September 2004

Revised

Environmental Technology Verification Report

OPSIS AB
LD500 CONTINUOUS EMISSION MONITOR FOR AMMONIA

Prepared by
Battelle

Battelle
The Business of Innovation

Under a cooperative agreement with

EPA **U.S. Environmental Protection Agency**

ETV ETV ETV

September 2004

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Opsis AB
LD500 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. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support 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. Battelle conducted this verification under a follow-on agreement to the original cooperative agreement. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

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List of Abbreviations

AEP	American Electric Power
A	agreement
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 Opsis AB LD500 (LD500).

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 Opsis LD500. Following is a description of the LD500, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The LD500 is an optical open-path monitoring system designed to measure ammonia, water vapor, hydrochloric acid, hydrogen fluoride, oxygen, and temperature. The LD500 allows multiplexing of monitoring paths and can be configured with up to eight individual paths.

The LD500 (Figure 2-1), housed in a 19-inch rack cabinet, is the central unit of a laser diode gas monitoring system. Up to four laser diode heads can be installed, each one a complete laser control and data sampling system monitoring a specific gas. The LD500's laser module emits near-infrared light, operates continuously, and is tunable. The laser is scanned rapidly (in kilohertz frequency range) over the absorption line of the gas to be measured for 10 to 30 seconds. An internal reference beam maintains the wavelength stability of the laser diode. At the end of the measurement interval, the averaged spectrum is evaluated. The results are compared through a least-squares fitting procedure with the known absorbance cross section of the gas. The Beer-Lambert absorption law is used to determine the gas concentration from the absorption measured in the monitoring path, using the known monitoring path length.

Figure 2-1. Opsis LD500 Ammonia CEM

A schematic of the LD500 is shown in Figure 2-2. The LD500 includes an emitter and a receiver to be mounted on ports on the flue gas duct. The laser signal is sent through a fiber optic cable to the receiver where it is divided into two fiber optic cables, one providing the signal to the emitter and the second providing the light signal for calibration. The emitter projects the infrared energy across the stack or duct. The receiver focuses the projected infrared energy to a solid-state detector. The raw signal is converted to a digital communication signal and transmitted through a communications optic fiber back to the LD500. The LD500 processes the final signal and presents a concentration. The receiver is equipped with a calibration/audit cell.

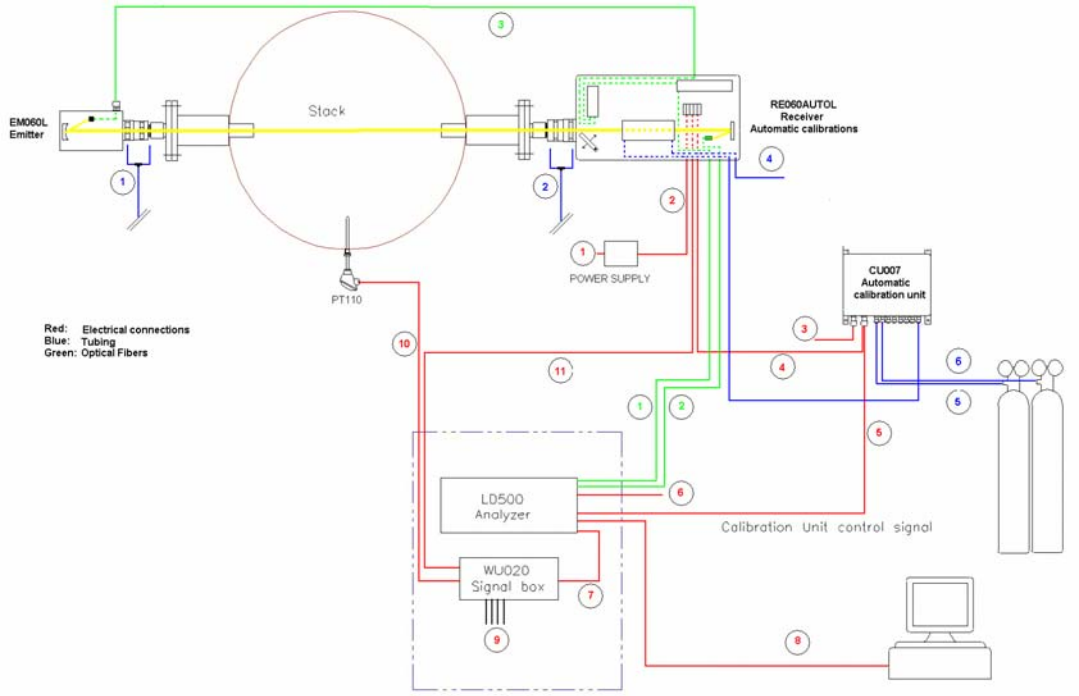


Figure 2-2. Schematic Diagram of the Opsis LD500

LD500 System Drawing Legend

Red

1	110 V AC power
2	DC power input cable
3	110 V AC power
4	DC power cable
5	Calibration control cable
6	Spare control signal
7	Communications cable for analog input/output
8	Communications cable to data system
9	Analog input/output signal
10	Temperature sensor signal
11	Calibration control signal

Blue

1,2,4	Purge air
5	Zero air
6	NH_3 span gas

Green

1	Laser source energy fiber optic
2	Detector signal fiber optic
3	Laser source energy fiber optic from splitter

The calibration cell is 5.11 inches (130.0 mm) long andheated to a constant temperature of 150°F. A solenoid valve unit is connected to the LD500, providing daily automatic zero and span calibration. In calibration mode, the gas is flushed at a low flow rate through the cell and vented through a ¼-inch tube at a secure point.

