July 2004

Environmental Technology Verification Report

PRANALYTICA, INC.

NITROLUX™ 1000 AMBIENT AMMONIA ANALYZER

Prepared by
Battelle

Battelle
The Business of Innovation

In collaboration with the
U.S. Department of Agriculture

Under a cooperative agreement with

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

ETV ETV ETV

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Pranalytica, Inc.
Nitrolux™ 1000 Ambient Ammonia Analyzer

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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 seven environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

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

Acknowledgments

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List of Abbreviations

AFO	animal feeding operation
AMS	Advanced Monitoring Systems
CI	confidence interval
cm	centimeter
CO_2	carbon dioxide
DL	detection limit
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FIA	flow injection analysis/analyzer
L	liter
Lpm	liters per minute
µg	microgram
µm	micrometer
mg	milligram
mL	milliliter
mm	millimeter
NIST	National Institute of Standards and Technology
NH_3	ammonia
NH_4^+	ammonium
ppb	part per billion
%D	percent difference
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RPD	relative percent difference
RSD	relative standard deviation
SD	standard deviation
TSA	technical systems audit
USDA	U.S. Department of Agriculture

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, in collaboration with the U.S. Department of Agriculture's (USDA) National Soil Tilth Laboratory, recently evaluated the performance of the Pranalytica, Inc. Nitrolux™ 1000 ambient ammonia (NH_3) analyzer.

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 Nitrolux 1000. The following is a description of the Nitrolux 1000, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The Nitrolux 1000 (Figure 2-1) is an ambient NH_3 analyzer that uses resonant photoacoustic spectroscopy and a line-tunable carbon dioxide (CO_2) laser to provide continuous or on-demand measurements. A CO_2 laser is useful to excite NH_3 because one of its laser lines is nearly coincident with one of NH_3's strongest spectral features. The excited NH_3 molecules undergo collisional deactivation, which converts the absorbed energy into periodic local heating at the modulation frequency of the laser. The resulting acoustic waves are detected with a low-noise microphone to quantify NH_3 with minimal interferences from carbon monoxide, hydrogen sulfide, methane, sulfur oxides, nitrogen oxides, ozone, and other contributors at their typical concentrations in a non-polluted atmosphere.

The Nitrolux 1000 is sensitive to NH_3 concentrations of 1 part per billion (ppb) and has a range of 0 to 2,000 ppb with full-scale ranges of 20 to 2,000 ppb by automatic or manual switching. The Nitrolux 1000 consists of a sealed-off radiofrequency-excited $^{13}CO_2$ laser, whose operating wavelength can be line-switched by using an intracavity grating, a flow-through analysis cell, a laser power meter, a signal processor, and a single-board computer for controlling all internal operations and analyzing the signals to produce concentration readings in real time. Optional analysis cells allow for simultaneous measurement of two to 16 input streams. Samples are extracted in a continuous mode at approximately 400 to 500 standard cubic centimeters (cm) per minute and pass through a 40-micrometer

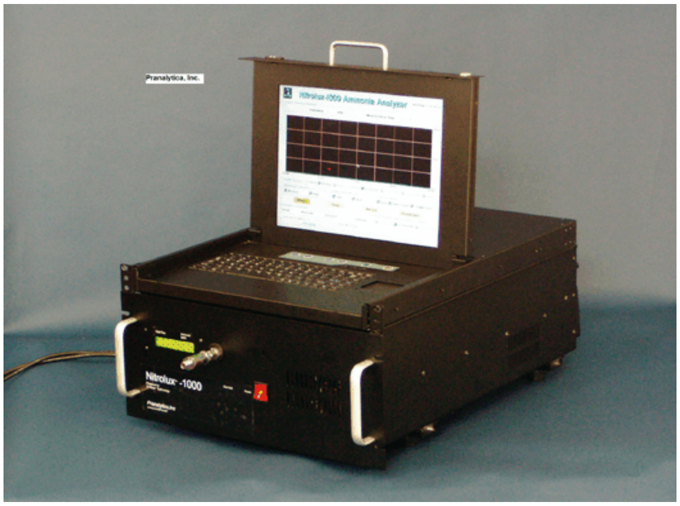

Figure 2-1. Pranalytica's Nitrolux 1000 Ambient NH_3 Analyzer

(µm) in-line filter to remove particulate matter. Time-stamped NH_3 concentration measurements are stored on an internal hard disk.

Power requirements of the Nitrolux 1000 are 150 Watts at 110 volts, 60 Hertz alternating current. It comes with a rack-mountable foldout 15-inch flat-panel video display, including keyboard and mouse. The rack mount is 48.3 cm (19 inches) wide, 61.0 cm (24 inches) deep, and 25.4 cm (10) inches high. It weighs 29.5 kilograms (65 pounds). The approximate cost of the Nitrolux 1000 with rack mount display is $24,000. Additional particulate filters cost $250 each, and mounting rails for installation are $150 per pair.

Chapter 3
Test Design and Procedures

3.1 Test Design

Livestock agriculture is thought to be the primary source of atmospheric NH_3 in the United States and accounts for approximately 70% of NH_3 emissions in the United States.(1) As a result, a means to accurately quantify these emissions is needed. The objective of this verification test was to verify the Nitrolux 1000's performance in measuring gaseous NH_3 in ambient air at animal feeding operations (AFOs).

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Ambient Ammonia Monitors at Animal Feeding Operations,*(2) with the exception of six deviations that are addressed later in this report. The verification test was conducted in two phases, each at separate AFOs. The first phase of testing was conducted between September 8 and October 3, 2003, at a swine finishing farm near Ames, Iowa. The second phase was conducted between October 20 and November 14, 2003, at a cattle feedlot in Carroll, Iowa. These sites were selected to provide realistic testing conditions, which were expected to exhibit a wide range of NH_3 concentrations during the test periods.

The verification test was designed to evaluate the following performance parameters:

- Relative accuracy
- Linearity
- Precision
- Response time
- Calibration/zero drift
- Interference effects
- Comparability
- Ease of use
- Data completeness.

During each phase of the verification test, the Nitrolux 1000 response to a series of NH_3 gas standards of known concentration was used to quantify relative accuracy (RA), linearity, precision (repeatability), and calibration/zero drift. The Nitrolux 1000 response time, the time to reach 95% of the stable signal, was also assessed during the delivery of the NH_3 standards. During Phase II, interference effects were quantified from the Nitrolux 1000 response to various chemical species that may be present at AFOs; the potential interferent gases were delivered both in the presence and absence of NH_3. The Nitrolux 1000 response to ambient air was also evaluated during both phases as the comparability to simultaneous determinations by an ambient NH_3 reference method (acid-coated denuders). Additionally, the ease of use of the Nitrolux 1000 was evaluated based on operator observations. Data completeness was determined based on the amount of data collected as a percentage of the amount of data that could have been collected.

3.2 Site Descriptions

The Nitrolux 1000 was installed at the Phase I and II testing locations by a vendor representative. Battelle and USDA staff worked with the vendor representative to establish procedures for operating the Nitrolux 1000 during this verification test. The vendor representative trained Battelle and USDA staff to check several instrument parameters to verify the operation of the Nitrolux 1000 and identify signs of malfunction. A checklist, provided by the vendor representative and included as Appendix A, was completed daily by Battelle and USDA staff. In the event of an instrument malfunction, Battelle and/or USDA staff could contact the vendor representative and conduct minor troubleshooting procedures upon request as necessary, but were not expected to make any major repairs. The vendor representative remained on-site until the installation was complete. All the testing activities were conducted by Battelle and/or USDA staff. The vendor representative returned to the test site after the completion of Phase I to install the Nitrolux 1000 at the Phase II test site.

3.2.1 Site Description—Phase I

Figure 3-1 shows a schematic diagram of the swine farm during Phase I of the verification test. The AFO included ten animal barns arranged in two parallel rows of five, with each barn housing up to 2,000 swine. The urine and feces from the swine exited the barns through metal gratings in the floor and were deposited in two nutrient lagoons located on the southern end of the AFO. The perimeter of the AFO was lined with trees, with agricultural fields surrounding the AFO perimeter. A temperature-regulated instrument trailer was placed on-site during the test to house the monitoring equipment and to provide a sheltered work space. The Nitrolux 1000 was installed inside the instrument trailer, and a Teflon inlet line was used to supply outside air to the Nitrolux 1000. The inlet was mounted on a tripod on the west side of the trailer at a height of approximately 2 meters. The platform shown in Figure 3-1 was installed to hold some of the monitoring equipment.

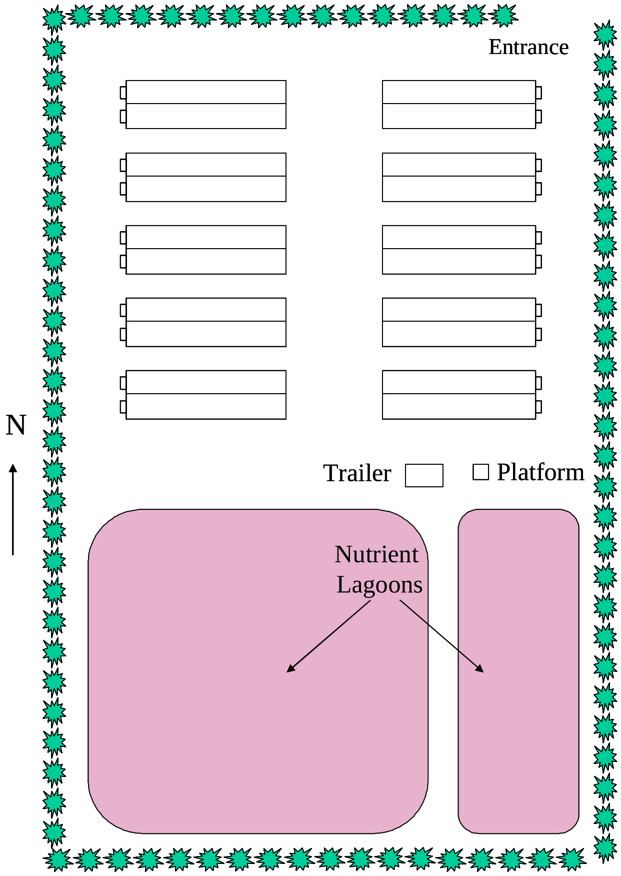

Figure 3-1. Phase I Test Site

3.2.2 *Site Description—Phase II*

Figure 3-2 shows a schematic diagram of the cattle feedlot during Phase II of the verification test. The instrument trailer used in Phase I of this verification test was also used in Phase II and was in a harvested corn field surrounded on three sides by cow pens. The farm was surrounded on all sides by corn fields, most of which had been harvested. Approximately 2,000 to 3,000 head of cattle were on the farm during the verification test. The Nitrolux 1000 was installed in the instrument trailer as in Phase I, with an inlet height of approximately 1.5 meters.

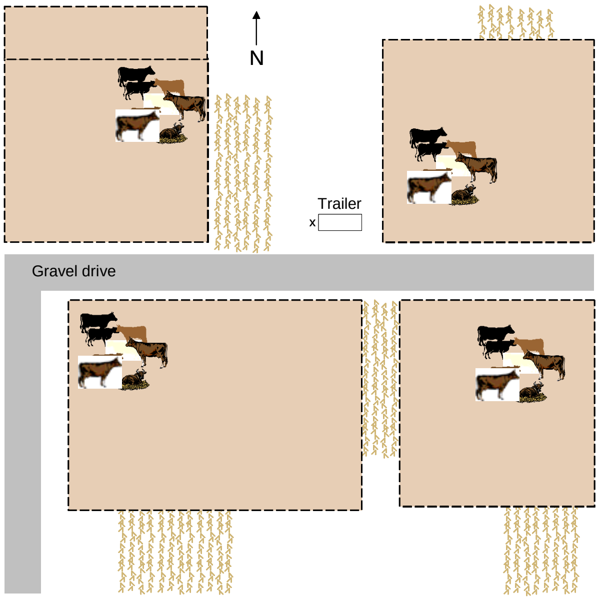

Figure 3-2. Phase II Test Site

3.3 Test Procedures

All tests utilized the continuous NH_3 measurement data record stored by the Nitrolux 1000 that were downloaded from the instrument and transferred digitally to computer spreadsheets for analysis.

3.3.1 *Accuracy, Linearity, Precision, and Response Time*

During the first and last (fourth) week of each phase of testing, the Nitrolux 1000 was independently supplied with compressed NH_3 gas standards to achieve NH_3 concentrations over a range from 0 to 10,000 ppb (Phase I) or 0 to 2,000 ppb (Phase II) to simulate the range expected in ambient air during each phase. The gases delivered to the Nitrolux 1000 were prepared by diluting higher-concentration NH_3 standard gases (i.e., 100 to 500 parts per million) in zero air using a calibrated dilution system provided by the USDA.

The NH_3 gas was supplied to the Nitrolux 1000 for between 30 minutes and two hours at each concentration level. Accuracy, linearity, and precision were established based on the continuous digital data set recorded by the Nitrolux 1000 during the periods when the NH_3 gas was supplied. Data were used for the calculations once the signal had stabilized at a constant concentration (i.e., the signal did not appear to be increasing or decreasing with time). The time required to reach 95% of the change in the stable reading for each concentration was also recorded for the Nitrolux 1000. These data were used to assess the response time of the Nitrolux 1000.

3.3.2 Calibration and Zero Drift

On Monday, Wednesday, and Friday of the first and last weeks of testing during each phase, the Nitrolux 1000 was supplied with a 1,000-ppb (nominal) NH_3 gas standard and zero air to check the calibration and zero drift of the Nitrolux 1000, respectively. Zero air and the 1,000-ppb NH_3 standard were each supplied to the Nitrolux 1000 for approximately one hour, during which time the measured concentrations were recorded by the Nitrolux 1000.

3.3.3 Interference Effects

During the second phase of testing, the Nitrolux 1000 was independently supplied with a series of potential interference gases (hydrogen sulfide, nitrogen dioxide, 1,3-butadiene, and diethylamine) to assess any impact the gases have on the Nitrolux 1000 response. The interferent gases were supplied from diffusion tubes (VICI Metronics, Poulsbo, Washington) at concentrations of approximately 100 to 300 ppb in zero air and a 500-ppb NH_3 standard as carrier gases.

