine the data completeness achieved by the LDS 3000. Data completeness was assessed by comparing the data recovered from the LDS 3000 with the maximum amount of data recoverable upon completion of all portions of these test procedures. The test was conducted over a period spanning approximately 746 hours.

Setup and maintenance needs were documented qualitatively, both through observation and through communication with the vendors and trained facility staff during the test. Factors included frequency of scheduled maintenance activities, downtime of the LDS 3000, and number of staff needed to operate or maintain it during the verification test. The approximate purchase cost of the LDS 3000 was also determined based on information provided by the vendor.

Chapter 4
Quality Assurance/Quality Control Results

This section summarizes the results of QA/QC efforts in this verification. Because the CTM027 reference data were not used, for the reasons described in Section 3.4.1, the QA/QC results for the reference method are not included here.

4.1 Equipment Calibrations

4.1.1 Host Facility Equipment

Monitoring devices in place at AEP's Mountaineer Plant, including an ammonia CEM of a type not verified in this test, were calibrated according to normal facility procedures. All calibration results were documented according to facility procedures and are available as supporting documentation for this test.

4.1.2 Calibration Check/Dynamic Spiking Equipment

The accuracy of the dry gas meter used for measuring the spike gas flow rate during the calibration checks and the dynamic spiking activities was confirmed by Battelle by comparison against an electronic bubble flow meter (M30 Mini-Buck Calibrator, A. P. Buck, Inc.). This calibrator has a flow rate range of 0.1 to 30 L/min. The range of flows confirmed with this calibrator was approximately 5 to 10 L/min. The M30 Mini-Buck was itself calibrated by the manufacturer against a NIST-traceable flow standard.

4.2 Audits

4.2.1 Performance Evaluation Audit

The PE audits of differential pressure and mass measurements showed results within the expected tolerances in Table 3-2. As noted in Section 3.4.1, the PE audit results of the reference method analyses were also within the tolerances in Table 3-2.

4.2.2 Technical Systems Audit

Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No major findings were noted. All minor findings were documented, and all required corrective actions were taken. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

4.2.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked during the technical review process.

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.(4) Once the audit report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the performance parameters listed in Section 3.1.

5.1 Agreement with Standards

The agreement (A) of the LDS 3000 with respect to the ammonia gas standards was assessed using Equation 1:

$$A = \frac{\left|\overline{d}\right| + t_{n-1}^{\alpha}\dfrac{S_d}{\sqrt{n}}}{\overline{x}} \times 100\% \qquad (1)$$

where *d* refers to the difference between the expected ammonia concentration from the dynamic spiking and the two-minute average LDS 3000 ammonia reading (corrected for the average background concentration) during the spiking period, and *x* corresponds to the expected ammonia concentration. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the 100(1 - α)th percentile of the distribution with n-1 degrees of freedom. The agreement was determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). The A value calculated in this way can be interpreted as an upper confidence bound for the relative bias of the LDS 3000, i.e., $\frac{\left|\overline{d}\right|}{\overline{x}}$, where the superscript bar indicates the average value of the differences or of the reference values. The agreement with standards was calculated separately at each of the spiking levels, using the 12 two-minute average spike results at each level. The three most outlying results (i.e., the three largest *d* values) were excluded in the calculation, i.e., the agreement was calculated with nine data points at each spike level.

5.2 Linearity

Linearity was assessed by a linear regression analysis of the two-minute averages from the dynamic spiking runs using the calculated ammonia concentrations as the independent variable and the LDS 3000 results as the dependent variable. Linearity is expressed in terms of slope, intercept, and coefficient of determination (r^2).