For absolute zero and span calibrations, a flat mirror is folded in to deflect the calibration laser beam through the calibration cell. At the beginning of the calibration cycle, the mirror is automatically folded in; it is folded out upon completion of the calibration cycle. The same laser source is used both for measurements and for calibration checks. An add-on spiking run is performed with the mirror folded out, i.e., the measurement light beam is measured on the detector. In this mode, a concentration entered in the calibration cell is added to the measured stack concentration.

A signal input and output unit is connected to the LD500. Signals include stack temperature entering the system and analog output signals being delivered to an outside data system. The LD500 stores all raw data, measurements, and logged data from the signal system on its internal hard drive. For data presentation, a personal computer provides real-time graphics of monitored results. In this verification test, the LD500 was set up to provide discrete readings of NH_3 concentration every 10 seconds, without averaging or smoothing the data.

Chapter 3
Test Design and Procedures

3.1 Introduction

The objective of this verification test of the LD500 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 LD500 based on the differences between LD500 readings and known concentrations of ammonia prepared from ammonia compressed gas standards. Relative accuracy refers to the degree of agreement of LD500 readings with flue gas ammonia measurements made by a reference method. Precision was assessed in terms of the repeatability of the LD500 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 LD500 was documented and used to assess ease of use. The amount of time the LD500 was operational and the maintenance activities performed were recorded to assess data completeness.

3.2 Test Design

The LD500 was installed at AEP's Mountaineer Plant approximately two weeks prior to testing, and a shakedown run was conducted before verification testing began. The LD500 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 LD500. The sampling ports were assigned so that the LD500 was unaffected by the operation of any other CEM or by the reference method sampling. The LD500 was equipped with a heated calibration cell that was used during dynamic spiking and for calibration.

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 LD500 continuously monitored ammonia over the five-week test period. The LD500 provided discrete integrated ammonia readings at 10-second intervals, with no smoothing or averaging of successive 10-second readings. The discrete 10-second readings were used directly or averaged over longer time periods to address each of the target performance parameters. The LD500 vendor provided a correction to the raw LD500 data that was applied to all LD500 data as follows:

Corrected LD500 concentration = (raw LD500 concentration - 0.2) x 0.13/0.12

The first correction was needed to address an incorrect baseline (zero) concentration that was part of the pre-test calibration. The factor of 0.13/0.12 was needed to adjust to the actual calibration cell length of 13 centimeters (cm).

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 10-second LD500 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 LD500 monitoring path traversed the duct approximately five feet from the duct wall, parallel to the 20-foot side. 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.