The process for supplying the interferent gases was as follows: zero air was supplied to the Nitrolux 1000 until a stable reading was achieved. The interferent gas was added to the zero air flow and supplied to the Nitrolux 1000 until a stable reading was observed (at least 2 minutes). The Nitrolux 1000 was flushed for at least 2 minutes with zero air, and the next interferent gas was delivered. This process was repeated for the four interferent gases. A 500-ppb NH_3 standard was then supplied to the Nitrolux 1000 until a stable reading was achieved. The interferent gas was added to the NH_3 standard for delivery to the Nitrolux 1000 and the process outlined above was repeated, delivering the 500-ppb NH_3 standard for at least 2 minutes between each interferent gas.

3.3.4 Comparability

The comparability of the Nitrolux 1000 with a standard reference method was established by comparing the average Nitrolux 1000 readings with time integrated NH_3 samples collected using citric-acid coated denuders. The reference samples were collected based on procedures described in the EPA Compendium Method IO-4.2, *Determination of Reactive Acidic and Basic Gases and Acidity of Fine Particles (< 2.5 μm).*(3)

For this test, NH_3 samples were collected using a ChemComb Model 3500 Speciation Sampling Cartridge (Rupprecht & Patashnick Co., East Greenbush, New York). Figure 3-3 shows a schematic illustration of the ChemComb sampling cartridge. Samples were collected by drawing ambient air through an impactor at a nominal rate of 10 liters per minute (Lpm) to remove particulate matter with aerodynamic diameters greater than 2.5 µm. The air was passed through two or more citric-acid-coated denuders to collect gaseous NH_3. A single Teflon filter was used to collect the particulate matter that passed through the denuder. For Phase I, air flow was controlled using diaphragm pumps with needle valves. During Phase II, automated Partisol^{M} Model 2300 speciation samplers (Rupprecht & Patashnick Co., East Greenbush, New York) were used. The Partisol samplers were equipped with mass-flow controlled sampling systems that were pressure- and temperature-corrected. This improved the accuracy of the sampled air volume and also reduced the overall labor requirements. The samplers had not been available during Phase I.

The procedures that were used for preparing and coating the denuders were based on the procedures given in the ChemComb Operating Manual(4) and the test/QA plan(2). The denuders were coated in an NH_3-free glove box at a USDA National Soil Tilth Laboratory facility in Ames, Iowa, and stored in an NH_3-free glove box until they were installed in the ChemComb sampling cartridge and transported to the test site. Cartridges were assembled in the laboratory and transported to the test site. All denuders were used within 72 hours of being coated and within 24 hours of being transported to the field.

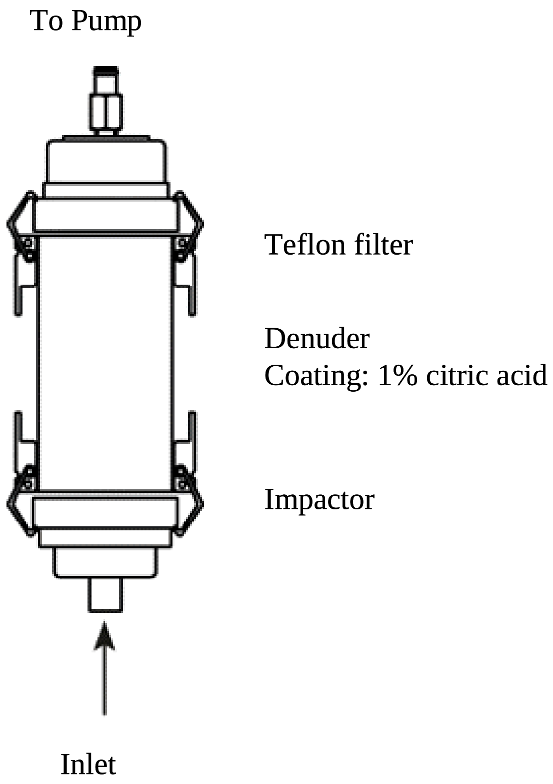

Figure 3-3. Reference Method Sampling Cartridge

Reference samples were collected during the second and third weeks of testing during each phase. To capture diurnal variations in NH_3 concentrations, sampling was conducted on approximately the following schedule: 8:00 a.m. to 12:00 p.m., 12:00 p.m. to 2:00 p.m., 2:00 p.m. to 4:00 p.m., 4:00 p.m. to 8:00 p.m., and 8:00 p.m. to 8:00 a.m., so that five sets of samples were collected in each 24-hour period. The short-term (2-hour and 4-hour) sampling captured the midday peaks in NH_3 concentrations, whereas the 12-hour sampling captured overnight, generally low, concentrations. After sampling, the sampling media were retrieved and transported to the USDA laboratory for extraction and analysis. During Phase I, sampling was conducted at two locations: the instrument trailer near the Nitrolux 1000 inlet and near the platform shown in Figure 3-1. Duplicate samples were obtained at each location. Sampling was conducted daily, Monday through Friday, during the two-week reference sampling period. During Phase II, the reference sampling for single-point monitors was conducted at one location near the monitor inlets at the instrument trailer. Duplicate samples were also obtained at this site. The sampling schedule for Phase II deviated from the test/QA plan in that sampling was conducted every other day, including weekends, during the two-week sampling period. The schedule allowed sufficient time for sample transportation and processing between sampling days.

Extraction and analysis of the denuders were performed as described in the test/QA plan,(2) with one exception. The water volume used to extract the denuders was increased from 10 milliliters (mL), as specified in the test/QA plan, to 20 mL. The volume was increased to accommodate the sample volume requirements of the analysis method described below. A deviation was filed to address this change, which does not impact the quality of the reference data. Samples were extracted in an NH_3-free glove box and stored in acid-washed scintillation vials to prevent contamination. The USDA analyzed the samples by flow injection analysis (FIA) using a Lachat QuikChem Automated Flow Injection Ion Analyzer (Lachat Company, Loveland, Colorado) according to QuikChem Method No. 10-107-06-2-A. The method involves heating the NH_3 sample with salicylate and hypochlorite in an alkaline phosphate buffer, which produces an emerald green color proportional to the NH_3 concentration. The color was intensified by adding sodium nitroprusside and monitored photometrically.

When possible, samples were analyzed within 24 hours of extraction, as specified in the test/QA plan. When analysis within 24 hours of extraction was not possible, the samples were stored frozen until the analysis could be performed, in accordance with the test/QA plan.

Chapter 4
Quality Assurance/Quality Control

QA/quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(5) and the test/QA plan for this verification test.(2)

Six deviation reports were filed during this test and have been addressed in this report. In summary, a change was made in the reference sampling schedule and equipment for Phase II (Section 3.3.4), the denuder extraction volume was increased (Section 3.3.4), some percent difference values measured for duplicate reference samples exceeded 10% (Section 4.2.3), laboratory blank tolerances were redefined (Section 4.2.4), the order in which laboratory blanks and calibration check standards were submitted for analysis was changed (Section 4.2.4 and 4.2.5), and not all of the test data were reviewed within two weeks of the end of the test phase (Section 4.5). None of these deviations have impacted the quality of this verification test.

4.1 Equipment Calibrations

4.1.1 Reference Method Sampling Equipment

Reference method sampling was conducted based on the procedures described in the EPA method(3) and the ChemComb operating manual.(4) A single-point calibration of the flow rate through each of the sampling systems (i.e., pump, flow controller, filter pack, denuder, impactor) was performed prior to starting each phase using a flow meter with a National Institute of Standards and Technology (NIST)-traceable calibration. The flow rate of each sampler was checked at the beginning and end of each sampling period using an in-line flow meter. The flow rate was readjusted if the flow check was not within ± 5% of the nominal flow rate of 10 Lpm (i.e., 9.5 Lpm to 10.5 Lpm). All calibration results were documented for inclusion in the verification test data files. For Phase II, flows were controlled by the pressure- and temperature-corrected mass flow controllers used in the USDA's Partisol samplers. These samplers shut off automatically if the flow deviated by ± 5% from the 10 Lpm setpoint for more than 5 minutes, and the data were flagged. Actual sample volumes were recorded by the samplers.

4.1.2 Analytical Equipment

The reference samples were analyzed in the USDA laboratory using FIA. A five-point calibration was measured on the FIA for the reference sample analysis prior to each analytical session by the USDA staff performing the analysis. The calibration was conducted according to the manufacturer's recommendations and included concentrations of NH_3 standard solutions throughout the operating range of the FIA. The calibration was acceptable if the coefficient of determination (r^2) of the calibration curve was greater than 0.99. The FIA detection limit (DL) was 0.03 milligrams per liter (mg/L) and was determined as three times the standard deviation of repeated measurements of a low-level NH_3 standard. Any analytical results that fell below the FIA DL were used without any further adjustment.

Calibration check standards were analyzed after every fifteenth sample in the batch. These calibration checks were considered acceptable if the measured concentration agreed within 10% of the standard solution concentration. If a calibration check failed to agree within 10% of the standard concentration, the FIA was recalibrated; all analyses since the last acceptable calibration check were repeated. All calibration results were documented for inclusion in the verification test data files.

4.1.3 Meteorological Equipment

The sensors used for meteorological monitoring had been calibrated by the manufacturer (Met One Instruments, Inc., Grants Pass, Oregon) within one year of their use in this verification test. The calibration results were included in the verification test data files.

4.1.4 Ammonia Dilution System

The USDA NH_3 dilution system (Environics, Tolland, Connecticut) employs three heated mass flow controllers and valves dedicated for the dilution of compressed NH_3 mixtures. The output flow rates were verified using an independent, NIST-traceable flow meter and agreed to within 10%.

4.2 QC Samples

4.2.1 Field Blanks

At least 10% of all reference samples collected were field blanks. The field blanks were collected by installing the sampling media (i.e., denuder and filters) in the sampling train without drawing any air through the train. The media were recovered and handled as normal samples. Field blanks were collected at each of the sampling locations and during each of the sampling periods (e.g., 8:00 a.m. to 12:00 p.m.). Field blank results were used to detect potential sample contamination (defined in the test/QA plan as field blank values greater than 5% of any reference samples for that day) and also to determine the reference method DL.

The reference method DL was determined from the field blank results and reported in terms of an NH_3 mass corresponding to three times the standard deviation of the NH_3 mass collected on the field blanks. Reference method DLs were determined for each phase and were more than six times higher than the equivalent FIA DL (0.6 microgram [µg] NH_3 per 20-mL sample).

The reference method DLs, reported as NH_3 masses, were used to determine the minimum detectable NH_3 concentration for each phase. Since the mass of NH_3 collected by the reference method is a function of the sampling time, flow rate, and the ambient NH_3 concentration, the minimum (time-integrated) ambient NH_3 concentration detectable by the reference method varies depending on the same period duration. (This assumes a constant flow rate.) For example, to collect 100 µg NH_3, the time-integrated ambient NH_3 concentration must be 20 ppb for a 12-hour sample and 120 ppb for a 2-hour sample. Accordingly, the minimum ambient NH_3 concentrations that could be detected from the collection of 2-, 4-, and 12-hour samples at a nominal flow rate of 10 Lpm were calculated from the reference method DL for each phase.

4.2.1.1 Phase I

During Phase I of testing, a total of 11 field blanks were collected (10% of reference samples). The sample cartridges were exposed to ambient air (caps removed) for approximately the time it would take to connect the cartridges to the pump tubing. The caps were then replaced and the cartridges handled in the same way as regular reference samples. The average NH_3 mass collected on the field blanks was 5.3 µg, with a range of 1.5 to 7.0 µg. This range of collected NH_3 corresponded to 0.5% to 6.5% of the NH_3 mass collected on any of the reference samples on the corresponding days during which the field blanks were collected. Two of the Phase I field blanks were above 5% of the minimum reference sample mass for that corresponding day. These field blanks collected 5.6 µg NH_3, which was slightly above the average field blank NH_3 mass during Phase I; however, the field blanks were collected on days that exhibited lower ambient NH_3 levels, resulting in a relatively large percentage of the reference mass (6.5% and 5.9%). These field blanks did not show unusually high levels of contamination, and it does not appear that they had a significant impact on the Phase I reference method results. The standard deviation of the NH_3 collected on field blanks for Phase I was 1.6 µg and the Phase I reference method DL was 10.1 µg NH_3. The minimum detectable ambient NH_3 concentrations are shown in Table 4-1 for 2-, 4-, and 12-hour samples. During Phase I, all measured NH_3 levels were greater than these minimum NH_3 concentrations, with a minimum measured value of 107 ppb for a 2-hour sample.

Table 4-1. Minimum Detectable Ambient NH_3 Concentrations During Phase I

	2-Hour Sample	**4-Hour Sample**	**12-Hour Sample**
Minimum detectable NH_3 concentration	12.1 ppb	6.0 ppb	2.0 ppb
Number of reference samples collected	46	45	19
Number less than the minimum detectable NH_3 concentration	0	0	0

4.2.1.2 Phase II

During Phase II of testing, the reference sampling was conducted somewhat differently than in Phase I, in that all the reference sampling cartridges and field blanks were installed in the sampler prior to the first sampling period on a given day. The reference sample and field blank cartridges were thus exposed to the ambient environment for a period of approximately 24 hours. Nonetheless, the average measured NH_3 mass in the field blanks for Phase II was somewhat lower than in Phase I. A total of 14 field blanks were collected in Phase II. The average NH_3 mass collected on these blanks was 2.5 µg NH_3, and the range was 0.5 to 4.6 µg NH_3. The mass collected on the field blanks ranged from 1.2% to 55.0% of the smallest reference sample mass collected on the same day, with an average of 19.2%. These percentages are not indicative of unusually high levels of contamination, but rather are a result of relatively low ambient NH_3 levels at the AFO. The impact of these blank levels on the results of this verification test may be manifested as a small positive bias of the reference method results relative to the readings of the technologies being verified. This bias would be most pronounced on days with low ambient NH_3 concentrations. The highest field blank percentages were measured on days when the integrated ambient NH_3 levels were as low as 6 ppb, which is approaching the 4.9-ppb minimum detectable ambient NH_3 concentration for a 2-hour sample. Assuming an ambient air sample volume of 1.2 cubic meters, the smallest volume collected during Phase II, the maximum field blank value corresponds to an ambient concentration of 5.5 ppb. Thus, the sample handling may account for up to 5.5 ppb of the measured values.

The standard deviation of the NH_3 collected from field blanks for Phase II was 1.4 µg, which resulted in a 6.6 µg NH_3 Phase II reference method DL. The minimum detectable ambient NH_3 concentrations for 2-, 4-, and 12-hour samples (at a nominal flow rate of 10 Lpm) are shown in Table 4-2. During Phase II, one measured NH_3 concentration in ambient air fell below the minimum detectable NH_3 concentration, as summarized in Table 4-2.