5.3 Precision

Precision was calculated in terms of the average % RSD of the LDS 3000 readings over the duration of each of the 12 spike and 12 zero two-minute periods during each dynamic spiking run. For each two-minute period during each dynamic spiking run, all 15-second readings from the LDS 3000 were recorded, and the mean and standard deviation of those readings were calculated. Precision (*P*) was then determined as:

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

where *SD* is the standard deviation of the LDS 3000 readings and $\overline{X}$ is the mean of the LDS 3000 readings in each period, and the overbar in Equation 2 indicates an average over all 12 periods. Precision was determined with both ammonia and zero gas provided to the wedge cell. Note that the calculated precision is subject not only to the LDS 3000 variability, but also to the variability of the flue gas ammonia background and the dynamic spiking procedure. The precision observed with zero gas in the wedge cell indicates the variability due to the flue gas background.

5.4 Calibration and Zero Drift

Calibration and zero drift are reported in terms of the mean, RSD, and range (maximum and minimum) of the stable readings obtained from the LDS 3000 in daily sampling of the same ammonia standard gas and zero gas supplied to the external calibration cell. As noted above, that cell was isolated from the cross-duct light path, i.e., the flue gas ammonia background was not a factor in these tests. Five ammonia standard readings in each week and 10 zero readings from both weeks combined were used for this calculation. This calculation, along with the range of the data, indicates the day-to-day variation in zero and standard gas readings.

5.5 Response Time

Response time was assessed in terms of both the rise and fall times of the LDS 3000 in the dynamic spiking runs. Rise time (i.e., 0% to 95% response time) was determined based on the 15-second LDS 3000 readings as the gas supplied to the wedge cell was switched from zero gas to the ammonia standard. Once a stable response was achieved with the gas standard, the fall time (i.e., the 100% to 5% response time) was determined based on the LDS 3000 readings as the gas supplied was switched from the ammonia standard back to zero gas. The observed rise and fall times are highly dependent on the replacement time of the gas standards or zero gas in the wedge cell, as well as on the smoothing of NH_3 readings imposed by the LDS 3000 software (Section 3.2). Rise and fall times were determined for the LDS 3000 using the data from the dynamic spiking runs at 14.4 ppmwv above background. Ten determinations of response time were obtained for the LDS 3000.

Chapter 6
Test Results

The results of the verification test of the LDS 3000 are presented in this section. The LDS 3000 outputs ammonia concentrations without correction for flue gas conditions. Therefore, the concentrations are on a wet volume basis, i.e., ppmwv. Note that all test results originate from LDS 3000 readings reported every 15 seconds, with the smoothing applied by the LDS 3000 software as described in Section 3.2.

6.1 Agreement with Standards

Table 6-1 presents the data and resulting percent agreement of the LDS 3000 with respect to each of three ammonia gas standards used for the dynamic spiking runs during Week 5 of the verification test. Shown in Table 6-1 are the two-minute average background-corrected LDS 3000 readings, the expected ammonia concentrations, the resulting differences, and the overall A values at each of the three spike concentrations calculated using Equation 1 in Section 5.1. The calculated A was 5.9% at a 3.78-ppmwv spike concentration, 7.7% at a 9.20-ppmwv spike concentration, and 6.1% at a 14.4-ppmwv spike concentration. Note that these A values arise from relatively small differences between the LDS 3000 and standard results. For example, the median of the differences listed in Table 6-1 is 0.59 ppmwv. Most often, the LDS 3000 readings were higher than the expected spike concentrations. In addition, since one average background concentration was used for the duration of the spiking runs at each concentration, normal variations in flue gas ammonia concentrations may have contributed to the difference between expected and observed concentrations.

6.2 Linearity

Figure 6-1 presents the linear regression of the LDS 3000 response, based on the two-minute averages obtained during the dynamic spiking runs versus the expected ammonia response. The linear regression equation is shown in the figure and includes the 95% confidence intervals of the slope and intercept in parentheses. This linear regression shows a slope of 1.054 (± 0.013), an intercept of 0.08 (± 0.13) ppm, and a coefficient of determination (r^2) of 0.995.