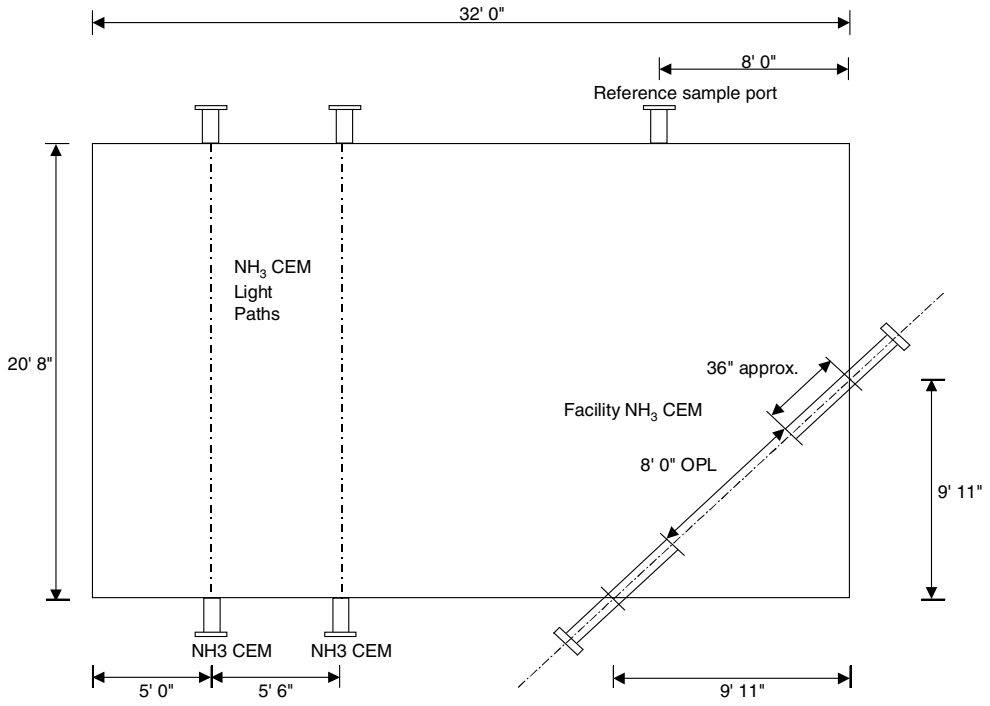


Figure 3-1. Schematic of CEM Locations in Ammonia CEM Verification

During the third week of testing, the LD500 was challenged with a series of dynamic spikes of a compressed ammonia gas standard and nitrogen zero gas using the calibration cell in line with the cross-duct light path. The LD500 responses to the ammonia spikes were determined by subtracting the average ammonia concentration observed without spiking from the average ammonia concentrations observed during spiking. The results of these runs were used to assess the agreement with standards, linearity, and precision of the LD500. Ten-second readings from the dynamic spiking also were used to assess the response time of the LD500.

During each day of reference method sampling, zero and span checks were conducted by challenging the LD500 with a commercial compressed ammonia gas standard and nitrogen zero gas using the LD500 calibration cell. These zero/span checks were used to assess the zero and calibration drift of the LD500 during the test period. During the second week of the test, the LD500 operated continuously without any performance testing. The LD500 was not operational during the fourth week of testing due to a hard drive failure.

Throughout the verification test, the LD500 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 LD500 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 LD500 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 optical windows in the duct on a

few occasions during the test. This maintenance was necessitated by the lack of an adequate supply of clean facility instrument air, and 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	0.8 to 2.5 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 679°F[c]

[a] Typical 15-minute values in ppmwv calculated from the LD500 10-second readings.
[b] Typical values supplied by AEP.
[c] As measured during reference method sampling.

3.4 Test Procedure

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 LD500. In this mapping study, reference method samples were collected simultaneously at the reference method port and at four locations along the LD500 monitoring path (32, 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 LD500 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 LD500. Consequently, no quantitative assessment of the relative accuracy of the LD500 and reference method results is made in this report.

3.4.2 Dynamic Spiking

During the third week of testing, the LD500 was challenged with a series of dynamic spiking runs using the calibration cell in line with the cross-duct light path. During these runs, the effective ammonia concentrations in the light path were increased by 2.14, 5.22, and 8.15 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 6.05 meters (m), whereas the path length of the calibration cell was 13 cm (i.e., 0.13 m). The internal volume of this cell was 0.5 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 1.3 L/minute (min), which produced approximately 2.6 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 calibration 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 two 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 calibration cell to purge for approximately five minutes with the ammonia standard (this yields 13 cell volume changes).

2. Select the next two minutes of 10-second LD500 readings and calculate a two-minute average value. This value is the first spiked sample measurement.

3. Allow the calibration cell to purge with the ammonia standard for an additional two minutes (this yields 5.2 cell volume changes).

4. Select the next two minutes of 10-second LD500 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 spiked and 36 unspiked observations). A single average unspiked reading was determined from all of the unspiked LD500 readings, and that unspiked average was subtracted from each spiked measurement before comparisons were made to the gas standard spike concentrations.

Linearity was evaluated using all 36 two-minute average spiked observations. The expected LD500 response was calculated based on the concentration of the ammonia standard gas and a 0.13-m/6.05-m factor to correct for the difference between the 13-cm light path in the calibration cell and the 6.05-m monitoring path in the flue gas duct. A temperature compensation factor of 1.84 and a spectral effects correction factor of 0.665, both supplied by the vendor, were applied to correct the expected LD500 response for the difference between the calibration cell temperature (150°F) and the flue gas temperature (350°C). The actual LD500 spike response was calculated by subtracting the average reading when zero gas passed through the calibration cell from the average reading when spike gas passed through the cell.

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 LD500 and the staff operating the LD500 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 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.

Table 3-3. Summary of Data Obtained in LD500 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	14
Response Time	Determine rise and fall times	Recording successive readings in dynamic spiking runs	11

The results of the dynamic spiking were used to assess the agreement of the LD500 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 LD500

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 LD500 results with the ammonia standard concentrations as described in Section 5.1.

Linearity of the LD500 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 2.14 to 8.15 ppmwv above background. A total of 36 data points (12 two-minute averages each at 2.14, 5.22, and 8.15 ppmwv above background) were used for this assessment.

Precision of the LD500 was assessed based on the average percent relative standard deviation (% RSD) of the 10-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 LD500 with an ammonia compressed gas standard and a nitrogen zero gas, respectively, during the first and fifth weeks of the test, as described in Section 5.4. In this procedure the LD500 light path passed through the calibration cell only (i.e., not across the duct). Consequently, the LD500 readings had to be adjusted (scaled up) to correct for the difference between the 0.13-m cell length and the 6.05-m path length programmed into the LD500 for cross-stack measurements. Seven data points were used to assess zero drift, and seven were used to assess calibration drift.