Table 4-2. Minimum Detectable Ambient NH_3 Concentrations During Phase II

	2-Hour Sample	**4-Hour Sample**	**12-Hour Sample**
Minimum detectable NH_3 concentration	7.9 ppb	4.0 ppb	1.3 ppb
Number of reference samples collected	56	56	29
Number less than minimum detectable NH_3 concentration	2	0	0

4.2.2 Denuder Breakthrough Checks

4.2.2.1 Phase I

Use of backup denuders is called for in the test/QA plan during periods when breakthrough greater than 10% of the front denuder is observed or expected. Owing to the high NH_3 levels observed during Phase I, all reference samples collected during Phase I included at least one backup denuder, and most samples (>70%) included two backup denuders. These backup denuders were used to check the degree of NH_3 breakthrough. The breakthrough checks were conducted at both of the sampling locations and included checks during each of the five

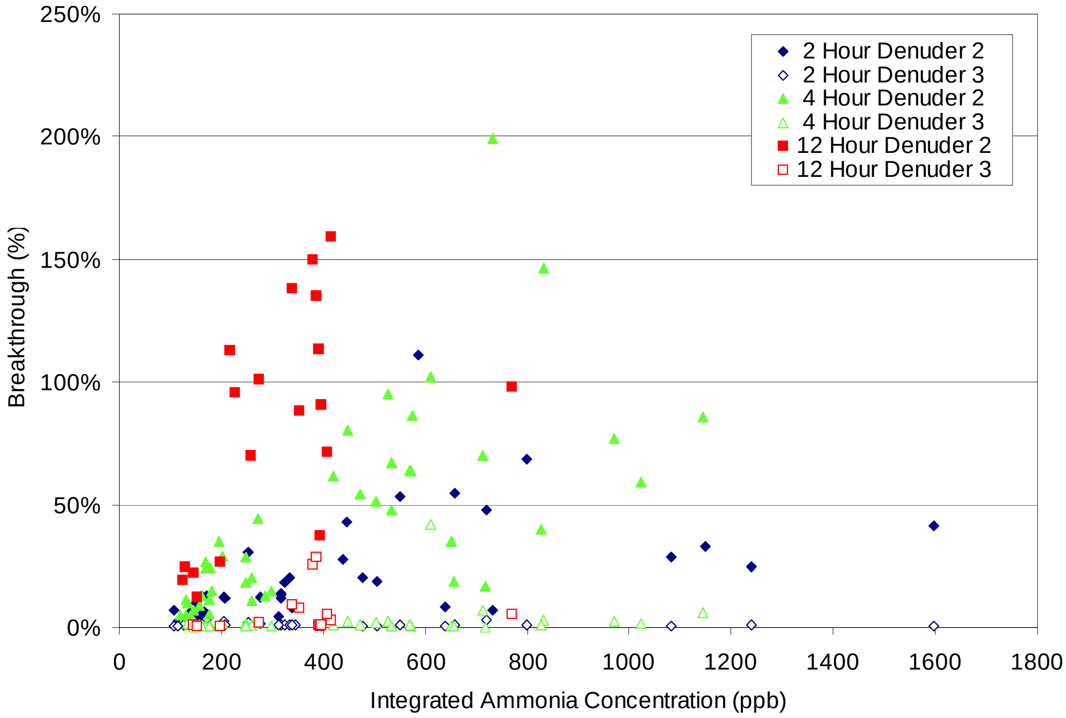

Figure 4-1. Denuder Breakthrough During Phase I as a Function of Integrated NH_3 Concentration

sampling periods (i.e., 8:00 p.m. to 8:00 a.m., 8:00 a.m. to 12:00 p.m., etc.). Figure 4-1 shows the percentage of NH_3 collected on the backup denuders relative to the front denuder (i.e., breakthrough) as a function of the average NH_3 concentration for each of the sampling period lengths (combined data from both sampling locations). The solid symbols in this figure represent the first backup denuder (identified as Denuder 2 in the legend). and the open symbols represent the second backup denuder (identified as Denuder 3 in the legend). This figure illustrates that the first backup denuder captured a significant fraction of NH_3 relative to the front denuder during many of the sampling periods (up to 200% of the front denuder). The second backup denuder captured more than 10% of the NH_3 on the front denuder in only three cases. It is unlikely that NH_3 was lost due to breakthrough of the second backup denuder for these or any of the reference samples. Therefore, these samples were not eliminated from the reference data. The relatively high collection of NH_3 on the first backup denuder may have been caused by displacement by species with a higher affinity for the citric acid coating. Presumably these species would remain on the front denuder, so it is unlikely that NH_3 was lost as a result. Table 4-3 summarizes the results of the breakthrough checks for Phase I.

4.2.2.2 Phase II

The NH_3 levels measured during Phase II were significantly lower than observed during Phase I. Thus, the sampling approach was changed such that all samples still included one backup denuder but only 19% of the samples collected during Phase II included two backup denuders. Figure 4-2 shows the percentage of NH_3 collected on the backup denuders relative to the front denuder as a function of the average NH_3 concentration during the corresponding sampling

Table 4-3. Denuder Breakthrough Checks During Phase I

	2-Hour Samples		4-Hour Samples		12-Hour Samples	
	1st Backup Denuder (%)	2nd Backup Denuder (%)	1st Backup Denuder (%)	2nd Backup Denuder (%)	1st Backup Denuder (%)	2nd Backup Denuder (%)
Percent of reference samples with denuder	100	72	100	80	100	74
Average concentration as % of concentration on front denuder	19.4	1.2	42.4	2.5	82.5	6.5
Maximum concentration as % of concentration on front denuder	111.0	3.6	199.3	41.7	159.2	28.8
Percent of samples with breakthrough greater than 10% of front denuder	57	0	82	3	100	14

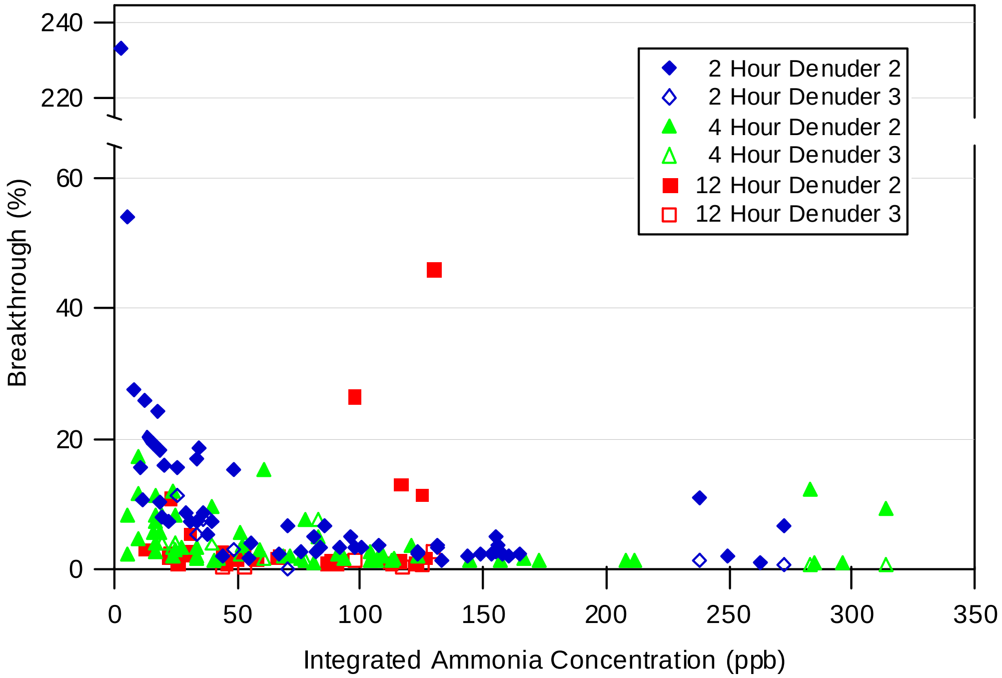

Figure 4-2. Denuder Breakthrough During Phase II as a Function of Integrated NH_3 Concentration

period, using the same symbols as in Figure 4-1. Data for all three Phase II sampling locations are included here. In general, breakthrough onto the first backup denuder (Denuder 2 in the figure legend) was low, with an average breakthrough of 8.6%. As shown in the figure, many of the high breakthrough values (i.e., greater than 10%) observed on the first backup denuder (Denuder 2 in the legend) occurred at very low NH_3 concentrations where the mass of NH_3 collected was similar to that collected for field blanks. The high values do not indicate that breakthrough occurred, but rather that the measurements were near the DL of the reference method. High breakthrough of the first backup denuder also occurred at higher NH_3 concentrations and/or long sample durations. Although these high breakthrough values may indicate that breakthrough of the first backup denuder occurred, the second backup denuder (Denuder 3 in the figure legend) was in place to collect the remaining NH_3. With the exception of one sample that occurred at a low ambient NH_3 concentration, breakthrough observed on the second backup denuder was always less than 10% of the amount collected on the front denuder. Thus, it is unlikely that NH_3 was lost as a result of breakthrough of the first or second backup denuders. Table 4-4 summarizes the results of the breakthrough checks for Phase II.

Table 4-4. Denuder Breakthrough Checks During Phase II

	2-Hour Samples		**4-Hour Samples**		**12-Hour Samples**	
	1st Backup Denuder (%)	**2nd Backup Denuder (%)**	**1st Backup Denuder (%)**	**2nd Backup Denuder (%)**	**1st Backup Denuder (%)**	**2nd Backup Denuder (%)**
Percent of reference samples with denuder	100	18	100	18	100	24
Average concentration as % of concentration on front denuder	8.6	4.1	4.4	2.8	5.2	1.1
Maximum concentration as % of concentration on front denuder	[233.3](a) 53.8	11.3	17.2	7.5	45.9	2.5
Percent of samples with breakthrough greater than 10% of front denuder	29	10	10.7	0	17.2	0

(a) Suspect value rejected based on Q-test and not included in other calculations. This value corresponded to an NH_3 concentration that was less than the minimum detectable NH_3 concentration.

4.2.3 Duplicate Samples

For at least 10% of the reference samples, duplicates were collected using a collocated sampling train (within 1 meter). These duplicate samples were collected at both of the sampling locations during Phase I, and only at the trailer location during Phase II, and were collected during each of the sampling periods. The relative percent difference (RPD) between the duplicate samples was calculated by dividing the absolute difference of the sample concentrations by the average of the sample concentrations.

Table 4-5 summarizes the results of the duplicate sampling for both Phases I and II. During Phase I, a total of 18 sets of duplicate samples were collected. Eight of the duplicate samples were collected at the sampling location next to the trailer, and the other 10 duplicate samples were collected at the sampling location next to the platform. For Phase I the duplicate samples showed absolute RPD values between 0.6% and 22%, and the average RPD was 9%. During Phase II, duplicate samples were collected during every sampling period at the sampling location next to the trailer, resulting in a total of 35 duplicate measurements. The absolute RPD varied between 0.7% and 32%, with an average of 7%. Although the average RPD values are comparable in Phases I and II, the absolute differences were significantly smaller during Phase II. For both phases combined, the absolute RPD for 13 of the duplicate samples exceeded the acceptance criterion of 10% specified in the test/QA plan. To verify the quality of the reference method, NH_3 gas standards were delivered to the reference method. Repeated delivery of the same concentration standard gave an average RPD of 1.3%. Thus, it is probable that the exceedences were caused by non-uniformity in the air sampled and did not impact the quality of the reference method itself. However, some contributions may result from small variations in sampling flow rates and analytical uncertainties.

Table 4-5. Duplicate Reference Method Samples

	Phase I		**Phase II**	
	RPD (%)	**Absolute Difference (ppb)**	**RPD (%)**	**Absolute Difference (ppb)**
Average	9	28	7	5
Maximum	22	109	32	18
Minimum	0.6	1	0.7	0.6
Number of duplicate samples	18		35	
Number with RPD >10%	6		7	

4.2.4 Laboratory Blanks

Laboratory blank solutions were prepared for the FIA using distilled, deionized water. In each analytical batch, at least 10% of the number of reference samples analyzed were laboratory blanks, and were submitted to the laboratory as blind samples. The analysis of the laboratory blanks deviated from the test/QA plan in that, rather than submitting the blanks routinely (e.g., every tenth sample), the blanks were interspersed among the other samples and submitted as blind samples.

During Phase I, a total of 31 laboratory blank samples were analyzed. The analytical results from the laboratory blanks indicated no apparent drift in the calibration of the FIA, and none of the blank values were greater than 5% of the lowest measured reference sample on that day. (Note:

The test/QA plan indicates that laboratory blanks should not exceed 5% of any concentration measured on that day. As written, this threshold includes field blanks and backup denuder samples. A deviation report has been filed to change this threshold so that it applies only to composite reference samples and does not include samples that would be expected to have low concentrations, such as field blanks.) During Phase II, a total of 27 laboratory blank samples were analyzed. Similarly, the analytical results from the laboratory blanks indicated no apparent drift in the baseline of the FIA, and none of the blank values was greater than 5% of the lowest measured reference sample on that day.

4.2.5 Calibration Checks

In addition to analyzing every 15th calibration check samples, as described in Section 4.1.2, at least 10% of the samples were submitted to the laboratory as blind calibration check samples. These blind calibration check samples were prepared by diluting NIST-traceable NH_4^+ standard stock solution.

During Phase I, 38 NH_4^+ blind calibration check samples were prepared from 15 different standard solutions, ranging in concentration from 0.4 to 8 mg/L NH_3. Measured concentrations for 10 of these calibration check samples differed from the delivered standard concentration by more than 10%, and the full set of measured values was on average 1.9% lower than the delivered concentration. It should be noted that the calibration check samples were prepared from NH_4^+ standards that were diluted from a 1,000-mg/L stock solution and that errors may have occurred during the dilution process. For example, nine of the 10 calibration check samples that failed were prepared from four different standard solutions. Of these four standard solutions, a total of 10 samples were submitted to the laboratory for analysis, and 9 of the samples fell outside the 10% acceptance criterion. Of the 28 additional samples submitted to the laboratory from the 11 other prepared standard solutions, only one fell outside the 10% acceptance criterion, and the concentration of that standard solution was near the quantitation limit of the FIA. As such, it is likely that the preparation of the standard solutions contributed to the failure of the calibration check samples, rather than the calibration of the FIA.