Table 6-1. Agreement of LDS 3000 with Ammonia Gas Standards

Zero-adjusted LDS 3000 response(a) (ppmwv)	Expected adjusted LDS 3000 response(b) (ppmwv)	Difference (ppmwv)	Zero-adjusted LDS 3000 response(a) (ppmwv)	Expected adjusted LDS 3000 response(b) (ppmwv)	Difference (ppmwv)	Zero-adjusted LDS 3000 response(a) (ppmwv)	Expected adjusted LDS 3000 response(b) (ppmwv)	Difference (ppmwv)
Spike Concentration 1(c)			**Spike Concentration 2(d)**			**Spike Concentration 3(e)**		
4.05	3.78	0.27	10.37	9.20	***1.18***	14.25	14.37	-0.12
4.25	3.78	***0.47***	10.74	9.20	***1.54***	15.36	14.37	***0.99***
3.72	3.78	-0.06	10.31	9.20	***1.11***	15.09	14.37	0.72
3.69	3.78	-0.09	10.14	9.20	0.94	15.41	14.37	***1.04***
4.27	3.78	***0.49***	9.37	9.20	0.17	15.15	14.37	0.78
4.00	3.78	0.23	9.51	9.20	0.31	15.46	14.37	***1.09***
4.01	3.78	0.23	9.71	9.20	0.51	15.22	14.37	0.85
4.05	3.78	0.27	9.76	9.20	0.56	15.10	14.37	0.73
3.81	3.78	0.03	9.67	9.20	0.48	15.17	14.37	0.80
4.28	3.78	***0.50***	9.85	9.20	0.66	15.08	14.37	0.71
3.72	3.78	-0.06	10.05	9.20	0.85	15.19	14.37	0.82
3.95	3.78	0.17	9.81	9.20	0.61	15.23	14.37	0.86
Agreement with standard		**5.9%**			**7.7%**			**6.1%**

Bold italics = Indicates this number was not included in the calculations.

(a) The LDS 3000 response was adjusted by subtracting the response when zero nitrogen was in the wedge cell.

(b) The expected LDS 3000 response includes the following correction to account for differences in the light path and temperature of the flow-through wedge cell compared with the flue gas duct:
Correction = [(wedge module length, 0.071 m)/(path length, 5.5 m)] x (temperature compensation factor, 2.399).

(c) Using a spike gas with an ammonia concentration of 122 ppmwv.

(d) Using a spike gas with an ammonia concentration of 297 ppmwv.

(e) Using a spike gas with an ammonia concentration of 464 ppmwv.

6.3 Precision

Table 6-2 presents the precision, calculated in terms of % RSD, of the 15-second LDS 3000 readings during each of the 12 spike and 12 zero two-minute averages during each dynamic spiking run. The observed % RSD of the LDS 3000 readings ranged from 2.3 to 5.4% RSD in the spiking runs, with higher % RSD values at lower spike concentrations. The variability of background flue gas ammonia readings is indicated by the average standard deviation of the zero spike concentration data points. These average standard deviations are tightly clustered around 0.28 ppmwv (ranging from 0.22 to 0.34) at flue gas background concentrations of 0.52 to 1.17 ppmwv. A similar, although not identical, range of standard deviations was observed during the spike runs. Without an independent measure of the variability of flue gas ammonia concentrations, it is not possible to determine how much of the observed variability in LDS 3000 readings is due to background variability and how much to the variability of the LDS 3000 itself. However, the results in Table 6-2 clearly show the capability of the LDS 3000 to monitor low ppm levels of ammonia with a precision (as measured by standard deviation) within about 0.4 ppm.