LD500 response time was assessed in the third week of the test based on the successive 10-second readings during the dynamic spiking runs, as described in Section 5.5. The data from the dynamic spiking run at the highest concentration (8.15 ppmwv above background) were used to provide the clearest indication of response time. Five measures of rise time and six of fall time were used in this evaluation.

No additional test activities were required to determine the data completeness achieved by the LD500. Data completeness was assessed by comparing the data recovered from the LD500 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 LD500, and number of staff needed to operate or maintain it during the verification test. The approximate purchase cost of the LD500 was also determined based on information provided by the vendor.

Chapter 4
Quality Assurance/Quality Control

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 01 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 LD500 with respect to the ammonia gas standards was assessed using Equation 1:

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

where d refers to the difference between the expected ammonia concentration from the dynamic spiking and the two-minute average LD500 ammonia readings (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 LD500, i.e., $\frac{\left|\bar{d}\right|}{\bar{x}}$, 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 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 LD500 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 percent RSD of the LD500 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 10-second readings from the LD500 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 LD500 readings and $\overline{X}$ is the mean of the LD500 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 cell. Note that the calculated precision is subject not only to the LD500 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 calibration 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 LD500 in daily sampling of the same ammonia standard gas and zero gas. These readings were obtained with the calibration cell isolated from the cross-duct light path, i.e., the flue gas ammonia background was not a factor in these tests. The readings were adjusted to account for the difference between the calibration cell length and the cross-duct path length programmed into the LD500. Seven ammonia standard readings and seven zero readings 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 LD500 in the dynamic spiking runs. Rise time (i.e., 0% to 95% response time) was determined based on the 10-second LD500 readings as the gas supplied to the calibration cell was switched from zero gas to the ammonia standard during the dynamic spiking run. 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 LD500 readings as the gas supplied was switched from the ammonia standard back to zero gas during the dynamic spiking run. The observed rise and fall times are highly dependent on the replacement time of the gas standard or zero gas in the calibration cell. Rise and fall times were determined for the LD500 using the data from the dynamic spiking run at 8.15 ppmwv above background. A total of 11 data points were obtained relevant to response time for the LD500.

Chapter 6
Test Results

The results of the verification test of the LD500 are presented in this section. The LD500 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 discrete 10-second readings reported by the LD500 without smoothing or averaging, as described in Section 3.2

6.1 Agreement with Standards

Table 6-1 presents the data and resulting percent agreement of the LD500 with respect to each of three ammonia gas standards used for the dynamic spiking runs during Week 3 of the verification test. Shown in Table 6-1 are the two-minute average background-corrected LD500 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 10.4% at a 2.14-ppmwv spike concentration,7.9% at a 5.22-ppmwv spike concentration, and 14.3% at an 8.15-ppmwv spike concentration. Note that these A values arise from relatively small differences between the LD500 and standard results. For example, the median of the differences listed in Table 6-1 is 0.43 ppmwv. Most often, the LD500 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 variation in flue gas ammonia concentrations may have contributed to the differences between expected and observed concentrations.

6.2 Linearity

Figure 6-1 presents the linear regression analysis of the LD500 response based on the two one-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 1.198 (± 0.036), an intercept near -0.52 (± 0.21) ppmwv, and a coefficient of determination (r^2) of 0.970.

Table 6-1. Agreement of LD500 with Ammonia Gas Standards

Zero-adjusted LD500 response[a] (ppmwv)	Expected adjusted LD500 response[b] (ppmwv)	Difference (ppmwv)	Zero-adjusted LD500 response[a] (ppmwv)	Expected adjusted LD500 response[b] (ppmwv)	Difference (ppmwv)	Zero-adjusted LD500 response[a] (ppmwv)	Expected adjusted LD500 response[b] (ppmwv)	Difference (ppmwv)
Spike Concentration 1[c]			**Spike Concentration 2[d]**			**Spike Concentration 3[e]**		
1.95	2.14	-0.19	5.74	5.22	0.52	9.48	8.15	1.33
2.13	2.14	-0.01	7.36	5.22	***2.14***	9.34	8.15	1.20
2.58	2.14	***0.44***	6.00	5.22	***0.78***	8.93	8.15	0.78
2.11	2.14	-0.03	5.74	5.22	0.52	9.39	8.15	1.24
2.13	2.14	-0.01	5.79	5.22	0.57	9.26	8.15	1.11
2.56	2.14	0.42	5.95	5.22	***0.73***	9.88	8.15	***1.73***
2.49	2.14	0.35	4.78	5.22	-0.44	9.25	8.15	1.10
2.07	2.14	-0.07	5.41	5.22	0.20	8.66	8.15	0.51
1.54	2.14	***-0.60***	4.60	5.22	-0.61	9.77	8.15	***1.62***
1.63	2.14	***-0.51***	5.00	5.22	-0.21	9.77	8.15	***1.62***
2.38	2.14	0.24	5.54	5.22	0.32	8.45	8.15	0.30
1.87	2.14	-0.27	4.98	5.22	-0.23	9.65	8.15	1.50
Agreement with standard		**10.4%**			**7.9%**			**14.3%**

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

[a] The LD500 response was adjusted by subtracting the average response when zero nitrogen was in the calibration cell.

[b] The expected LD500 response includes the following correction to account for differences in the light path and temperature of the flow-through calibration cell compared with the flue gas duct: Correction = (calibration cell length, 0.13 m)/(duct path length, 6.05 m) x [(temperature compensation factor, 1.84) x (spectral effects correction factor, 0.665)].

[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 percent RSD, of the discrete 10-second LD500 readings during each of the 12 spike and 12 zero two-minute averages during each dynamic spiking run. The observed precision of the LD500 readings ranged from 15.8 to 48.6% RSD in the dynamic spiking runs, with higher percent 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 clustered tightly around 1.0 ppmwv (ranging from 0.96 to 1.07 ppmwv) at flue gas background concentrations of 0.61 to 0.69 ppmwv. Slightly higher average standard deviations (1.37 to 1.59 ppmwv) were observed during the spike runs than during the zero gas 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 LD500 readings is due to background variability and how much to the variability of the LD500 itself. However, the results in Table 6-2 clearly show the capability of the LD500 to monitor low ppm levels of ammonia with a precision (as measured by standard deviation) within about 1 ppm even with discrete (unsmoothed) 10-second measurements.

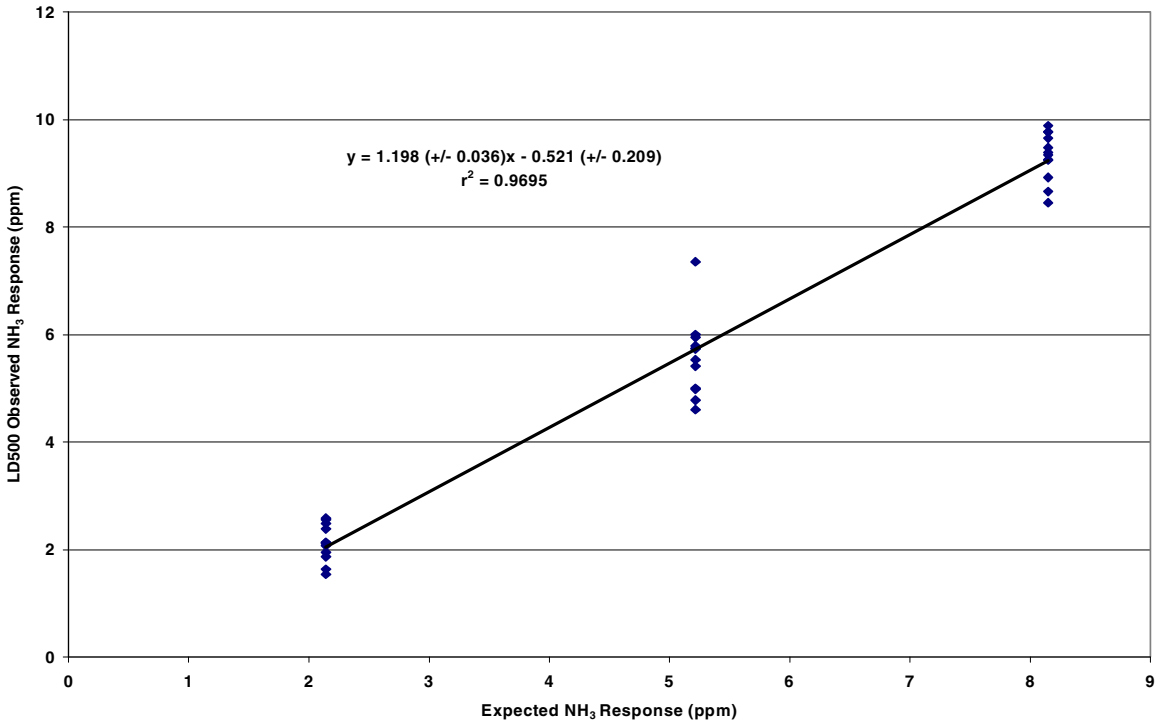


Figure 6-1. Linear Regression of the LD500 NH_3 Response vs. Expected Response

Table 6-2. Precision (% RSD) of LD500 During Dynamic Spiking Periods

Period	Average Reading (ppmwv)	Average SD (ppmwv)	Average RSD (%)
Spike 1[(a)]	2.82	1.37	48.6
Spike 2[(b)]	6.26	1.49	24.1
Spike 3[(c)]	10.12	1.59	15.8
Zero	0.69	1.00	–
Zero	0.61	0.96	–
Zero	0.68	1.07	–

[(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 during Weeks 1 and 5 of the verification test. These checks were conducted by flowing either a zero gas or a standard gas through the calibration cell, with that cell isolated from the cross-duct light path. The 10-second LD500 readings were then adjusted to account for the fact that the cell path length was only 0.13 m, rather than the 6.05-m cross-duct path length used in the LD500 software. Table 6-3 presents the results of these checks, showing the NH_3 concentration in the cell, the LD500 readings, and the average, standard deviation, %RSD, maximum, and minimum of those readings. Zero values determined during the test show individual results from -0.46 to 14.0 ppmwv, though most results were zero. The span values show standard deviations of 11.4 and 4.66 ppmwv in the two weeks, with no significant trend with time. These standard deviations result in RSD values of 2.43% in Week 1 and 0.96% in Week 5.

6.5 Response Time

LD500 response time was estimated using the 10-second readings generated during the dynamic spiking runs. Because these checks were performed in an external calibration cell with a light path through both the duct and the calibration cell, the LD500 readings were subject not only to the LD500's time response, but also to the adsorptive nature of ammonia and the physical changeover due to gas replacement in the calibration cell. The internal volume of the calibration cell was 0.5 L, and the gas flow rate through the cell was 1.3 L/min. The LD500 would be expected to display the final concentration only after the reference cell had changed volumes several times. Therefore, the final concentration would not have been displayed until the standard gas or zero gas had been flowing through the calibration cell for at least one minute. Consequently, the response times indicated below should be taken as procedural changeover times and not as the instrument response times of the LD500. Vendor-supplied information indicates that true LD500 response times are generally a few seconds.

Table 6-4 presents the CEM rise and fall times during the dynamic spiking in Week 3. Figure 6-2 presents examples of the Week 3 rise and fall curves. Table 6-4 shows that the rise times observed with the LD500 averaged 53 seconds. The observed fall times averaged 57 seconds. The data leading to both of these average response times varied considerably. Because these measurements were recorded with a light path through both the calibration cell and the flue gas, these readings reflect both the variability of flue gas concentrations and the time needed to replace the gas in the calibration cell. The observed response times are consistent with the concentration profiles expected based on the cell volume and gas flow rate.

Table 6-3. Calibration and Zero Drift for LD500 During Weeks 1 and 5

Gas Standard Concentration (ppmwv)	LD500 Reading (ppmwv)	LD500 Average (ppmwv)	Standard Deviation (ppmwv)	Relative Standard Deviation (%)	LD500 Minimum (ppmwv)	LD500 Maximum (ppmwv)
Weeks 1 and 5 Zeros						
0	0.0					
0	-0.01 (-0.46)[(a)]					
0	0.0					
0	0.0					
0	0.3 (14.0)					
0	-0.01 (-0.46)					
0	0.0					
		0.04 (1.86)	0.115 (5.36)	—	-0.01 (-0.46)	0.3 (14.0)
Week 1 Spans						
479	10.4 (484.6)					
479	10.1 (470.6)					
479	10.1 (470.6)					
479	9.8 (456.6)					
		10.1 (470.6)	0.245 (11.4)	2.43	9.8 (456.6)	10.4 (484.6)
Week 5 Spans						
479	10.4 (484.6)					
479	10.3 (479.9)					
479	10.5 (489.3)					
		10.4 (484.6)	0.100 (4.66)	0.96	10.3 (479.9)	10.5 (489.3)

(a) First value shown is actual reading of the LD500; value in parentheses is corrected to adjust for the fact that the light path passed through only the 0.13 m calibration cell, and not the 6.05 m path programmed in the LD500.

6.6 Ease of Use

The LD500 has some features that make it easy to use. Other features add complexity to its use. Once the LD500 was set up and calibrated, it required very little maintenance. Zero and span checks (Section 6.4) revealed that the LD500 did display a slight variation around zero but maintained its calibration setting very well. Other specific aspects of installation and operation are discussed below.

6.6.1 Installation

Installation and LD500 setup at the site required two Opsis engineers. The engineers set up the LD500 central unit in the instrument trailer along with a desktop computer, bundled cable to reach from the analyzer to the duct (100 m), mounted and strung cable connecting the emitter/ receiver modules at the duct, aligned the optics, plumbed in purge air, and verified LD500 performance.

Table 6-4. LD500 Rise and Fall Times

Week 3 Rise/Fall[(a)]	Time	Rise/Fall Time (seconds)
Rise	12:29:09	93
Rise	12:54:26	66
Rise	13:22:19	31
Rise	14:04:18	42
Rise	14:39:52	32
	Average Rise	53
Fall	12:10:39	54
Fall	12:40:16	28
Fall	13:07:53	73
Fall	13:49:17	47
Fall	14:22:06	106
Fall	14:57:19	31
	Average Fall	57

[(a)] Flue gas background concentration approximately 1 ppmwv; dynamic spike concentration 8.15 ppmwv above background.

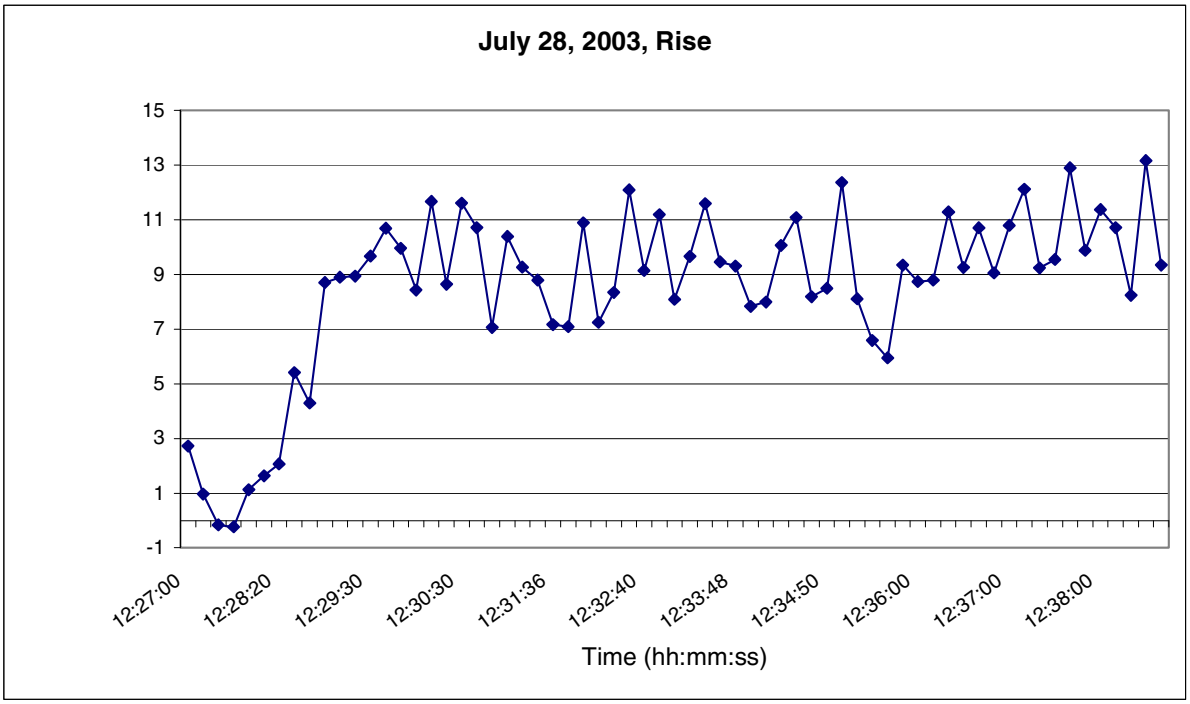
Additional support from plant personnel was required to provide power at the duct for the emitter/receiver, drop the cabling from the duct to the trailer, install a support bracket provided by the vendor for the large receiver module, and mount the lenses on the flanges at the duct. Teardown/demobilization required only one engineer and proceeded much more quickly.

6.6.2 Zero and Span Checks

As noted above, the emitter/receiver module of the LD500 has a built-in, temperature-controlled, calibration gas cell (0.5 L volume, 13 cm length). A useful feature of the LD500 is that the laser light can be directed along any of the following three paths: 1) through the duct alone, 2) through the calibration cell alone, or 3) through both the duct and calibration cell. Such functionality in combination with electronically operated solenoid valves allows for unattended zero/span checks. The small size of the gas cell ensured that a stable response was achieved in a relatively short time after the ammonia or zero nitrogen gas was introduced.

6.6.3 Dynamic Spiking

The laser light paths discussed in Section 6.7.2 also are useful when conducting dynamic spiking studies. The variable laser light path makes it possible to perform dynamic spiking without further LD500 modification. In this verification test, spiking was conducted manually, requiring that trained personnel operate the LD500 data acquisition software in manual mode. However, the LD500 system can be set up to carry out such spiking (known as an “add on” calibration) automatically. The data adjustment after collection during dynamic spiking runs was somewhat



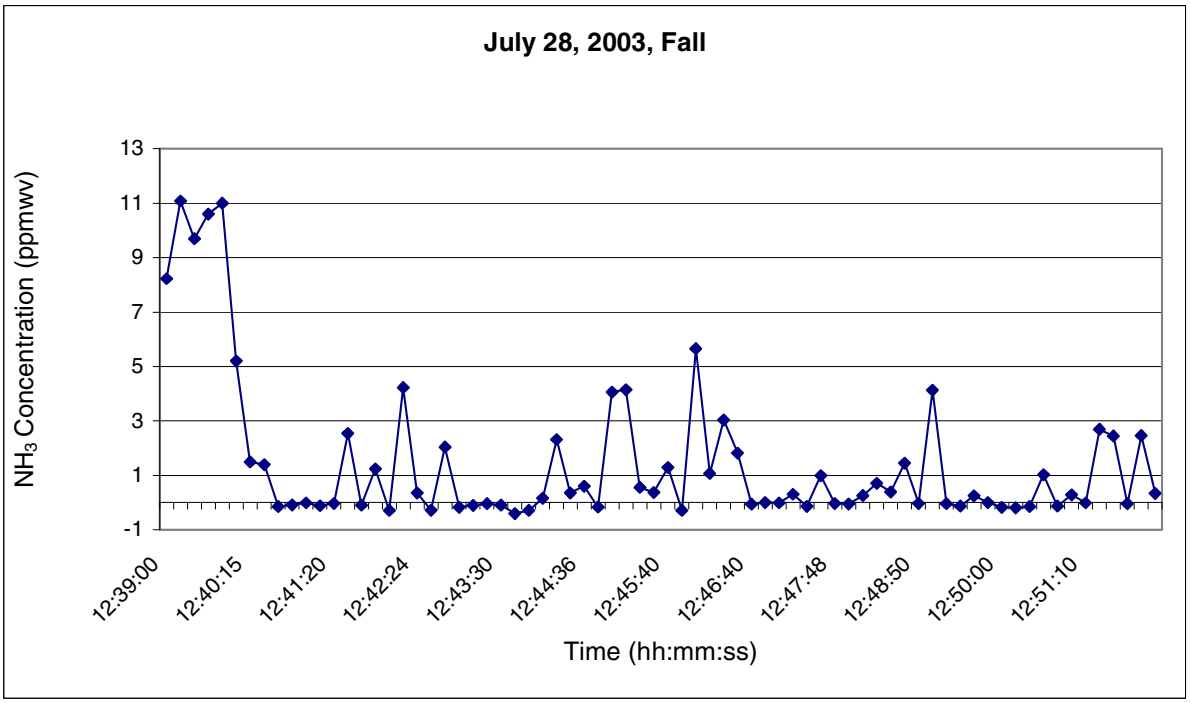


Figure 6-2. Example LD500 Rise and Fall Time Plots

cumbersome and required a correction for temperature to be recalculated at every duct temperature observed during the dynamic spiking period. This adjustment can be done in the LD500 data software; the vendor indicates that this capability will be in all future LD500 systems.

6.6.4 Data Handling

Data files were extracted from the data logging program by Opsis staff and copied onto floppy discs for transfer to a Battelle laptop. The tab-delimited ASCII files were suitable for importing directly to spreadsheet software.

6.7 Data Completeness

Data completeness was approximately 70% over the five-week test period. The LD500 required intervention by vendor engineers in two instances to rectify errors that caused the data system to lock up and, on one occasion, also caused the loss of data.

The first instance occurred when the LD500's autocalibration sequence failed. A feature of the LD500 is its ability to conduct, at user-determined times, automatic zero/span checks using compressed calibration gases. These calibration checks are typically scheduled during off-peak hours as the LD500 cannot simultaneously measure duct ammonia concentrations and calibration gases. On Monday morning of Week 1, the first scheduled zero/span failed and the LD500 froze, thereby halting all data collection. After consultation with Opsis engineers, Battelle staff rebooted the LD500 and successfully restarted data collection. The problem recurred later Monday afternoon and early Tuesday morning. By later Tuesday morning, the Opsis engineer had arrived on site, remedied the problem, and run a zero/span. No data correlating to reference sampling runs were lost, but one zero/span was lost.

The second instance occurred on Monday of Week 4, when the hard disk in the LD500 failed. Because the site was unattended, this failure was not detected until an Opsis staff member arrived on site on Monday of Week 5, at which time he diagnosed the problem and ordered replacement parts. The LD500 functioned intermittently throughout the day Tuesday, but it was not until early Wednesday morning of Week 5 that the LD500 system was running normally. Approximately nine days of data were lost, in addition to two scheduled daily zero/span checks.

6.8 Cost

The vendor indicated that the purchase cost of the complete LD500 system, as implemented for this verification test, was approximately $55,000.

Chapter 7
Performance Summary

Table 7-1 summarizes the results for each of the LD500 performance parameters. Note that all quantitative results originate from discrete 10-second readings reported by the LD500 without smoothing or averaging, as described in Section 3.2.

Table 7-1. Summary of LD500 Verification Results

Parameter	Performance Results	Comments
Agreement with Standards	10.4% at 2.14 ppmwv 7.9% at 5.22 ppmwv 14.3% at 8.15 ppmwv	Results of three concentration levels with 12 data points each; nine data points used in each calculation; median difference from expected value = 0.43 ppmwv
Relative Accuracy	Not calculated	Reference sampling location unrepresentative of duct ammonia concentrations[(a)]
Linearity	Regression line = 1.198 (± 0.036)x - 0.521 (±0.209) ppmwv, r^2 = 0.970	Calculated over range of 2.14 to 8.15 ppmwv, 36 total data points
Precision	48.6% RSD at 2.82 ppmwv 24.1% RSD at 6.26 ppmwv 15.8% RSD at 10.12 ppmwv	Discrete 10-second data, no smoothing; variability due partly to the variability of background ammonia concentration in the duct
Calibration and Zero Drift	Zero drift averaged 1.86 ppmwv Span RSD values = 0.96 to 2.43%	Minimal span drift over the five-week test
Response Time	Rise times average 53 seconds Fall times average 57 seconds	Observed response times largely due to concentration changeover in the test cell
Ease of Use	Generally easy to use	
Completeness	70% data capture	Missing data due to data system lock up and hard drive failure

[(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.