During Phase II, 24 calibration check samples were prepared from four different standard solutions. Measured concentrations for six of these calibration check samples differed from the delivered standard concentration by more than 10%, and the full set of measured values was on average 4.4% lower than the delivered concentration. Of the six calibration check samples that failed, five were prepared from two of the four standard solutions. It is possible that the failures may be attributable to inadvertent dilution or degradation of the standard solutions used, since these standards were prepared prior to submission of the first samples and failed consistently only near the end of the analysis period. The sixth calibration check sample that failed may be associated with a transcription error in the submission log.

4.2.6 Gas Standard Dilution Checks

At each of the nominal NH_3 levels to be used for the accuracy and linearity checks, at least one sample of the dilution of the NH_3 gas standard was collected using the reference method. These samples were analyzed as regular samples and used to check the accuracy of the dilution system.

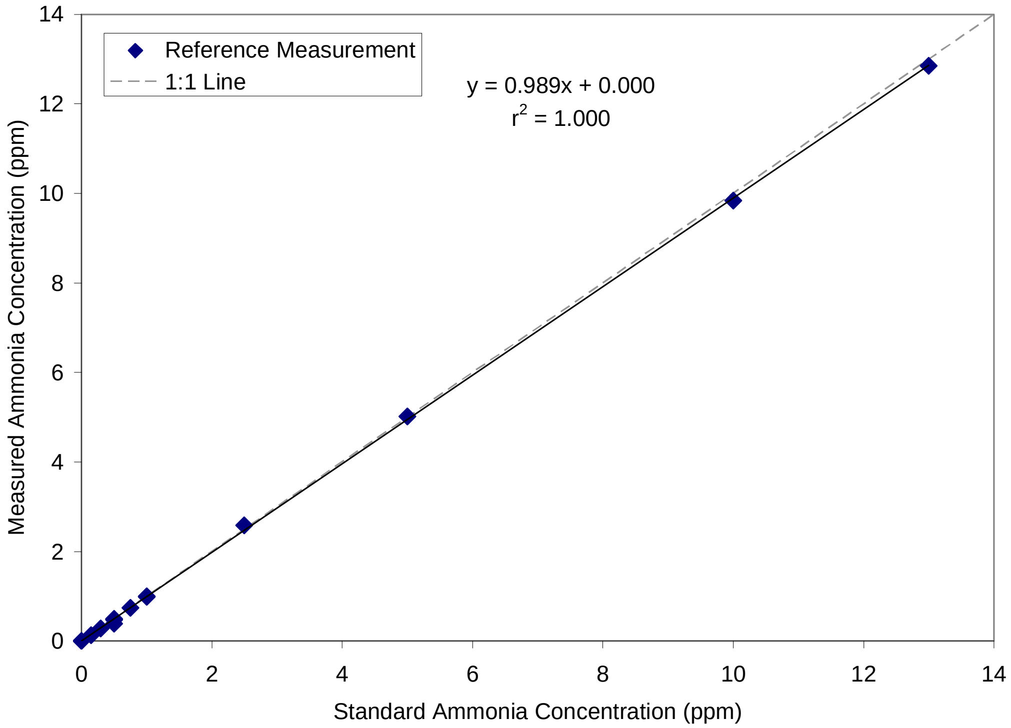

Figure 4-3. Analysis of Diluted NH_3 Standards Using the Denuder Reference Method

Figure 4-3 shows the measured NH_3 captured by the sampling cartridges versus the NH_3 delivered during the dilution checks.

A dilution check was conducted before Week 2 of Phase I. However, the sampling line was thought to have not been flushed with the diluted NH_3 sample prior to collecting the check samples, and the measured concentrations did not agree within 10% of the expected concentration. Consequently, the dilution check was repeated prior to Phase II, and the results are shown in Figure 4-3. The average RA of the measured concentrations was 4% and indicates that the NH_3 gas standards as delivered by the dilution system were accurate with respect to the reference method.

4.3 Audits

4.3.1 Performance Evaluation Audit

A performance evaluation audit was conducted to assess the quality of the measurements made in this verification test. This audit addressed only those measurements that factor into the data used for verification, i.e., the sample flow rate and the analytical laboratory measurements. This audit was performed once during the verification test by analyzing a standard or comparing a reading to a reference that was independent of standards used during the testing.

The flow rates of the reference method sampling assemblies were audited once during each phase of testing using a flow meter independent of the meter used to calibrate the flow rate. During Phase I, agreement between the audit flow rate and the nominal flow rate indicated a bias in the calibrated flow rates. The flow rates were recalibrated. The bias was later attributed to a faulty audit flow meter, and the original flow calibrations were verified against a second audit flow meter.

The performance of the FIA was audited by analyzing an NH_4^+ standard independent of those used for the calibration, but were the same as those used for the calibration checks described in Section 4.2.5. These samples were provided as blind audit samples, and the operator of the FIA was not aware of the concentrations of the samples. In several cases, agreement between the measured concentration and the standard concentration was not within ±10% (ranged from -43% to 64%). The cause of the discrepancy was investigated but could not be identified. It is possible that some of the discrepancy is attibutable to uncertainties associated with dilution of the stock 1,000 mg/L NH_4^+ standard solution. Multiple solutions were prepared, and only some of those solutions showed discrepancies with the analytical results. The relative agreement between the reference samples collected during the gas standard dilution check (performed between Phases I and II) and their expected values provide additional verification of the accuracy of the FIA.

4.3.2 Technical Systems Audit

Battelle's ETV Quality Manager performed a technical systems audit (TSA) of the performance of this verification test during each phase of the test. The purpose of this TSA was to ensure that the verification test was being performed in accordance with the test/QA plan(2) 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 to those specified in the test/QA plan, and reviewed data acquisition and handling procedures. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

4.3.3 Audit of Data Quality

At least 10% of the data acquired during the verification test was 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.

4.4 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.(5) 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.

4.5 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-6 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed. In some cases, entries in the laboratory record books or on field data sheets were not reviewed within two weeks after completion of each phase. A deviation report was filed to address this.

Table 4-6. Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[(a)]
Dates, times of test events (site activities, etc.)	USDA/ Battelle staff	Laboratory record books/field data sheet.	Start/end of test, and at each test activity.	Used to organize/ check test results; manually incorporated in data spreadsheets as necessary.
Reference method sampling data	USDA/ Battelle staff	Laboratory record books, chain-of-custody forms, or file data sheets as appropriate.	At least at start/end of reference sample, and at each change of a test parameter.	Used to organize/ check test results; manually incorporated in data spreadsheets as necessary.
Meteorological conditions	Battelle	Meteorological station data logger.	Continuously.	Used to assess meteorological conditions during testing as necessary.
NH_3 analyzer readings	Vendor or designee	Data acquisition system (data logger, personal computer, laptop, etc.).	Continuously at specified acquisition rate throughout analyzer operation.	Electronically transferred to spreadsheets.
Reference sample analysis and results	USDA/ Battelle staff	Laboratory record books, data sheets, or data acquisition system, as appropriate.	Throughout sample handling and analysis process.	Transferred to spreadsheets.

(a) All activities subsequent to data recording were carried out by Battelle.

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 Relative Accuracy

The percent difference (%D) of the average Nitrolux 1000 response to each NH_3 gas standard was calculated according to Equation 1:

$$\%\mathrm{D} = \frac{\bar{x} - x_n}{x_n} \times 100 \qquad (1)$$

where $\bar{x}$ is the average Nitrolux 1000 response to an NH_3 gas standard of concentration x_n. For each phase of testing, the RA with respect to all of the gas standards (n) delivered to the Nitrolux 1000 was calculated using Equation 2:

$$\text{Average RA} = \frac{1}{n}\left(\sum_{i=1}^{n} \left|\%\mathrm{D}_{\iota}\right|\right) \times 100 \qquad (2)$$

5.2 Linearity

Linearity was assessed by a linear regression analysis using the compressed gas standard concentrations as the independent variable and results from the Nitrolux 1000 as the dependent variable. Linearity was expressed in terms of slope, intercept, and r^2 and was calculated independently for each phase of the verification test. The 95% confidence interval (CI) for the slope and intercept was also calculated.

5.3 Precision

Precision was calculated in terms of the percent relative standard deviation (RSD) of Nitrolux 1000 measurements of several NH_3 gas standards. The mean and standard deviations of those readings were calculated. The RSD was then determined as:

$$\mathrm{RSD} = \frac{\mathrm{SD}}{\bar{x}} \times 100 \qquad (3)$$

where SD is the standard deviation of the Nitrolux 1000 readings and $\bar{x}$ is the mean of the Nitrolux 1000 readings. Precision was calculated independently for each phase of testing and the overall precision was calculated by averaging the precision for all four check periods.

5.4 Response Time

Response time was assessed in terms of both the rise and fall times of the Nitrolux 1000 when sampling NH_3 gas standards or zero air. Rise time (i.e., 0% to 95% response time for the change in NH_3 concentration) was determined from the Nitrolux 1000 response to a rapid increase in the delivered NH_3 concentration. Once a stable response was achieved with the gas standard, the fall time (i.e., the 100% to 5% response time) for the change in NH_3 concentration was determined in a similar way, switching from the NH_3 standard back to zero air or a lower concentration NH_3 gas standard. Rise and fall times were determined for the Nitrolux 1000 during each phase of testing. Response times are reported in seconds (s). It should be noted that response times include the time associated with equilibration of NH_3 on the tubing and inlet surfaces during delivery of the gas standards.

5.5 Calibration and Zero Drift

Calibration and zero drift are reported in terms of the mean, RSD, and range (minimum and maximum) of the readings obtained from the Nitrolux 1000 in the repeated sampling of the same NH_3 standard gas and of zero air. For zero drift, the SD is reported instead of the RSD since dividing the SD by a value approximately equal to zero is not meaningful. The calibration and zero drift were calculated independently during each phase of testing so that up to six NH_3 standard and zero readings (Monday, Wednesday, and Friday for two weeks) were used in each phase. The results of these checks indicate the day-to-day variation in zero and standard readings.

5.6 Interference Effects

The extent of interference was calculated in terms of the ratio of the response of the Nitrolux 1000 to the interfering species, relative to the actual concentration of the interfering species. For example, if 100 ppb of an interfering species resulted in a 1-ppb increase in the NH_3 reading of the Nitrolux 1000, the interference effect was reported as 1% (i.e., 1 ppb/100 ppb). The interference effect was reported separately for each interferent, both in the absence and in the presence of NH_3.

5.7 Comparability

Comparability between the Nitrolux 1000 results and the reference method results with respect to ambient air was assessed by linear regression using the reference method NH_3 concentrations as the independent variable and results from the Nitrolux 1000 as the dependent variable. Comparability was expressed in terms of slope, intercept, and r^2 and was calculated independently for each phase of the verification test.

Chapter 6
Test Results

The results of the verification test of the Nitrolux 1000 are presented in this section. The values presented in this section are based on discrete measurements recorded every 60 seconds by the Nitrolux 1000.

Meteorological conditions collected using the meteorological monitoring station during Phase I are presented in Figure 6-1. The ambient data set collected by the Nitrolux 1000 is shown in the bottom panel, along with the wind direction, wind speed, and ambient temperature data. The shaded regions indicate the NH_3 reference method sampling periods. The average ambient NH_3 concentration measured by the Nitrolux 1000 was 563 ppb, with a range of 16 to 8,477 ppb. The meteorological conditions, which were recorded as 1-hour averages, varied widely over the duration of Phase I. The average ambient temperature during Phase I of the test was 14°C, with a range of -4 to 29°C. The average relative humidity was 66%. Winds were predominantly from

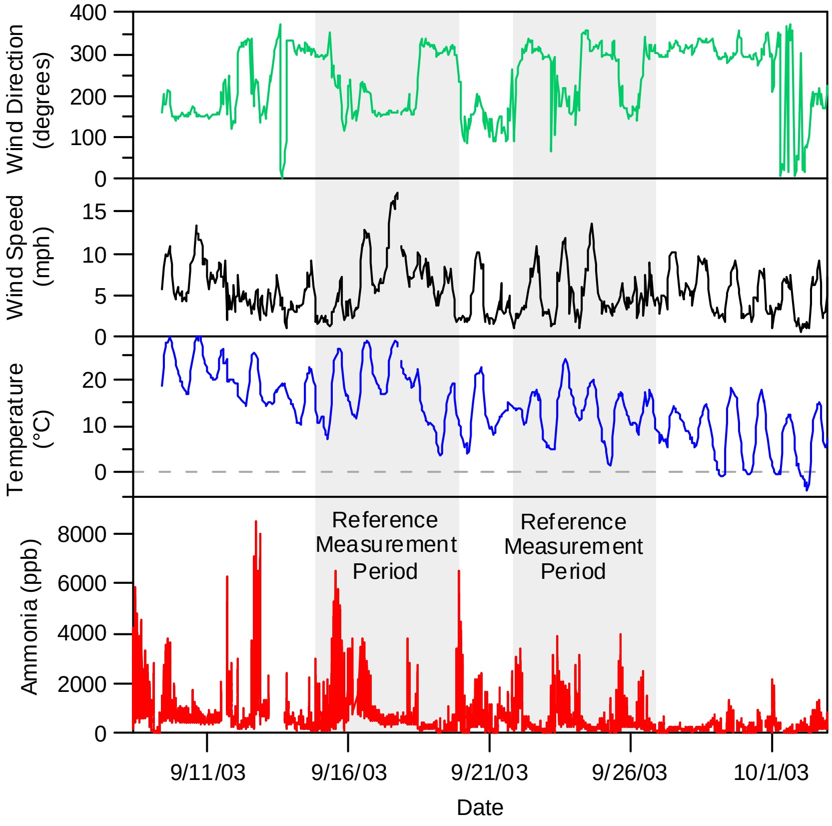

Figure 6-1. Phase I Meteorological Conditions and Nitrolux 1000 Ambient NH_3 Measurements

the southeast and northwest, with wind speeds up to 17 miles per hour (6 miles per hour average). When winds were observed from the southeast, the monitors were exposed to emissions from the nutrient lagoons, whereas the monitors sampled barn emissions during periods of northerly winds.

Meteorological conditions during Phase II are presented in Figure 6-2. The average ambient temperature was 4.5°C (range: -10 to 29°C), and the average relative humidity was 75%. Winds were predominantly from the northwest and quite variable in speed, averaging 7 miles per hour (30 miles per hour maximum). Figure 6-2 shows the Phase II wind direction, wind speed, and ambient temperature data and the ambient NH_3 data set collected by the Nitrolux 1000 (bottom panel). The shaded region shows the period during which NH_3 reference measurements were conducted. The Nitrolux 1000 NH_3 measurements ranged from 4 to 879 ppb during Phase II, and averaged 88 ppb.