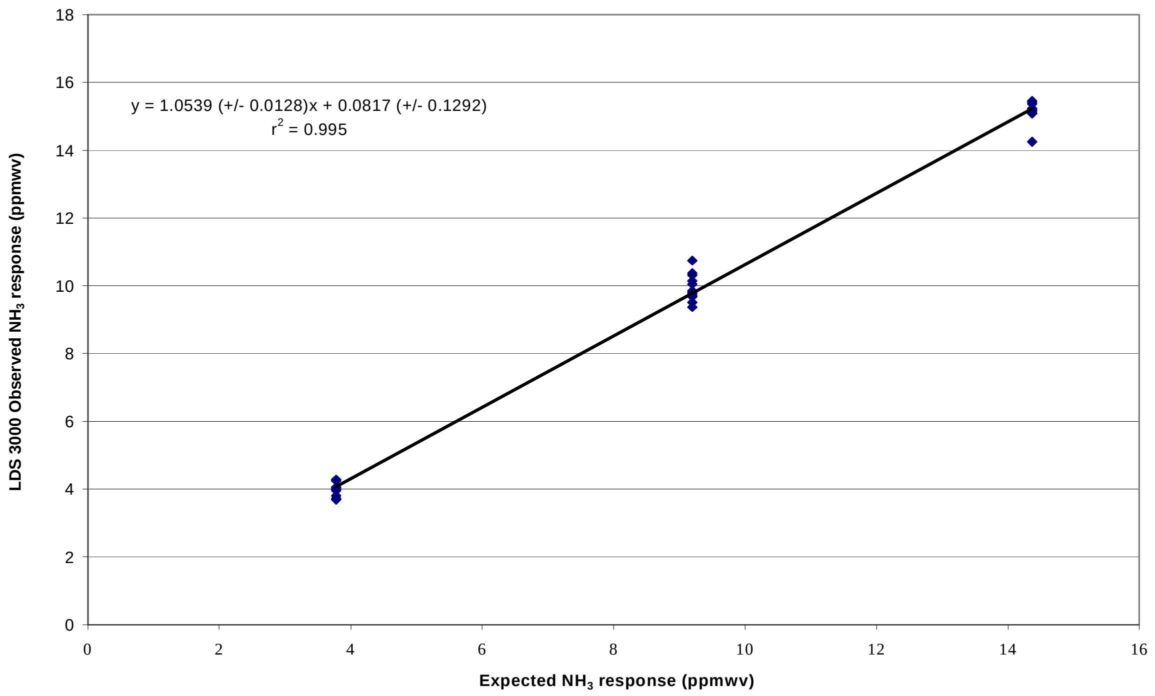

Figure 6-1. Linear Regression of the LDS 3000 NH_3 Response vs. Expected Response

Table 6-2. Precision (% RSD) of LDS 3000 During Dynamic Spiking Periods

Period	Average Number of Data Points	Average Concentration (ppm)	Average SD	Average RSD (%)
Spike 1[a]	9	4.85	0.26	5.4%
Spike 2[b]	9	10.47	0.30	2.9%
Spike 3[c]	9	16.31	0.37	2.3%
Zero	9	0.92	0.28	–
Zero	9	0.52	0.22	–
Zero	9	1.17	0.34	–

(a) Using a spike gas with an ammonia concentration of 122 ppmwv.
(b) Using a spike gas with an ammonia concentration of 297 ppmwv.
(c) Using a spike gas with an ammonia concentration of 464 ppmwv.

6.4 Calibration and Zero Drift

Span and zero checks were conducted five times each during Weeks 1 and 5 of the verification test. These checks were conducted by flowing either a zero gas or a standard gas through a separate calibration gas cell, with that cell isolated from the cross-duct light path. Table 6-3 presents the results of these checks, showing the NH_3 concentration in the cell, the LDS 3000 readings, and the average, standard deviation, %RSD, maximum, and minimum of those readings. Zero values determined during the test indicate no drift in the measurement (all zero results are 0.000 ppmwv). The span values show standard deviations of 0.581 and 0.319 ppmwv in the two weeks, with no significant trend with time. These standard deviations result in RSD values of 0.12 to 0.26%.

6.5 Response Time

LDS 3000 response time was estimated using the 15-second readings generated during dynamic spike procedures. Since these readings are mathematically smoothed values (see Section 3.2), the response times reported here are influenced by the smoothing algorithm. Also, because these checks were performed in the wedge cell, the LDS 3000 readings were subject not only to the LDS 3000’s response time, but also to the adsorptive nature of ammonia and the physical changeover due to gas replacement in the module. The internal volume of the wedge cell was 0.216 L, and the gas flow rate through the cell was approximately 1 L/min. A stable response would be expected only after the cell volume has changed gas volumes several times. Therefore, a stable response would not have been achievable until the standard gas had been flowing through the cell for about one minute. Consequently, the response times indicated below should be taken as procedural changeover times and not as the instrument response times of the LDS 3000. Vendor-supplied information indicates that true LDS 3000 response times are about 2 to 5 seconds.

Table 6-4 presents the LDS 3000 rise and fall times observed during the dynamic spiking in Week 5. Figure 6-2 presents examples of the Week 5 fall and rise time plots. Table 6-4 shows that the rise and fall times observed with the LDS 3000 were variable, with rise times and fall times averaging 67 and 108 seconds, respectively. The variability of these times may be partly due to adsorption of ammonia on the unheated walls of the wedge cell. Because these measurements were recorded with a light path through both the wedge cell and the flue gas, these readings reflect both the variability in flue gas concentrations and the time needed to replace the gas in the cell. The rise times in Table 6-4 are consistent with the concentration profile expected based on the cell volume and gas flow rate.

Table 6-3. Calibration and Zero Drift for LDS 3000 During Weeks 1 and 5

Gas Standard Concentration (ppmwv)	LDS 3000 Reading (ppmwv)	LDS 3000 Average (ppmwv)	Standard Deviation (ppmwv)	Relative Standard Deviation (%)	LDS 3000 Minimum (ppmwv)	LDS 3000 Maximum (ppmwv)
Weeks 1 and 5 Zeros						
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
0	0.000					
		0.000	0.000	–	0.000	0.000
Week 1 Spans						
479	466.5					
479	467.1					
479	467.3					
479	467.8					
479	466.4					
		467.0	0.581	0.12	466.4	467.8
Week 5 Spans						
122	125.6					
122	125.1					
122	124.7					
122	125.1					
122	125.1					
		125.1	0.319	0.26	124.7	125.6

Table 6-4. LDS 3000 Rise and Fall Times

Week 5 Rise/Fall[a]	Time (hh:mm:ss)	Rise/Fall Time (seconds)
Rise	21:38:14	66
Rise	22:02:32	83
Rise	22:26:17	68
Rise	22:54:15	65
Rise	23:18:08	54
	Average Rise	67
Fall	21:51:09	123
Fall	22:14:44	94
Fall	22:38:45	94
Fall	23:07:25	133
Fall	23:28:50	97
	Average Fall	108

[a] Flue gas background concentration approximately 1 ppmwv; dynamic spike concentration 14.4 ppmwv above background.

6.6 Ease of Use

The LDS 3000 has some features that make it easy to use. Other features add complexity to its use. Once the LDS 3000 was set up and calibrated, it required very little maintenance. Zero and span checks (Section 6.4) revealed that the LDS 3000 maintained its calibration very well. Other specific aspects of installation and operation are discussed below.

6.6.1 Installation

Installation of the LDS 3000 central unit, laptop computer, and external calibration cell in the instrument trailer proceeded smoothly with the aid of one Siemens engineer. The hybrid cable needed to be run from the central unit in the trailer to the transmitter/receiver assembly mounted on the duct, requiring the aid of plant personnel. Electric power was required at the duct for the two air blower fans that kept particulate matter from accumulating on the optics. There is no power requirement when compressed air is used for that purpose. Transmitter/receiver modules were mounted easily to standard 4-inch American National Standards Institute flanges. Another fiber-optic cable, wrapped around the duct, connected the modules.

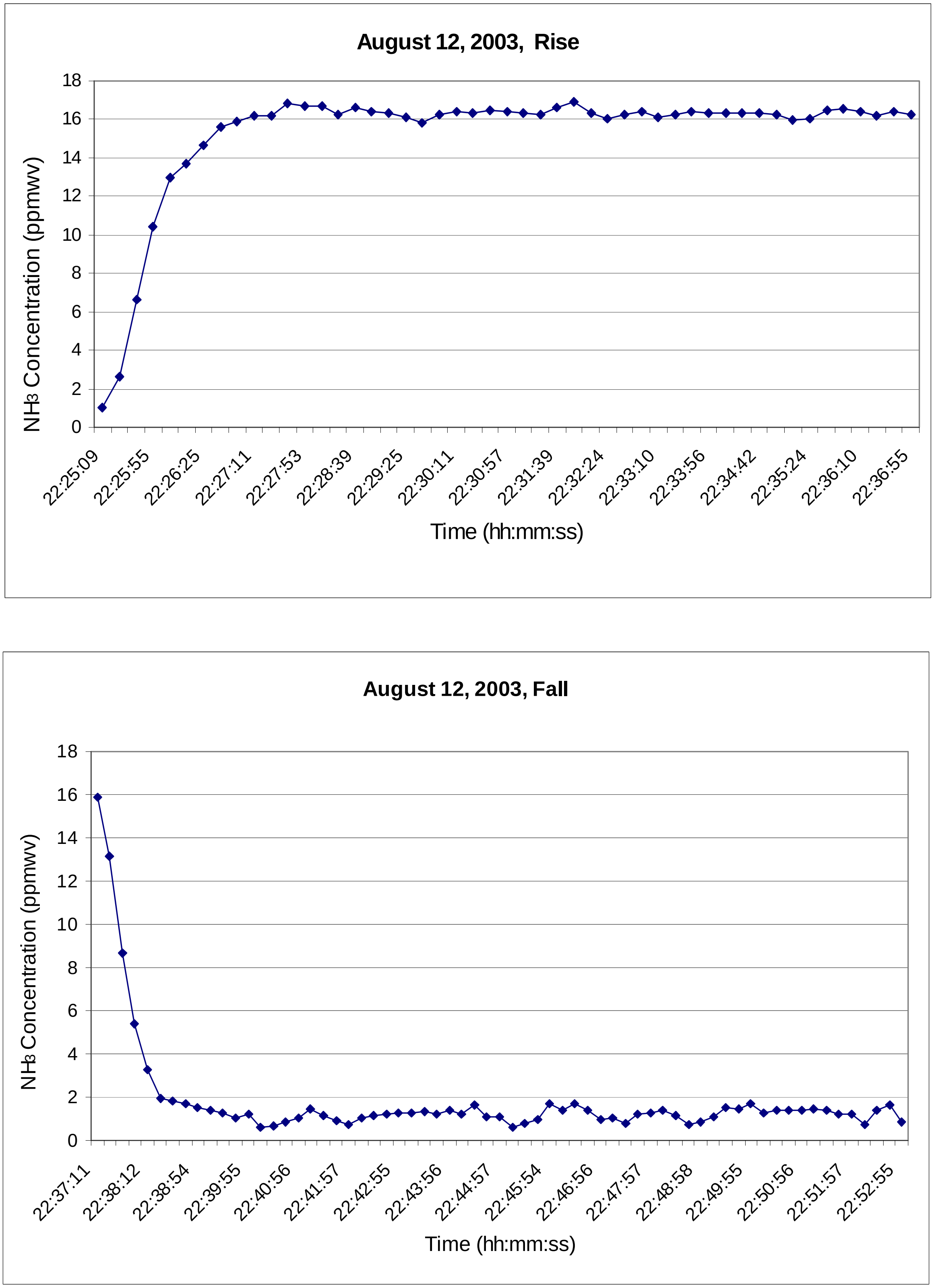

Figure 6-2. Example LDS 3000 Rise and Fall Time Plots

6.6.2 Zero and Span Checks

The LDS 3000 vendor, when asked to make it possible to perform external zero/span checks using compressed gases, provided Battelle with a 1-m path length, cylindrical, flow-through calibration cell (internal volume approximately 4.6 L) made of stainless steel and coated internally with Teflon. The analyzer monitored the ammonia concentrations in the duct and in this reference cell independently. Because of the large internal volume of this calibration cell, performing the zero and span checks required a large flow of standard or zero gas and long times to equilibration as the gas purged the cell. In addition, slow return to baseline readings was observed following completion of span checks, possibly due to absorption or adsorption of ammonia on the cell walls. Siemens representatives acknowledged this problem with the Teflon coating and stated that the next version of such a cell would be coated with a more inert substance such as deactivated fused silica.

6.6.3 Dynamic Spiking

A 216-mL, non–temperature–controlled gas cell was located in the wedge module of the LDS 3000 as an optional part of the transmitter/receiver unit mounted on the duct. As originally installed, there was no way to introduce or control zero/span gases in the gas cell to allow for dynamic spiking. However, a solenoid valve gas-switching device was fashioned that could be operated from the instrument trailer and that allowed either zero or span gas to be introduced through the wedge cell. Light always passed through both the wedge cell and the duct and could not be switched around the wedge cell.

Using the wedge cell to determine agreement with gas standards made the system slightly difficult to use. Since the LDS 3000 uses molecular absorption along the light path as its basis of detection, using the wedge cell when determining that agreement required an adjustment for the short light path through the wedge cell compared with the long path through the duct (7.1 cm v 5.5 m). In addition, the extent of light absorption varies with temperature, such that a temperature correction also must be provided or calculated. Because the wedge cell operates at ambient temperatures, no single temperature correction can be developed.

6.6.4 Data Handling

The LDS 3000 data were downloaded easily from the laptop computer (required for data logging from the central unit) onto a laptop memory card. The latter could then be inserted into any computer running a Windows operating system. Files in tab-delimited ASCII format were suitable for importing directly to spreadsheet software. All data for the five-week test period were recovered easily as requested.

6.7 Data Completeness

The LDS 3000 operated without interruption for the entire five-week test period. Thus, the data completeness was essentially 100%. Light beam transmittance was checked periodically (generally every two to three days; occasionally as many as five days passed without checking). The filters on the air blower motors became clogged on this schedule, leading to a decrease in blower performance and consequent accumulation of particulate matter on the lenses, ultimately causing decreased light transmittance across the duct. The only required maintenance, therefore, was to check light levels and clean or replace the blower motor filters on a two- to three-day schedule. For a permanent installation, this maintenance would not be required because a plant would use a continuous flow of pressurized clean instrument air to purge the lenses.

6.8 Cost

The vendor indicated that the purchase cost of the complete LDS 3000 system, implemented in a single-path configuration as for this verification test, was approximately $40,000 to $50,000.

Chapter 7
Performance Summary

Table 7-1 summarizes the results for each of the LDS 3000 performance parameters. Note that all quantitative results originate from LDS 3000 readings reported every 15 seconds, with the smoothing applied by the LDS 3000 software as described in Section 3.2.

Table 7-1. Summary of LDS 3000 Verification Results

Parameter	Performance Results	Comments
Agreement with Standards	5.9% at 3.78 ppmwv 7.7% at 9.20 ppmwv 6.1% at 14.4 ppmwv	Results of three concentration levels with 12 data points each; nine data points used in each calculation; median difference from expected value = 0.59 ppmwv
Relative Accuracy	Not calculated	Reference sampling location unrepresentative of duct ammonia concentrations(a)
Linearity	Regression slope = 1.054 (± 0.013)x +0.082 (± 0.129) ppmwv, $r^2 = 0.995$	Calculated over range of 3.78 to 14.4 ppmwv, 36 total data points
Precision	5.4% RSD at 4.85 ppmwv 2.9% RSD at 10.5 ppmwv 2.3% RSD at 16.3 ppmwv	Data smoothed per Section 3.2; variability due partly to the variability of background ammonia concentration in the duct
Calibration and Zero Drift	No zero drift Span RSD values = 0.12 to 0.26%	Minimal drift over the five-week test
Response Time	Rise times average 67 seconds Fall times average 108 seconds	Observed response times largely due to concentration changeover in the test cell
Ease of Use	Generally easy to use	
Completeness	100% data capture	

(a) Reference sampling port was improperly located and did not allow sampling across width of duct. Mapping of ammonia concentrations at points along the CEM light path confirmed that sampling at reference port could not adequately determine duct ammonia concentrations.

Chapter 8
References

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