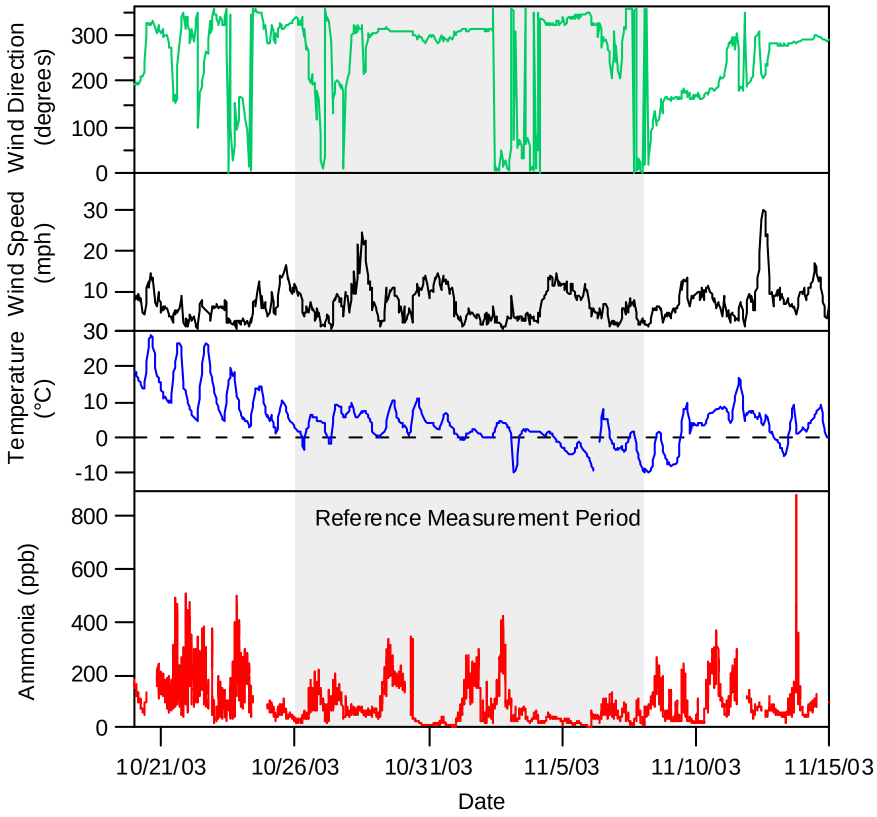

Figure 6-2. Phase II Meteorological Conditions and Nitrolux 1000 Ambient NH_3 Measurements

6.1 Relative Accuracy

During each phase of the verification test, the Nitrolux 1000 was supplied with compressed NH_3 gas standards at several concentrations. The NH_3 gas standards were diluted in zero air and delivered to the inlet of the Nitrolux 1000 at a flow rate of 3 to 5 Lpm. Relative accuracy checks were conducted once during the first week (Week 1) and again during the last week (Week 4) of each phase of testing. The results presented here are based on the factory calibration of the Nitrolux 1000, since calibrations were not performed on the Nitrolux 1000 at either test location. On-site calibration is part of the typical installation procedure recommended by the vendor, but an independent NH_3 standard was not available during the verification test and, consequently, the vendor did not conduct on-site calibration.

Figures 6-3(a, b) and 6-4(a, b) present the NH_3 concentrations recorded by the Nitrolux 1000 during the RA checks, along with the nominal NH_3 concentration levels supplied to the Nitrolux 1000 for Phase I and Phase II, respectively. The averages of the measurements at each nominal NH_3 concentration, the calculated %D, and the number of data points are presented in Tables 6-1 and 6-2, along with the average RA for each phase.

As shown in Table 6-1 for Phase I, the Nitrolux 1000 showed %Ds that ranged from 20% to 34% for the Week 1 RA check (between 300 and 5,000 ppb). The average RA over all the measurements was 27% during this check. The Nitrolux 1000 %Ds ranged from -21% to -7% for the Week 4 RA check (between 600 and 10,000 ppb). The average absolute RA over all the concentration ranges was 10% during the check conducted during the last week. The overall Nitrolux 1000 Phase I RA (the average of all the %Ds measured during Phase I) was 20%.

As shown in Table 6-2, during the Phase II RA checks (between 300 and 2,000 ppb), the %Ds of the Nitrolux 1000 ranged from -48% to -41% during the Week 1 RA check and from -54% to -28% during the Week 4 relative accuracy check. The average RA was 44% during Week 1 and 40% during Week 4, with a Phase II average RA of 42%.

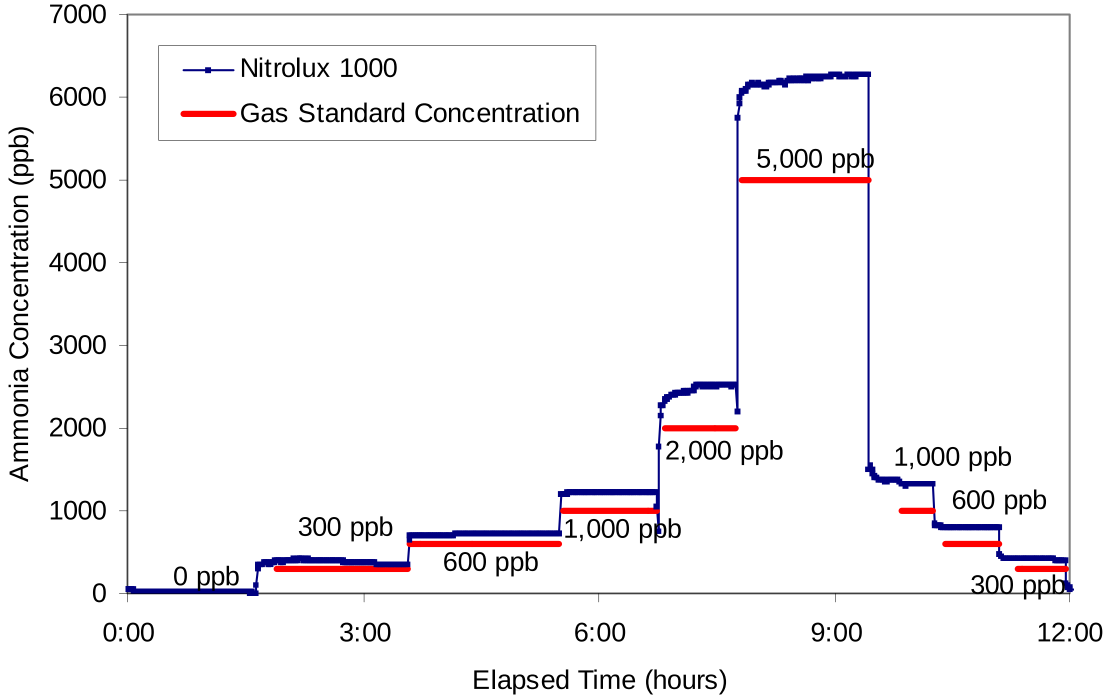

Figure 6-3a. Week 1, Phase I Accuracy Results for the Nitrolux 1000

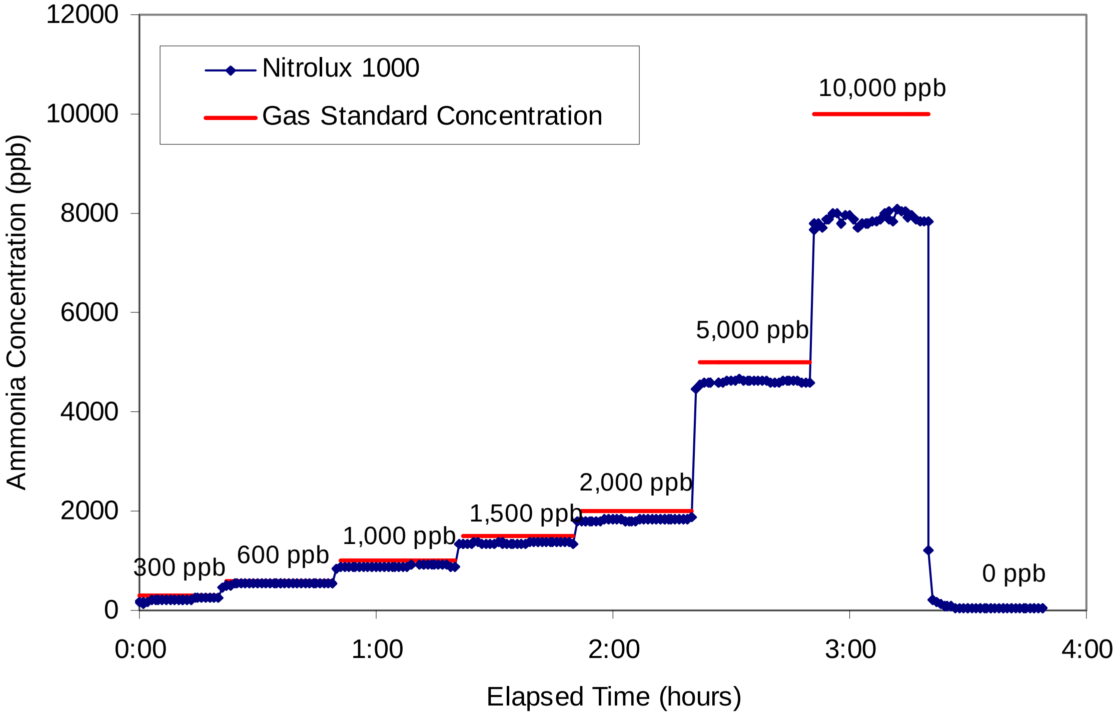

Figure 6-3b. Week 4, Phase I Accuracy Results for the Nitrolux 1000

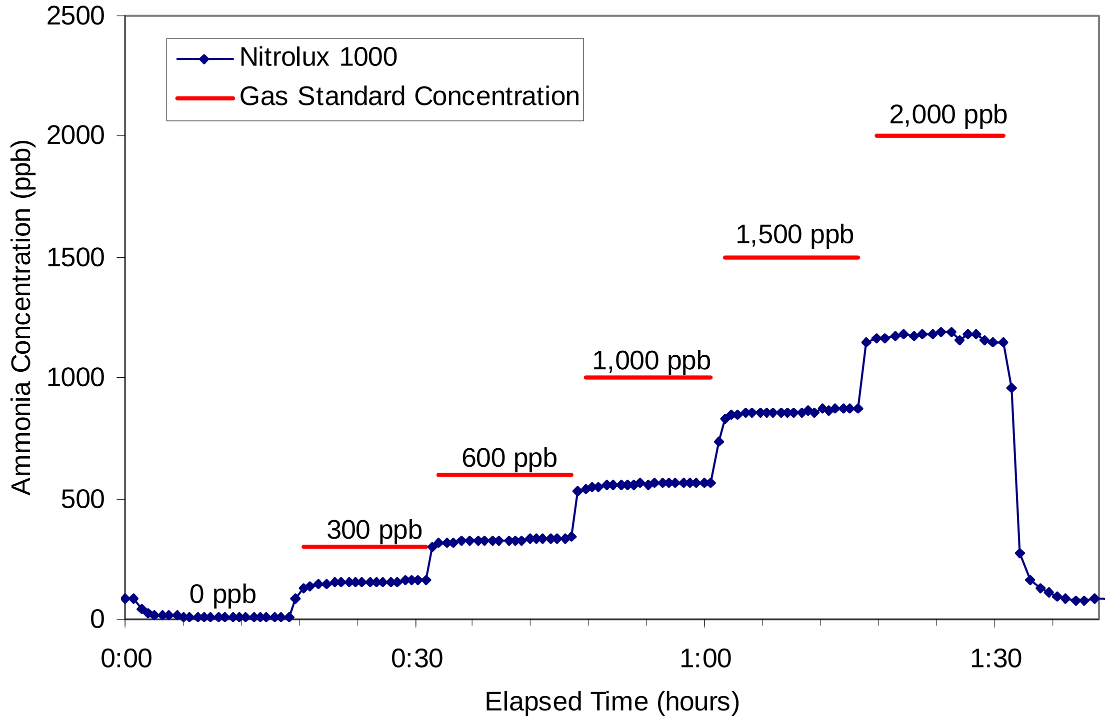

Figure 6-4a. Week 1, Phase II Accuracy Results for the Nitrolux 1000

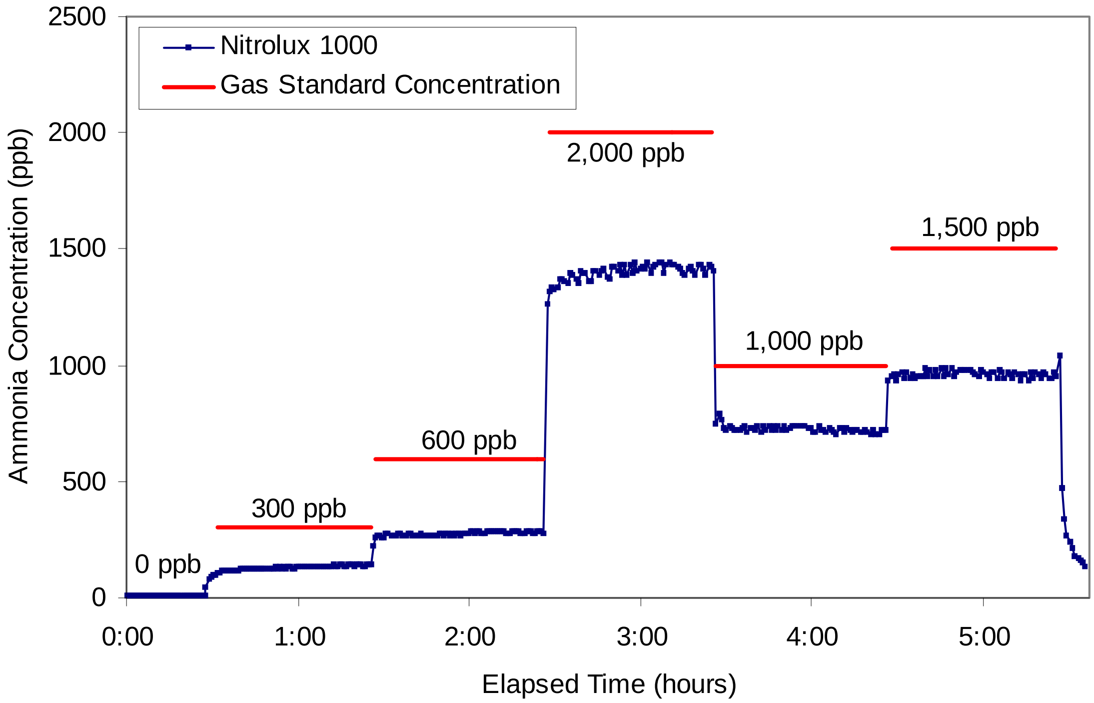

Figure 6-4b. Week 4, Phase II Accuracy Results for the Nitrolux 1000

Table 6-1. Relative Accuracy Results During Phase I

	Week 1			Week 4		
NH_3 Gas Standard Concentration (ppb)	**Average Measured Concentration (ppb)**	**Number of Data Points**	**%D (%)**	**Average Measured Concentration (ppb)**	**Number of Data Points**	**%D (%)**
0	13	20	NA	26	10	NA
300	359	20	20	(a)		
600	727	20	21	556	10	-7
1,000	1,236	20	24	900	10	-10
1,500	(b)			1,369	10	-9
2,000	2,520	20	26	1,835	10	-8
5,000	6,267	20	25	4,605	10	-8
10,000	(b)			7,924	10	-21
1,000	1,319	20	32	(b)		
600	806	20	34	(b)		
300	392	9	30	(b)		
Average RA	27%			10%		
Overall Phase I RA	20%					

(a) Gas standard not delivered for a sufficient amount of time to reach a stable reading.

(b) The concentration levels and sequence of NH_3 concentrations supplied to the Nitrolux 1000 were changed for the RA checks conducted during each phase. Consequently, not all concentration levels were measured during both RA checks.

NA = not applicable.

Table 6-2. Relative Accuracy Results During Phase II

	Week 1			Week 4		
NH_3 Gas Standard Concentration (ppb)	Average Measured Concentration (ppb)	Number of Data Points	%D (%)	Average Measured Concentration (ppb)	Number of Data Points	%D (%)
0	6	5	NA	5	10	NA
300	157	10	-48	139	20	-54
600	330	10	-45	280	20	-53
1,000	564	10	-44	716	20	-28
1,500	864	10	-42	956	20	-36
2,000	1,172	10	-41	1,417	20	-29
Average RA	44%			40%		
Overall Phase II RA	42%					

NA = not applicable.

6.2 Linearity

Figures 6-5a and 6-5b show the results of the linearity check for Week 1 and Week 4 of Phase I, respectively. During Week 1 of Phase I, a linear regression of the Nitrolux 1000 response versus the gas standard concentration, over the range from 0 to 5,000 ppb, showed a slope of 1.25 (± 0.02), an intercept of 13.2 ppb (± 34.1) ppb, and an r^2 of 0.9997, where the numbers in parentheses represent the 95% CI. During Week 4 of Phase I, a linear regression of the Nitrolux 1000 response versus the gas standard concentrations over the range from 0 to 10,000 ppb showed a slope of 0.798 (± 0.071), an intercept of 167 ppb (± 310) and an r^2 value of 0.9940. However, as shown in Figure 6-5b, if the highest concentration value is not included (since it is above the Nitrolux 1000 measurement range), the linear regression shows a slope of 0.919 (± 0.013), an intercept of 2.02 ppb (± 29.3), and an r^2 value of 0.9999.

Figures 6-6a and 6-6b show the results of the linearity checks for Week 1 and Week 4 of Phase II, respectively. The linear regression of the Nitrolux 1000 response versus the gas standard concentration for Week 1 of Phase II , showed a slope of 0.586 (± 0.022), an intercept of -12.2 ppb (± 24.9), and an r^2 of 0.9993. The linear regression results from Week 4 of Phase II, showed a slope of 0.716 (± 0.121), an intercept of -58.5 ppb (± 137), and an r^2 of 0.9854

The results presented here are based on the factory calibration of the Nitrolux 1000, since no calibrations of the Nitrolux 1000 were performed in the field. Typically, on-site calibrations are included in the Nitrolux 1000 installation procedure.

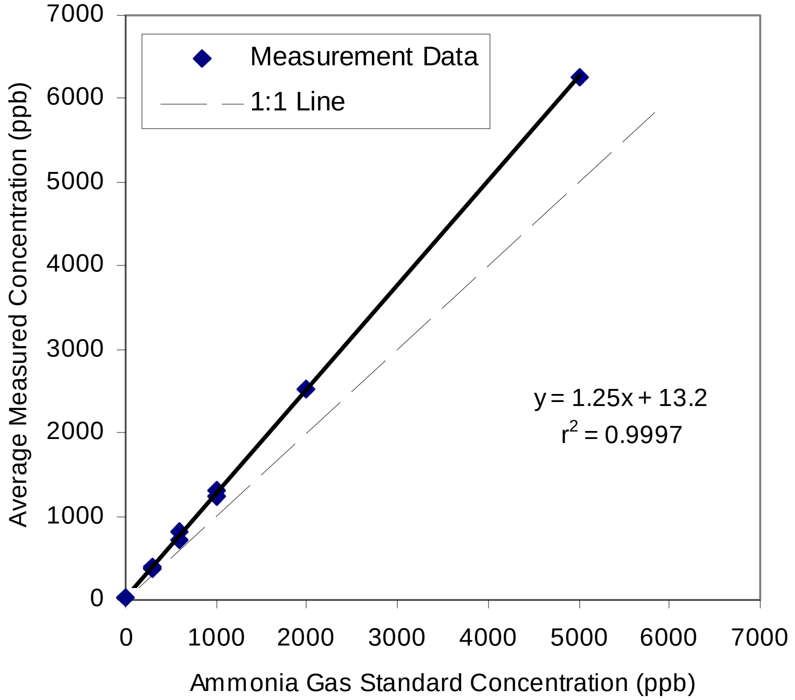

Figure 6-5a. Nitrolux 1000 Linearity Check During Week 1 of Phase I

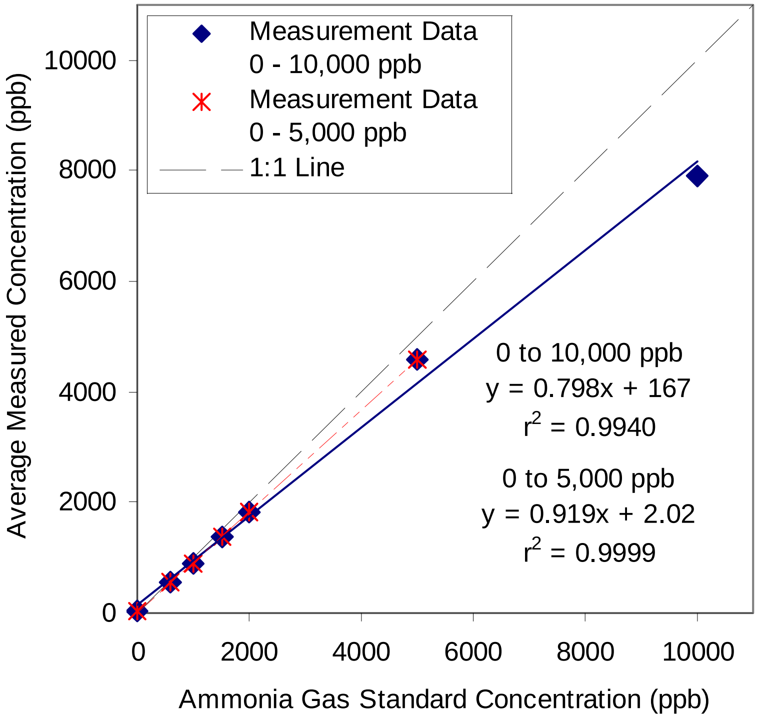

Figure 6-5b. Nitrolux 1000 Linearity Check During Week 4 of Phase I

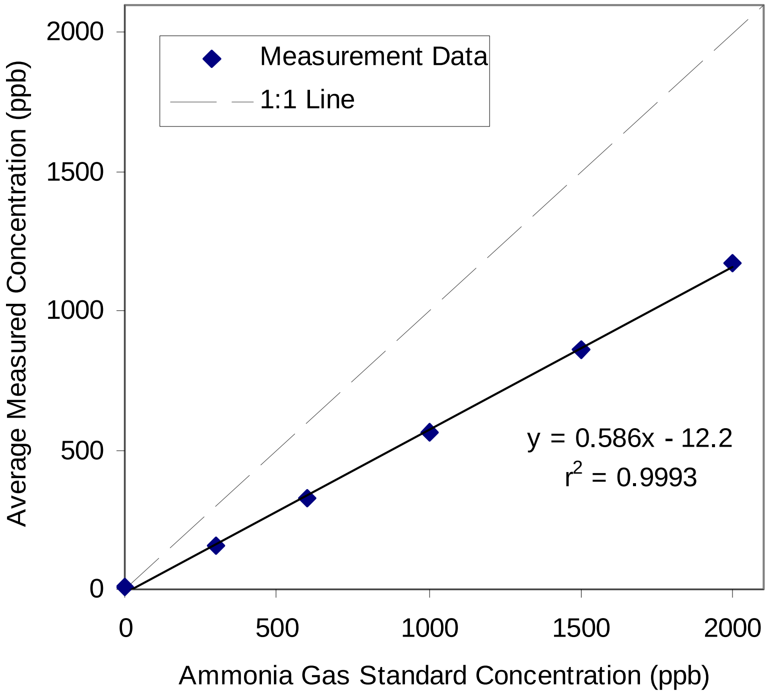

Figure 6-6a. Nitrolux 1000 Linearity Check During Week 1 of Phase II

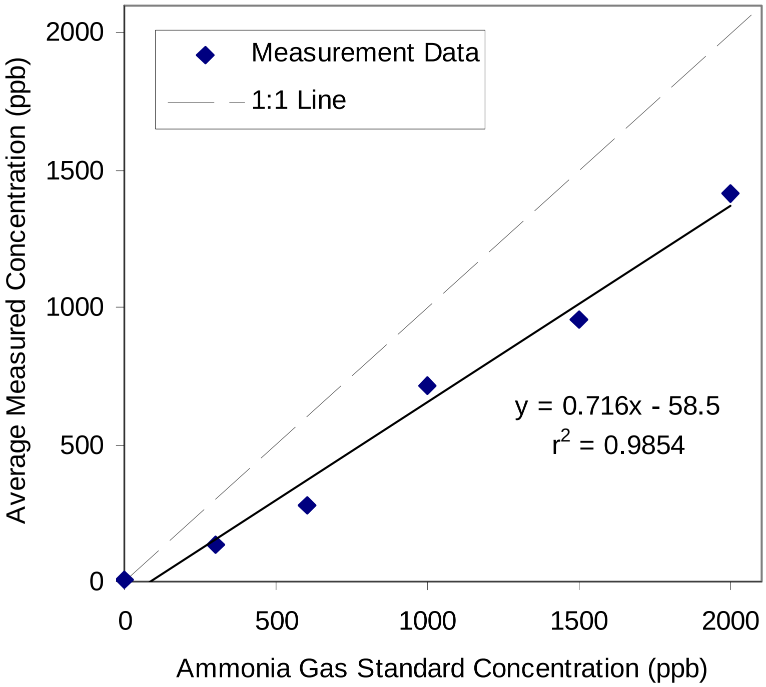

Figure 6-6b. Nitrolux 1000 Linearity Check During Week 4 of Phase II

6.3 Precision

Tables 6-3 and 6-4 present the calculated precision of the Nitrolux 1000 measured during the accuracy and linearity checks during Phase I and Phase II, respectively. During Phase I, the precision of the Nitrolux 1000 readings varied from 0.1% to 0.5% RSD in the first accuracy/ linearity check (Week 1) and from 0.2% to 1.3% RSD in the second check (Week 4). During Phase II, the precision of the Nitrolux monitor readings ranged from 0.3% to 2.3% during the first accuracy/linearity check (Week 1) and varied from 1.2% to 1.5% RSD in the second accuracy/linearity check (Week 4). The average overall precision, calculated by taking the average of all RSDs from all four check periods, during both phases, was 0.7% RSD.

Table 6-3. Calculated Precision of the Nitrolux 1000 During Phase I

	Week 1		Week 4	
NH_3 Gas Standard Concentration (ppb)	Average Measured Concentration (ppb)	RSD (%)	Average Measured Concentration (ppb)	RSD (%)
300	359	0.2	(a)	
600	727	0.2	556	0.9
1,000	1,236	0.1	900	0.5
1,500	(b)		1,369	0.6
2,000	2,520	0.4	1,835	0.4
5,000	6,267	0.1	4,605	0.2
10,000	(b)		7,924	1.3
1,000	1,319	0.1	(b)	
600	806	0.2	(b)	
300	392	0.5	(b)	
Average RSD		0.2		0.6

(a) Gas standard not delivered for a sufficient amount of time to reach a stable reading.

(b) The concentration levels and sequence of NH_3 concentrations supplied to the Nitrolux 1000 were changed for the RA checks conducted during each phase. Consequently, not all concentration levels were measured during both RA checks.

Table 6-4. Calculated Precision of the Nitrolux 1000 During Phase II

NH_3 Gas Standard Concentration (ppb)	Week 1		Week 4	
	Average Reading (ppb)	RSD (%)	Average Reading (ppb)	RSD (%)
300	157	2.3	139	1.5
600	330	0.3	280	1.2
1,000	564	0.4	716	1.2
1,500	864	0.7	956	1.3
2,000	1,172	1.5	1,417	1.3
Average RSD		1.0		1.3

6.4 Response Time

Response time was determined during each phase from the amount of time required for the Nitrolux 1000 to reach 95% of the change in stable concentrations during the accuracy/linearity checks. Table 6-5 presents a summary of the response time determinations for the Nitrolux 1000. Rise times during Phase I ranged from 54 to 1,893 seconds, with fall times between 54 and 214 seconds. Response times measured during Phase II were in approximately the same range as during Phase I. Phase II rise times ranged from 108 to 1,808 seconds and measured fall times were 108 and 231 seconds. It should be noted that the response times include the time associated with equilibration of NH_3 on the tubing and inlet surfaces during delivery of the gas standards.

6.5 Calibration and Zero Drift

The calibration/zero drift checks were conducted by supplying a 1,000 ppb NH_3 (nominal) gas standard and zero air to the Nitrolux 1000 on Monday, Wednesday, and Friday during the first and last week of each phase. The results of the calibration and drift checks during Phase I and Phase II are summarized in Tables 6-6 and 6-7, respectively. The values reported in these tables for the calibration drift checks are based on the average readings during the delivery of the 1000-ppb NH_3 gas standard when the readings of the Nitrolux 1000 had stabilized (i.e., the signal was neither visibly increasing nor decreasing); thus, the calculations for each check span somewhat different time periods that ranged from 4 to 55 minutes in Phase I and 5 to 65 minutes in Phase II. During the zero drift checks, although it was not apparent while the checks were being performed, the Nitrolux 1000 response was still decreasing at the end of each zero air delivery period, even after delivery durations of 60 minutes. The one exception to this is the first

Table 6-5. Response Time Determinations

	Phase I		Phase II	
Change (ppb)	**Rise Time (seconds)**	**Fall Time (seconds)**	**Rise Time (seconds)**	**Fall Time (seconds)**
0 – 300	183	—	277(a) 1,808(b)	—
300 – 600	1,893(b)	—	229(a) 532	—
600 – 1,000	380(a) 489	—	261	—
1,000 – 1,500	328	—	173(a) 108	—
1,000 – 2,000		—		
1,500 – 2,000	499	—	167	—
2,000 – 5,000	123	—	(d)	
5,000 – 10,000	54	—	(d)	
10,000 – 0	—	113	(d)	
5,000 – 1,000	—	54	(d)	
2,000 – 1,000	(d)		—	108
2,000 – ambient(e)	(d)		—	231
1,000 – 600	—	107	(d)	
600 – 300	—	214	(d)	

(a) For concentration changes that were repeated during Weeks 1 and 4 (for both phases), both values are reported.
(b) For this transition, there was an initial sharp increase in response, followed by a steady rise until the readings stabilized.
(c) Zero air was inadvertently delivered briefly between the two NH_3 standards; no response time is reported.
(d) Not measured since the sequence of NH_3 concentrations supplied to the Nitrolux 1000 was different for the two phases.
(e) Ambient NH_3 concentration was ~80 ppb.

zero check of Phase II, during which a stable response of 2.6 ppb was achieved. For the other checks, the mean values reported in Tables 6-6 and 6-7 do not represent stable responses, which may have been reached with longer zero air delivery periods. The values reported for all zero drift checks were calculated from data for the last 5 minutes of each zero air delivery period. No obvious drift in the response to zero air was apparent during Phase I or Phase II. The response to the 1,000 ppb NH_3 gas standard increased by approximately 44% during Week 1 of Phase I, but no drift was apparent during Week 4. No obvious calibration drift was observed during Week 1 or Week 4 of Phase II, but a decrease of approximately 13% was observed between the average Week 1 and Week 4 responses to a 1,000-ppb NH_3 standard. The average response to the 1,000 ppb NH_3 gas standard (the average of the values from each phase) decreased from 961 ppb during Phase I to 511 ppb during Phase II.

Table 6-6. Calibration and Zero Checks During Phase I

	Zero Check					Calibration Check(a)				
Check Number	**Mean (ppb)**	**SD(b) (ppb)**	**Minimum (ppb)**	**Maximum (ppb)**	**Number of Data Points**	**Mean (ppb)**	**RSD (%)**	**Minimum (ppb)**	**Maximum (ppb)**	**Number of Data Points**
Week 1 Monday	13.6	0.9	12.8	15.1	5	865	0.1	864	866	4
Week 1 Wednesday	7.8	0.2	7.7	8.2	5	1,004	0.9	993	1,016	5
Week 1 Friday	9.5	0.3	9.1	10.0	5	1,247	1.3	1,217	1,274	20
Week 4 Monday	4.3	0.3	3.9	4.5	5	892	2.1	861	916	55
Week 4 Wednesday	9.5	0.1	9.4	9.6	5	911	1.5	880	935	54
Week 4 Friday	4.7	0.1	4.7	4.8	5	845	1.4	830	866	49

(a) 1,000 ppb NH_3 nominal concentration.

(b) Standard deviation reported for zero drift since the RSD is not meaningful for near-zero values.

Table 6-7. Calibration and Zero Checks During Phase II

	Zero Check					Calibration Check(a)				
Check Number	**Mean (ppb)**	**SD(b) (ppb)**	**Minimum (ppb)**	**Maximum (ppb)**	**Number of Data Points**	**Mean (ppb)**	**RSD (%)**	**Minimum (ppb)**	**Maximum (ppb)**	**Number of Data Points**
Week 1 Monday	2.6	0.0	2.5	2.6	5	(c)				
Week 1 Wednesday	2.0	0.3	1.7	2.4	5	567	1.5	554	581	45
Week 1 Friday	2.4	0.1	2.3	2.6	5	542	1.7	525	561	56
Week 4 Monday	3.5	0.2	3.2	3.8	5	479	1.5	468	493	52
Week 4 Wednesday	2.2	0.2	1.9	2.3	5	486	1.6	470	500	51
Week 4 Friday	5.3	0.2	5.1	5.5	5	480	1.3	469	490	41

(a) 1,000 ppb NH_3 nominal concentration.

(b) Standard deviation reported for zero drift since the RSD is not meaningful for near-zero values.

(c) NH_3 gas standard not delivered for a sufficient amount of time to reach a stable reading.

6.6 Interference Effects

The effect of potential interferent gases on the response of the Nitrolux 1000 was assessed by supplying the Nitrolux 1000 with a series of four gases (hydrogen sulfide, nitrogen dioxide, 1,3-butadiene, diethylamine) in zero air and a 500-ppb NH_3 standard. The response of the Nitrolux 1000 during the introduction of these gases is summarized in Table 6-8. The interferent gas concentrations carry an uncertainty of approximately ±15% (as reported by the manufacturer for uncertified permeation tubes).

The response of the Nitrolux 1000 to hydrogen sulfide, nitrogen dioxide, and 1,3-butadiene was negligible. The Nitrolux 1000 showed no significant response to diethylamine in a 500-ppb NH_3 standard, but an interference effect of 19% to diethylamine was observed in zero air. However, the presence of an NH_3 impurity in the diethylamine standard or the release of NH_3 from the sample lines during delivery could not be ruled out.

Table 6-8. Interference Effect Evaluation

Gas	Interferent Gas Concentration (ppb)	Interference Effect (%)	
		Zero-Air Matrix	500-ppb NH_3 Matrix
Hydrogen sulfide	285	0(a)	0.1(a)
Nitrogen dioxide	95	0.4(a)	1.1(a)
1,3-Butadiene	95	0.8(a)	(b)
Diethylamine	96	19(c)	(b)

(a) Signal not significantly different from baseline without interferent gas.
(b) Noise introduced from testing activities prevented reliable quantification of the interference from these compounds. However, no significant response was observed.
(c) The presence of an NH_3 impurity in the diethylamine gas standard or the release of NH_3 from the sample lines during delivery could not be ruled out.

6.7 Comparability

Figures 6-7 and 6-8 show the NH_3 concentrations measured using the reference method, along with the corresponding average readings of the Nitrolux 1000 for the reference sampling periods, during Phase I and Phase II, respectively. In general, the Nitrolux 1000 appeared to track changes in NH_3 concentrations measured with the reference method. These data also are presented in Figures 6-9 and 6-10 as scatter plots to illustrate the correlation between the reference and Nitrolux 1000 data.

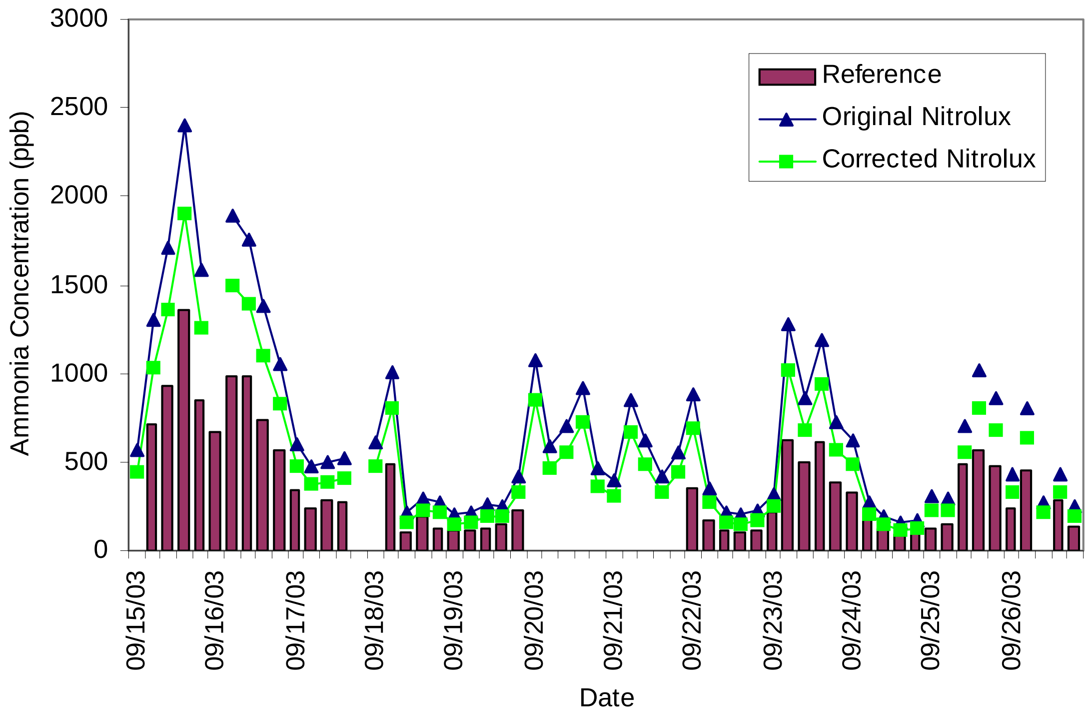

Figure 6-7. Comparison of Ambient Reference Measurements with Averages from the Nitrolux 1000 During Phase I

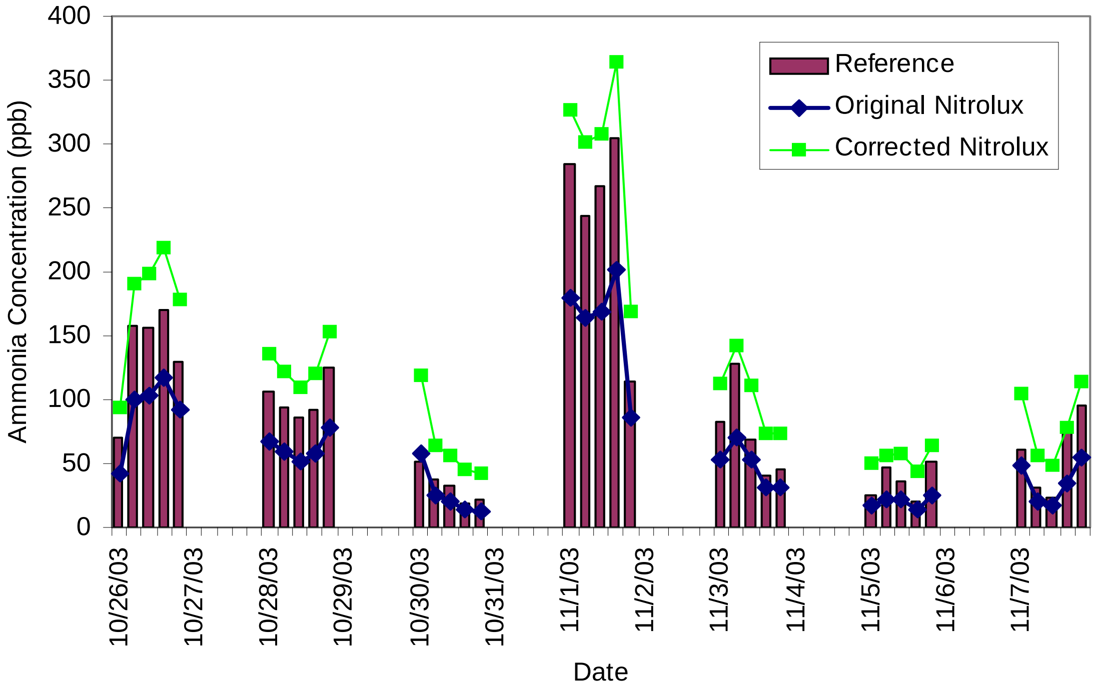

Figure 6-8. Comparison of Ambient Reference Measurements with Averages from the Nitrolux 1000 During Phase II

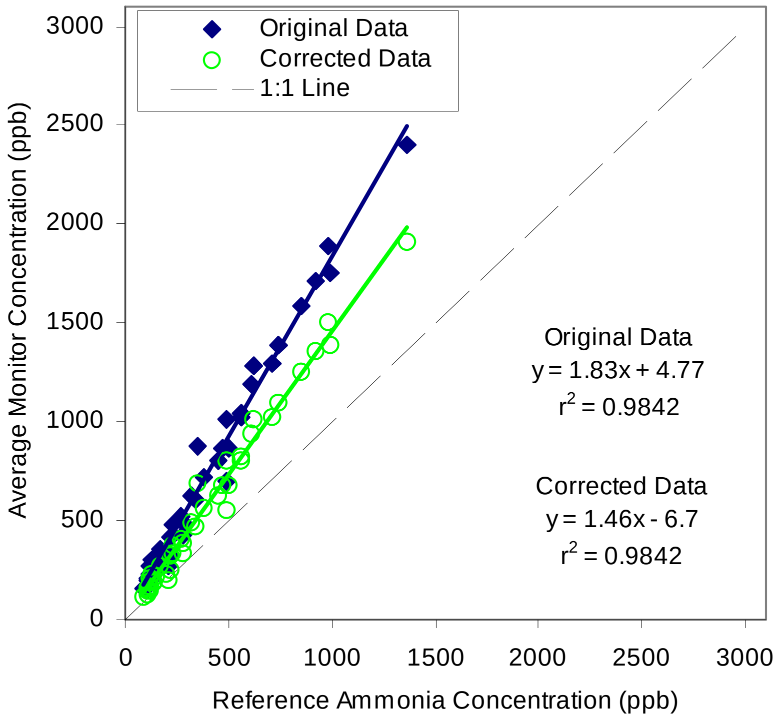

Figure 6-9. Scatter Plot of Averages from the Nitrolux 1000 versus Ambient Reference Measurements During Phase I

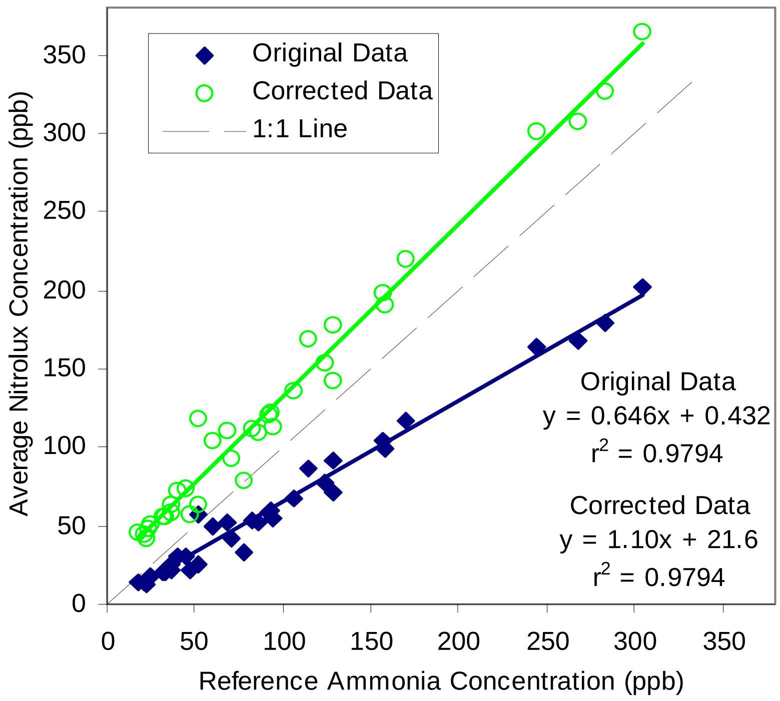

Figure 6-10. Scatter Plot of Averages from the Nitrolux 1000 versus Ambient Reference Measurements During Phase II

The Phase I Nitrolux 1000 average readings were consistently higher than the reference method, while during Phase II the Nitrolux 1000 readings were consistently lower than the reference method results. However, during both phases, the Nitrolux 1000 average readings and the reference method results were highly correlated.

A linear regression of the Nitrolux 1000 responses during the reference sampling periods versus the NH_3 determined from the reference method was calculated for each phase. For Phase I, the linear regression results showed a slope of 1.83 (± 0.07), an intercept of 4.77 ppb (±34.01), and an r^2 value of 0.9842, where the numbers in parentheses represent the 95% CI. For Phase II, the linear regression results showed a slope of 0.646 (± 0.03), an intercept of 0.432 ppb (± 4.10), and an r^2 value of 0.9794. Since no calibration was performed on-site during either phase of the verification test, these results are based on the factory calibration of the Nitrolux 1000. In the absence of an on-site calibration, the results of the first linearity checks conducted during each phase can be used to apply calibration corrections to the Nitrolux 1000 data. If such a calibration correction were applied to the data used to establish comparability, the results of the linear regression for Phase I would show a slope of 1.46 (±0.06), an intercept of -6.7 (±27.2), and an r^2 of 0.9842. Similarly, the results of the linear regression for Phase II would show a slope of 1.10 (±0.06), an intercept of 21.6 (±7.0), and an r^2 of 0.9794. The corrected Nitrolux 1000 measurements are also shown in Figures 6-7, 6-8, 6-9, and 6-10.

6.8 Ease of Use

The Nitrolux 1000 was installed at the Phase I and Phase II testing locations by the vendor representative. The Nitrolux 1000 could be installed and operated by a user with minimal experience and the Nitrolux 1000 manual. Although the Nitrolux 1000 was not calibrated on-site with an NH_3 gas standard during this test, a gas phase calibration is generally included in the installation procedure. The installation took less than one day. A checklist was provided by the vendor representatives to establish whether the instrument was in proper working order. The checklist, shown in Appendix A, was completed by Battelle or USDA staff during daily checks of the Nitrolux 1000 operating status. No routine maintenance was required for the Nitrolux 1000. The vendor representative replaced the inlet particulate filter before each phase of testing.

The Nitrolux 1000 was very easy to operate. The software was very user-friendly, automatically rebooted the PC on a daily basis, and accounted for daylight savings time without intervention. The system was found to not be responding once during each phase; once the operator rebooted the computer, the Nitrolux 1000 resumed measurements without further input. The Nitrolux 1000 software displayed a 4- or 8-hour record of NH_3 measurements, which were updated in real time. Data were automatically saved as text files containing the time and NH_3 concentration at a frequency of approximately one point per minute. New files were saved for each day of the verification test, each with approximately 25 kilobytes of data. The full data set for each 4-week phase was approximately 800 kilobytes in size. The personal computer stored all of the measurement data, which could be downloaded to a USB “thumb drive” (supplied by the vendor). Once the thumb drive was plugged into the personal computer, the data were automatically downloaded to the device without operator prompt or intervention. A summary of the activities performed to the Nitrolux 1000 during Phase I and Phase II are presented in Tables 6-9 and 6-10, respectively.

Table 6-9. Activities Performed During Phase I

Date	Time Offline [(a)] (minutes)	Down Time [(b)] (minutes)	Service Time [(c)] (minutes)	Activity
9/08/03	45			Supplied zero air and NH_3 standard[(d)]
9/10/03	130			Supplied zero air and NH_3 standard[(d)]
9/11/03	270			Supplied zero air and NH_3 standards[(d)]
9/12/03	120			Supplied zero air and NH_3 standard[(d)]
9/13/03	250			Supplied zero air and NH_3 standards[(d)]
9/16/03		340	5	System stopped responding overnight. Rebooted computer.
9/17/03		120 [(e)]		Power loss. Instrument recovered without user intervention.
9/29/03	145			Supplied zero air and NH_3 standard[(d)]
9/30/03	240			Supplied zero air and NH_3 standards[(d)]
10/01/03	120			Supplied zero air and NH_3 standard[(d)]
10/03/03	120			Supplied zero air and NH_3 standard[(d)]
Totals	1,440	340[(e)]	5	99% data completeness[(f)] and 5-minute service time.

(a) Time Offline = time that the Nitrolux 1000 was taken offline for zero or standard gas measurements. The period over which time offline was evaluated began at 8:00 a.m. on 9/8/03 and ended at the conclusion of testing at 5:00 p.m. on 10/3/03. The amount of time was rounded to the nearest 5 minutes.

(b) Down Time = time that the Nitrolux 1000 was not operating or was operating but not reporting reliable measurements. The period over which down time was evaluated began at 8:00 a.m. on 9/8/03 and ended at the conclusion of testing at 5:00 p.m. on 10/3/03. The amount of time was rounded to the nearest 5 minutes. Down time that did not result in loss of data is not included in the availability determination.

(c) Service Time = time spent conducting routine operation and maintenance activities and troubleshooting problems. The period over which service time was evaluated began at 8:00 a.m. on 9/8/03 and ended at the conclusion of testing at 5:00 p.m. on 10/3/03. The amount of time was rounded to the nearest 5 minutes.

(d) Testing activity performed by Battelle/USDA operator.

(e) The 120-minute down time that resulted from the absence of power at the test site was not included in the down time calculation as it does not reflect on the performance of the Nitrolux 1000.

(f) Data Completeness = the ratio of time that the Nitrolux 1000 was not experiencing down time to the total time available for monitoring ambient NH_3 mixing ratios from the start of testing on 9/8/03 to the end of testing on 10/3/03. The total time that was available for monitoring was 36,540 minutes or 609 hours.

6.9 Data Completeness

The Nitrolux 1000 was operating and collecting data for 99% of the available time during both Phase I and Phase II. As discussed in Section 6.8, the 1% data loss was attributed to software/computer failures.

Table 6-10. Activities Performed During Phase II

Date	Time Offline [(a)] (minutes)	Down Time [(b)] (minutes)	Service Time [(c)] (minutes)	Activity
10/20/03	260			Delivered zero air and NH_3 standard[(d)]
10/22/03	110			Delivered zero air and NH_3 standard[(d)]
10/23/03	90			Delivered zero air and NH_3 standards[(d)]
10/24/03	120			Delivered zero air and NH_3 standard[(d)]
10/26/03				System automatically adjusted time for daylight savings.
10/30/03		350	5	System stopped responding overnight. Rebooted computer.
11/10/03	120			Delivered zero air and NH_3 standard[(d)]
11/11/03	535			Performed interference tests[(d)]
11/12/03	120			Delivered zero air and NH_3 standard[(d)]
11/14/03	470			Delivered zero air and NH_3 standards[(d)]
Totals	1,825	350	5	99% data completeness[(e)] and 5-minute service time.

[(a)] Time Offline = time that the Nitrolux 1000 was taken offline for zero or standard gas measurements. The period over which time offline was evaluated began at 8:00 a.m. on 10/20/03 and ended at the conclusion of testing at 5:00 p.m. on 11/14/03. The amount of time was rounded to the nearest 5 minutes.

[(b)] Down Time = time that the Nitrolux 1000 was not operating or was operating but not reporting reliable measurements. The period over which down time was evaluated began at 8:00 a.m. on 10/20/03 and ended at the conclusion of testing at 5:00 p.m. on 11/14/03. The amount of time was rounded to the nearest 5 minutes.

[(c)] Service Time = time spent conducting routine operation and maintenance activities and troubleshooting problems. The period over which service time was evaluated began at 8:00 a.m. on 10/20/03 and ended at the conclusion of testing at 5:00 p.m. on 11/14/03. The amount of time was rounded to the nearest 5 minutes.

[(d)] Testing activity performed by Battelle/USDA operator.

[(e)] Data Completeness = the ratio of time that the Nitrolux 1000 was not experiencing down time to the total time available for monitoring ambient NH_3 mixing ratios from the start of testing on 10/20/03 to the end of testing on 11/14/03. The total time that was available for monitoring during Phase 2 was 35,280 minutes or 588 hours.

Chapter 7
Performance Summary

The performance of the Nitrolux 1000 was evaluated in two phases in this verification test. Table 7-1 presents a summary of the performance of the Nitrolux 1000 NH_3 during this verification test.

Table 7-1. Nitrolux 1000 Performance Summary

	Results					
	Phase I			**Phase II**		
Parameter		Week 1	Week 4		Week 1	Week 4
Relative accuracy[(a)(b)]	Average RA %D range	27% 20 to 34%	10% −21 to -7%	Average RA %D range	44% −48 to −41%	40% −54 to −28%
Linearity[(a)]	Range Slope Intercept r^2	0 to 5,000 ppb 1.25 (±0.02) 13.2 ppb (±34.1) 0.9997	0 to 10,000 ppb 0.798 (±0.071)[(c)] 167 ppb (±310) 0.9940	Range Slope Intercept r^2	0 to 2,000 ppb 0.586 (±0.022) −12.2 ppb (±24.9) 0.9993	0 to 2,000 ppb 0.716 (±0.121) −58.5 ppb (±137) 0.9854
Precision[(a)]	Average RSD Range	0.2% 0.1 to 0.5%	0.6% 0.2 to 1.3%	Average RSD Range	1.0% 0.3 to 2.3%	1.3% 1.2 to 1.5%
Response time	Rise time = 54 to 1,893 seconds Fall time = 54 to 214 seconds			Rise time = 108 to 1,808 seconds Fall time = 108 to 231 seconds		
Calibration/ zero drift	■ No apparent drift in response to zero air during Week 1 or Week 4. ■ Apparent drift of approximately 44% in response to 1,000 ppb NH_3 observed during Week 1. No apparent drift observed during Week 4.			■ No apparent drift in response to zero air during Week 1 or Week 4. ■ Apparent drift of approximately 13% in response to 1,000 ppb NH_3 between Week 1 and Week 4.		
Interference effects[(d)]	Interference check conducted during Phase II.			■ Hydrogen sulfide (285 ppb): no apparent effect ■ Nitrogen dioxide (95 ppb): no apparent effect ■ 1,3-Butadiene (95 ppb): no apparent effect ■ Diethylamine (96 ppb): ~19% response in zero air, no apparent effect in 500 ppb NH_3[(e)]		
Comparability		Raw Data[(a)]	Corrected Data[(f)]		Raw Data[(a)]	Corrected Data[(f)]
	Slope Intercept r^2	1.83 (± 0.07) 4.77 (± 34.01) 0.9842	1.46 (± 0.06) -6.7 (± 27.2) 0.9842	Slope Intercept r^2	0.646 (± 0.03) 0.43 (± 4.1) 0.9794	1.10 (±0.06) 21.6 (± 7.0) 0.9794
Ease of use	■ Daily checks were simple and quick ■ Little skill required to operate ■ No maintenance required ■ User-friendly software					
Data completeness	99%			99%		

(a) Results based on Nitrolux 1000 factory calibration since an on-site calibration was not performed. On-site calibration is generally included in Nitrolux 1000 installation procedures, but an independent NH_3 standard was not available during the verification test.

(b) Relative accuracy is expressed as an average absolute value of the percent difference from NH_3 gas standards.

(c) Including only data from 0 to 5,000 ppb, the slope was 0.919 (±0.013), with an intercept of -12.8 (±34.4) and an r^2 of 0.9998. The linear range for the Nitrolux 1000 is reported to be 0 - 2,000 ppb by the manufacturer.

(d) Calculated as the change in signal divided by the interferent gas concentration, expressed as a percentage.

(e) The presence of an NH_3 impurity in the diethylamine gas standard or the release of NH_3 from the sample lines during delivery could not be ruled out.

(f) Results of Week 1 linearity check were used to apply a calibration correction to the Nitrolux 1000 ambient data.

Chapter 8
References

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3. *Determination of Reactive Acidic and Basic Gases and Acidity of Fine Particles (<2.5 μm),* Environmental Protection Agency Compendium Method IO-4.2, EPA/625/R-96/010A, U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, Ohio, 45268.

4. *Operating Manual, ChemComb Model 3500 Speciation Sampling Cartridge*, Revision A, January 2000, Rupprecht & Patashnick Co., Inc. East Greenbush, New York, 12061.

5. *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.

Appendix A

Nitrolux 1000 Checklist

ETV Verification of Ambient Ammonia Monitors
Pranalytica Nitrolux 1000 Ambient Ammonia Analyzer
Daily Checklist

Vendor Contact Information

Operational Instructions:

1. Use the touchpad to “wake up” screensaver

2. Observe that readings have been continuous over the last 4 or 8 hours ☐

3. Record the following readings

   a. Pressure ______________

   b. Flow ______________ (Normal range is 400-500 sccm. If flow is steady at 350 sccm, change inlet filter)

   c. Cell Temp ______________

   d. Laser Temp ______________

4. Are all warning lights green? ____________ (Contact Pranalytica if not)

5. Is the timestamp of display and screen the same as LCD? ___________

Signature ____

Date ______________________

Comments:
