July 2004

Environmental Technology Verification Report

THERMO ELECTRON CORPORATION
MODEL 17C 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

Thermo Electron Corporation Model 17C Ammonia Analyzer

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Notice

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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
DL	detection limit
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FIA	flow injection analysis/analyzer
kg	kilogram
L	liter
Lpm	liter per minute
mL	milliliter
µg	microgram
µm	micrometer
mg	milligram
mm	millimeter
NIST	National Institute of Standards and Technology
NH_3	ammonia
NH_4^+	ammonium
NO	nitric oxide
NO_2	nitrogen dioxide
N_t	nitric oxide, nitrogen dioxide, and ammonia
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 Thermo Electron Corporation Model 17C 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 Model 17C. The following is a description of the Model 17C, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The Model 17C (Figure 2-1) is a chemiluminescence analyzer that uses the reaction of nitric oxide (NO) with ozone (O_3) to measure NH_3 concentrations in the atmosphere. A sample is drawn into the Model 17C by an external pump. After the sample reaches the reaction chamber, it mixes with O_3, which is generated internally. The reaction of NO with O_3 produces a characteristic luminescence with an intensity proportional to the concentration of NO. Light is emitted when electronically excited nitrogen dioxide (NO_2) molecules decay to lower energy states. The light emission is detected by a photomultiplier tube, which in turn generates an electronic signal. The signal is processed by the microcomputer into a NO concentration reading.

To measure the NO, NO_2, and NH_3 concentrations, NO_2 and NH_3 are transformed to NO in a stainless steel converter heated to approximately 775°C before reaching the reaction chamber. Upon reaching the reaction chamber, the converted molecules, along with the original NO molecules, react with O_3. The resulting signal represents the total NO, NO_2, and NH_3 reading (N_t). Separately, NO_2 is transformed into NO in a molybdenum converter heated to approximately 340°C. The NO, plus converted NO_2 concentrations are measured as NO_x. The NO_2 concentration is determined by subtracting the signal obtained in the NO mode from the signal obtained in the NO_x mode. The NH_3 concentration is determined by subtracting the signal obtained in the N_t mode from the signal obtained in the NO_x mode.

Figure 2-1. Model 17C Ammonia Analyzer

NO, NO_2, and NH_3 concentrations are displayed on the front panel of the Model 17C as analog output. The Model 17C has a 1-part-per-billion (ppb) detection limit and operates manually or automatically, with a sample flow rate of 0.6 liters per minute (Lpm). The Model 17C requires 500 Watts of power from 90 to 110, 105 to 125, or 210 to 250 volts alternating current. The Model 17C consists of two components: the analyzer and the converter. The analyzer dimensions are 426 millimeters (mm) by 219 mm by 584 mm, and the converter dimensions are 426 mm by 175 mm by 389 mm. The analyzer weighs 27 kilograms (kg), and the converter weighs 9 kg. The Model 17C costs about $17,000.

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 Model 17C'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 Model 17C 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 Model 17C 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 Model 17C 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 Model 17C 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 Model 17C 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 Model 17C 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 Model 17C during this verification test. The vendor representative trained Battelle and USDA staff to check several instrument parameters to verify the operation of the Model 17C and identify signs of malfunction, which was done on a daily basis. A checklist, provided by the vendor representative and included as Appendix A, was completed by Battelle and USDA staff when regular maintenance activities were performed. In the event of an instrument malfunction, Battelle and/or USDA staff could contact the vendor representative and conduct minor trouble-shooting 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 Model 17C 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 Model 17C was installed inside the instrument trailer, and a Teflon inlet line was used to supply outside air to the Model 17C. Ambient air passed through a Teflon filter before entering the Teflon inlet line. 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.

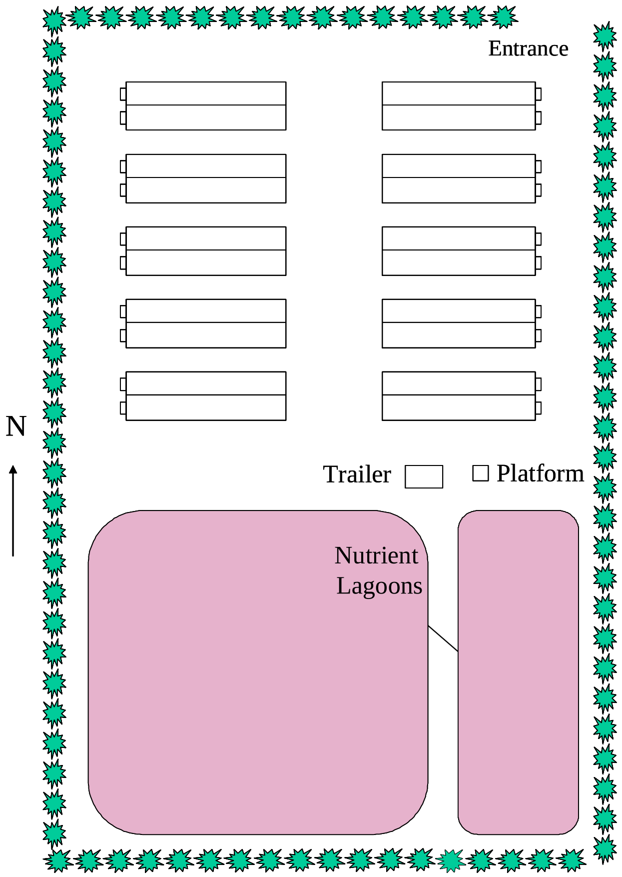

Figure 3-1. Phase I Test Site

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 Model 17C was installed in the instrument trailer as in Phase I, with an inlet height of approximately 1.5 meters.

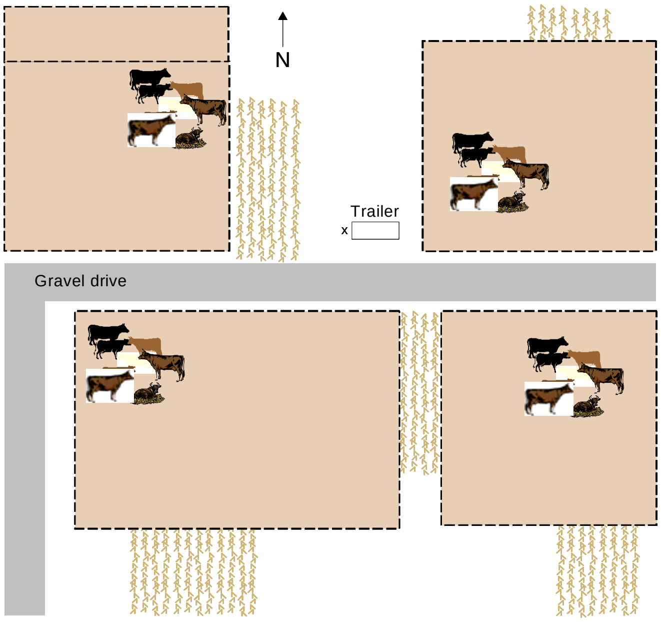

Figure 3-2. Phase II Test Site

3.3 Test Procedures

All tests utilized the continuous NH_3 measurement data record stored by the Model 17C 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 week of each phase of testing, the Model 17C 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 Model 17C 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 Model 17C for between 30 minutes and three hours at each concentration level. Accuracy, linearity, and precision were established based on the continuous digital data set recorded by the Model 17C 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 stable reading for each concentration was also recorded for the Model 17C. These data were used to assess the response time of the Model 17C.

3.3.2 Calibration and Zero Drift

On Monday, Wednesday, and Friday of the first and last weeks of testing during each phase, the Model 17C was supplied with an NH_3 gas standard at nominally 1,000 ppb and zero air to check the calibration and zero drift of the Model 17C, respectively. Zero air and the 1,000-ppb NH_3 standard were each supplied to the Model 17C for approximately one hour, during which time the measured concentrations were recorded by the Model 17C.

3.3.3 Interference Effects

During the second phase of testing, the Model 17C 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 Model 17C 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 in 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 Model 17C until a stable reading was achieved. The interferent gas was then added to the zero air flow and supplied to the Model 17C until a stable reading was observed (at least 2 minutes). The Model 17C was then 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 Model 17C until a stable reading was achieved. The interferent gas was then added to the NH_3 standard for delivery to the Model 17C 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 Model 17C with a standard reference method was established by comparing the average Model 17C 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 Lpm to remove particulate matter with aerodynamic diameters greater than 2.5 micrometers (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 Model 2300 speciation samplers (Rupprecht & Patashnick Co., East Greenbush, New York) were used. The Partisol samplers were equipped with mass-flow controlled

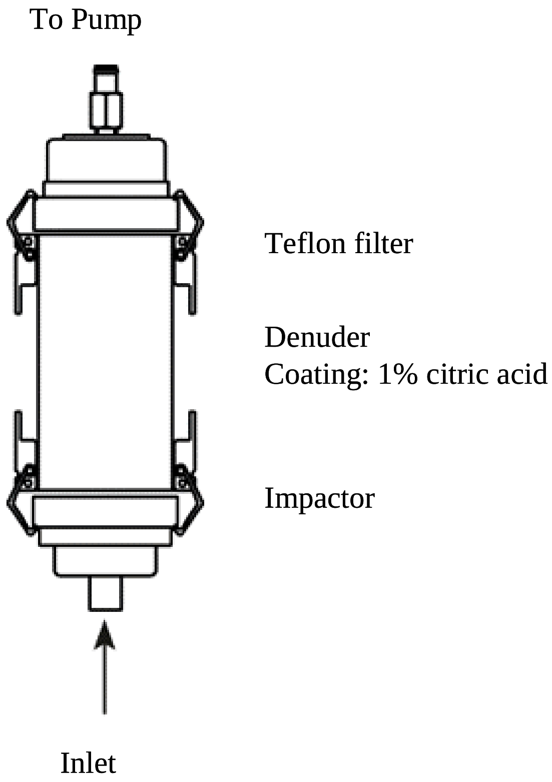

Figure 3-3. Reference Method Sampling Cartridge

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.

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 Model 17C 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 samples were analyzed by USDA 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. This 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, and 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 (as 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 sample 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 was 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 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

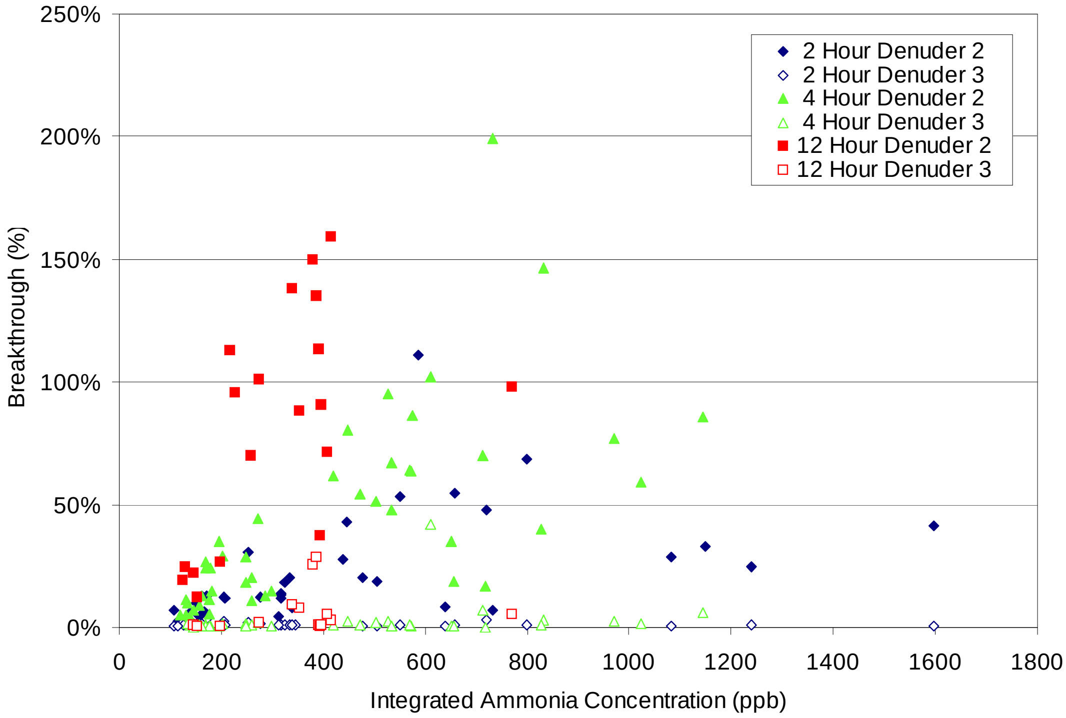

Figure 4-1. Denuder Breakthrough During Phase I as a Function of Integrated Ammonia Concentration

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 period, using the same symbols as in Figure 4-1. Data for all three Phase II sampling locations are included here. As shown in the figure, any high breakthrough values observed on the second backup denuder (Denuder 3 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 overall reference method. In general, breakthrough onto the first backup denuder (Denuder 2 in the figure legend) was low. 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. Table 4-4 summarizes the results of the breakthrough checks for Phase II.

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

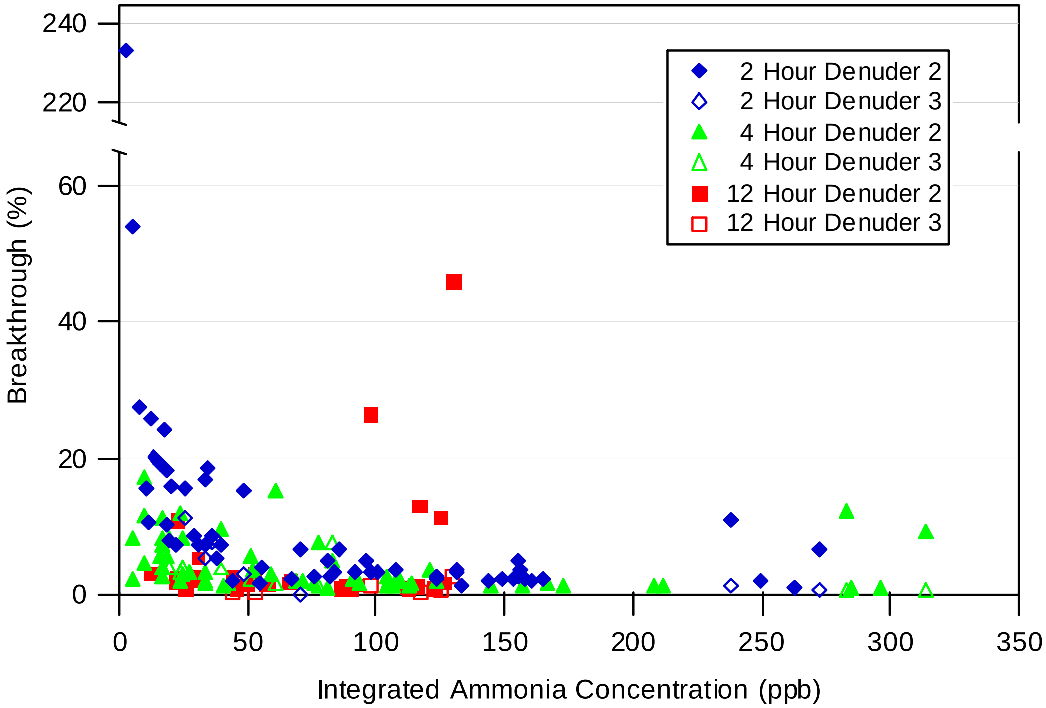

Figure 4-2. Denuder Breakthrough During Phase II as a Function of Integrated Ammonia Concentration

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 11 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 QA limit 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 shows the measured NH_3 captured by the sampling cartridges versus the NH_3 delivered during the dilution checks.

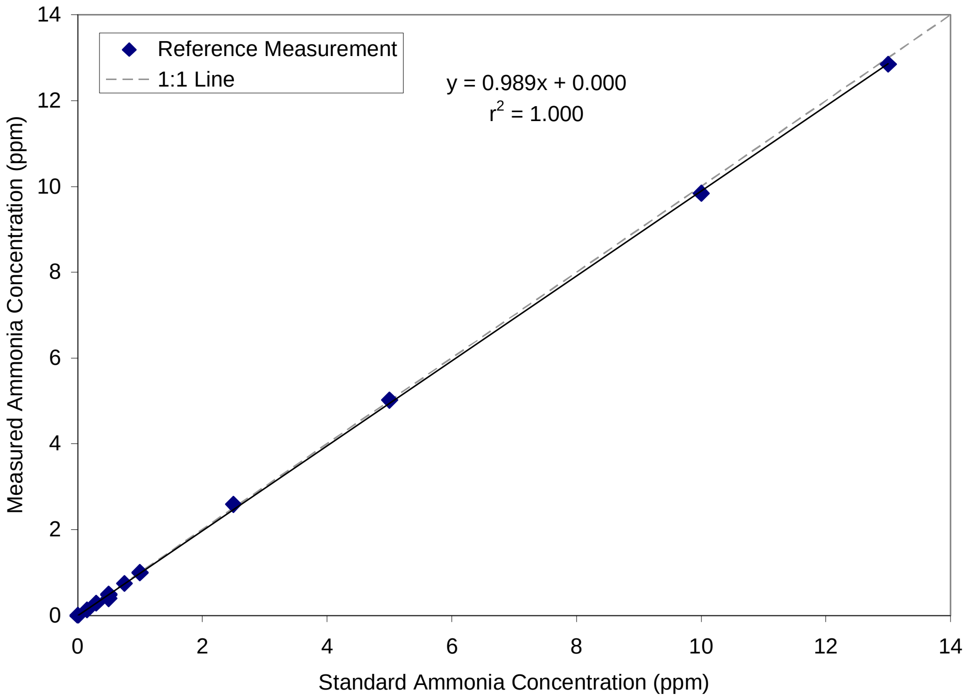

Figure 4-3. Analysis of Diluted Ammonia Standards Using the Denuder Reference Method

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 attributable 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.
Ammonia 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 Model 17C response to each NH_3 gas standard was calculated according to Equation 1

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

where $\overline{x}$ is the average Model 17C response to an NH_3 gas standard of nominal concentration x_n. For each phase of testing, the RA with respect to all of the gas standards (n) delivered to the Model 17C was calculated using Equation 2:

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

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 Model 17C 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 Model 17C measurements of several NH_3 gas standards. The mean and standard deviations of those readings were calculated. The RSD was then determined as:

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

where SD is the standard deviation of the Model 17C readings and $\bar{x}$ is the mean of the Model 17C readings. Precision was calculated independently for each phase of testing.

5.4 Response Time

Response time was assessed in terms of both the rise and fall times of the Model 17C 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 Model 17C 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) 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 Model 17C during each phase of testing. Response times are reported in terms of 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 were reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the Model 17C 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 for this calculation 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 Model 17C 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 Model 17C, 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 Model 17C 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 Model 17C 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. If the measured concentration of NH_3 did not vary by at least a factor of five during each phase of testing, then comparability for that phase was calculated using Equation 1 and reported as a percent difference rather than in terms of the linear regression results.

Chapter 6
Test Results

The results of the verification test of the Model 17C are presented in this section. The Model 17C stored NH_3 measurement data as both 1- and 5-minute averages. When available, 1-minute averaged data were used for the relative accuracy, linearity, precision, calibration/zero drift, response time, and interference tests. The comparability tests utilized 5-minute averaged data.

Meteorological conditions collected using the meteorological monitoring station during Phase I are shown in Figure 6-1. The ambient data set collected by the Model 17C is shown in the bottom panel, along with the wind direction, wind speed, and ambient temperature data. The shaded regions indicate the ammonia reference method sampling periods. The average ambient NH_3 concentration measured by the Model 17C was 515 ppb, with a range of 20 ppb to 3,564 ppb. The

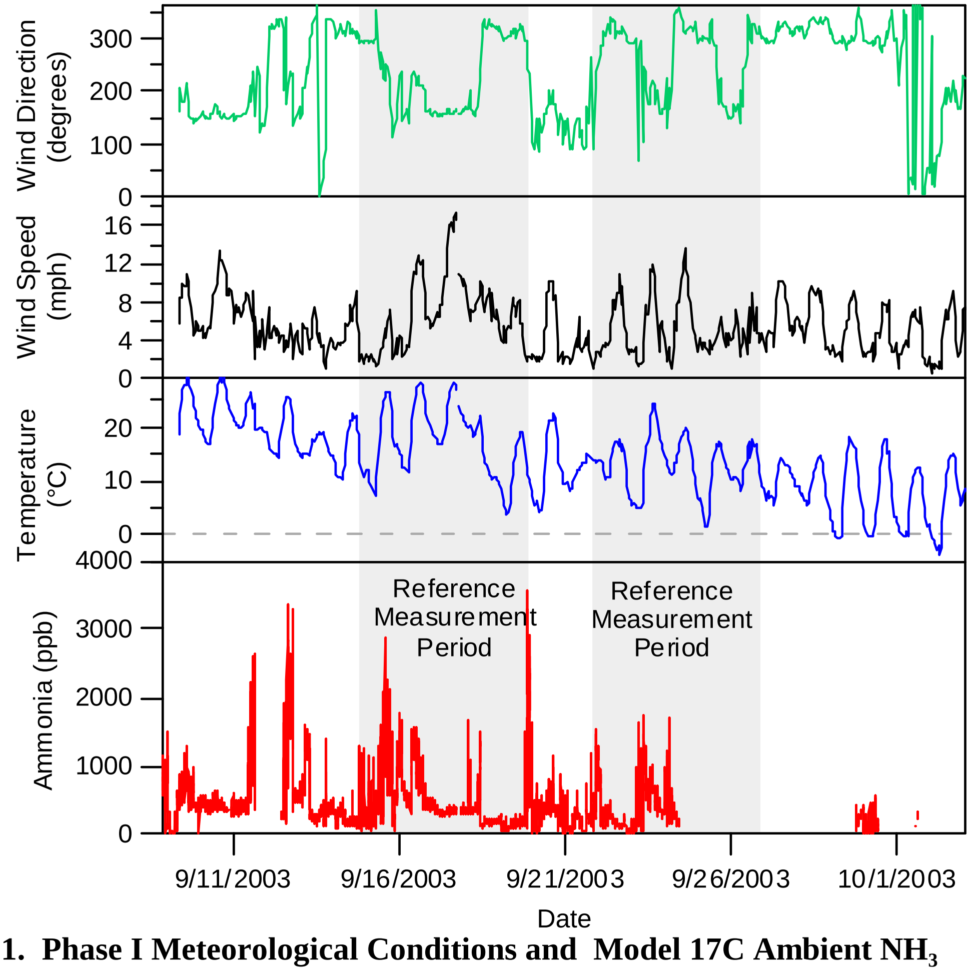

Figure 6-1. Phase I Meteorological Conditions and Model 17C Ambient NH_3 Measurements

large gaps in the Model 17C ambient NH_3 data set are discussed in Section 6.8, although some gaps appear because data points were not plotted for periods when Battelle or USDA staff were performing testing activities on the Model 17C. 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 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.

The ambient temperatures during Phase II, presented in Figure 6-2 along with other meteorological conditions, were significantly cooler than during Phase I, with an average ambient temperature of 4.5°C (range -10 to 29°C) and an average relative humidity of 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 Model 17C (bottom panel). The shaded region shows the period during which NH_3 reference measurements were conducted. The Model 17C NH_3 measurements ranged from 5 ppb to 667 ppb during Phase II and averaged 114 ppb.

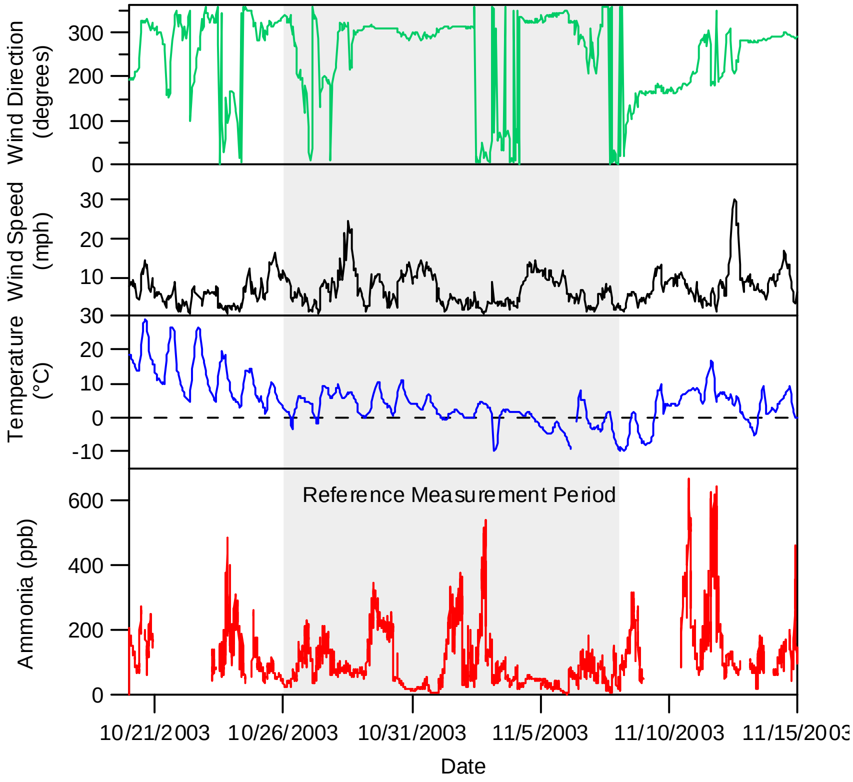

Figure 6-2. Phase II Meteorological Conditions and Model 17C Ambient NH_3 Measurements

6.1 Relative Accuracy

During the first week of each phase of the verification test, the Model 17C 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 Model 17C at a flow rate of 5 Lpm.

Figures 6-3 and 6-4 present the NH_3 concentrations recorded by the Model 17C during the RA checks, along with the nominal NH_3 concentration levels supplied to the Model 17C for Phase I and Phase II, respectively. The averages of the measurements at each nominal NH_3 concentration are presented in Table 6-1 along with the calculated %D, the number of data points, and the average RA for each phase.

As shown in Table 6-1, during Phase I, the %Ds of the Model 17C ranged from -10.2% to 2.8% over the seven concentration levels measured, and the average RA over all the measurements was 3.7%. During Phase II, the %D of the Model 17C ranged from -11.5% to -8.9%, and the average RA was 10.5%. It should be noted that, although the Model 17C was calibrated prior to Phase I, it was not recalibrated prior to Phase II after being transferred to the cattle feedlot.

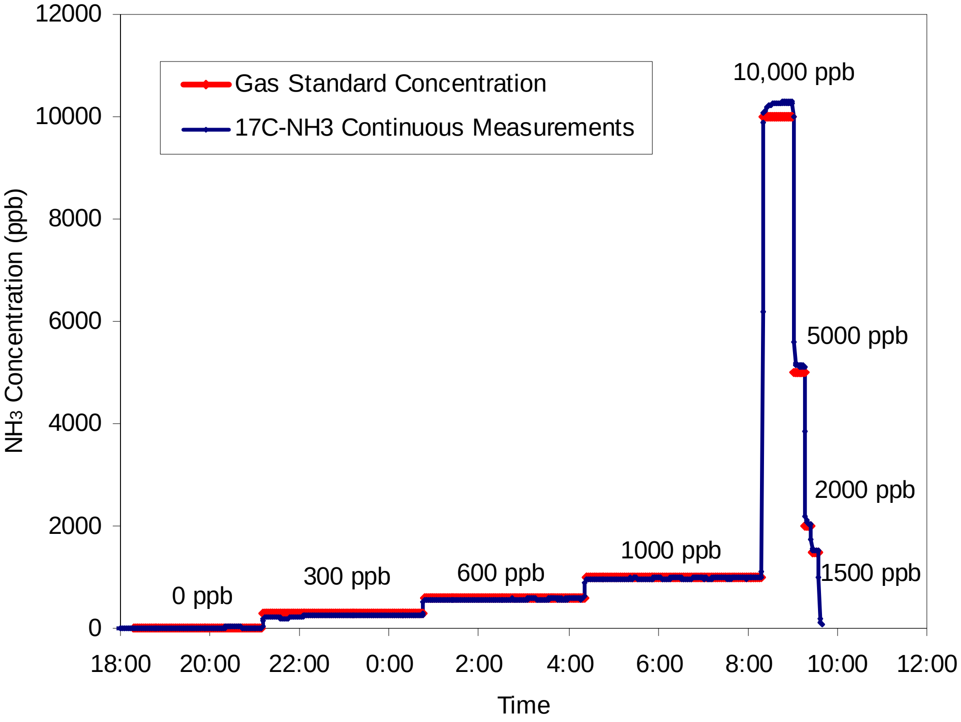

Figure 6-3. Phase I Accuracy Results for the Model 17C

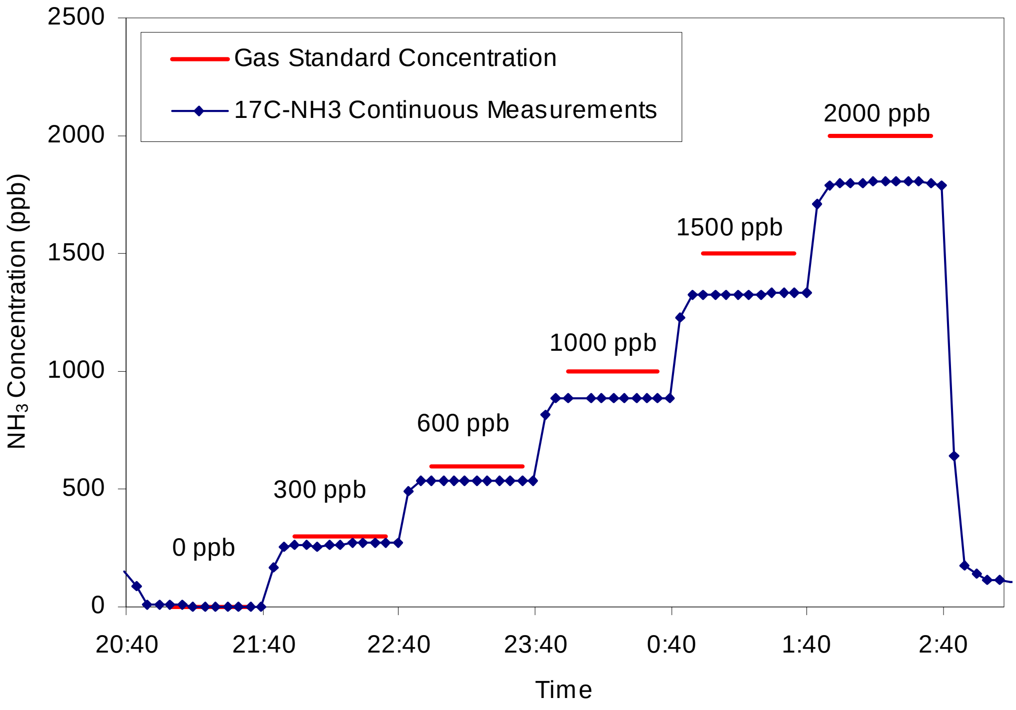

Figure 6-4. Phase II Accuracy Results for the Model 17C

Table 6-1. Relative Accuracy Results

	Phase I			Phase II		
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	5.7	52	NA	3	6	NA
300	269	51	-10.2	273	4	-8.9
600	576	46	-4.1	535	11	-10.9
1,000	984	123	-1.6	886	10	-11.4
1,500	1,527	31	1.8	1,328	11	-11.5
2,000	2,051	12	2.6	1,802	9	-9.9
5,000	5,140	5	2.8	(a)	(a)	(a)
10,000	10,270	8	2.7	(a)	(a)	(a)
Average RA			3.7%			10.5%

(a) The concentration levels and sequence of NH_3 concentrations supplied to the Model 17C were changed for the RA checks conducted during each phase. Consequently, not all concentration levels were measured during both RA checks.

NA = not applicable.

6.2 Linearity

Figures 6-5 and 6-6 show the results of the linearity check for Phase I and Phase II, respectively. During Phase I, a linear regression of the Model 17C response versus the gas standard concentration, over the range from 0 to 10,000 ppb, showed a slope of 1.03 (± 0.01), an intercept of -24 (± 23) ppb, and a coefficient of determination (r^2) of 1.000, where the numbers in parentheses represent the 95% CI. During Phase II, the Model 17C showed a linear response, over the range from 0 to 2,000 ppb, with a slope of 0.90 (± 0.02), an intercept of -0.6 ppb (± 20.3), and an r^2 of 1.000.

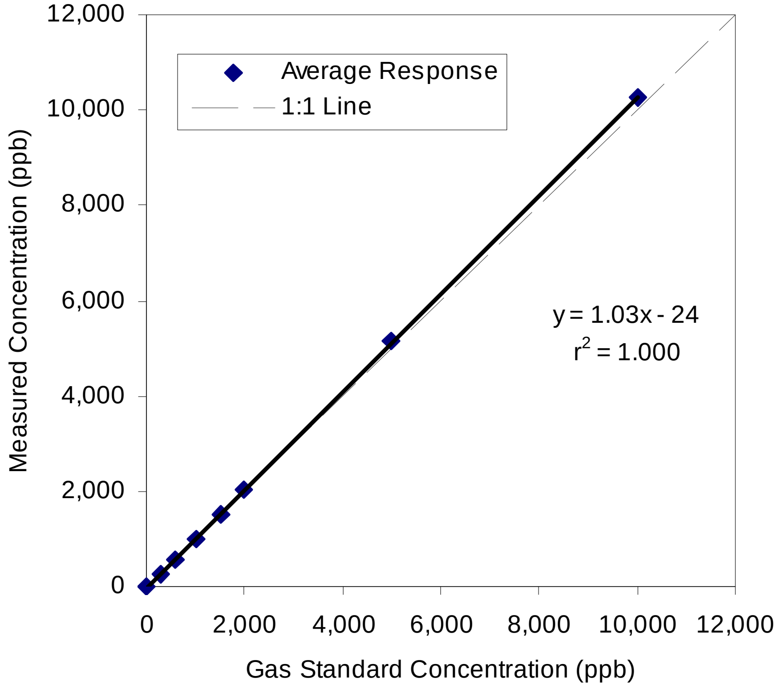

Figure 6-5. Results of Linearity Check of the Model 17C During Phase I

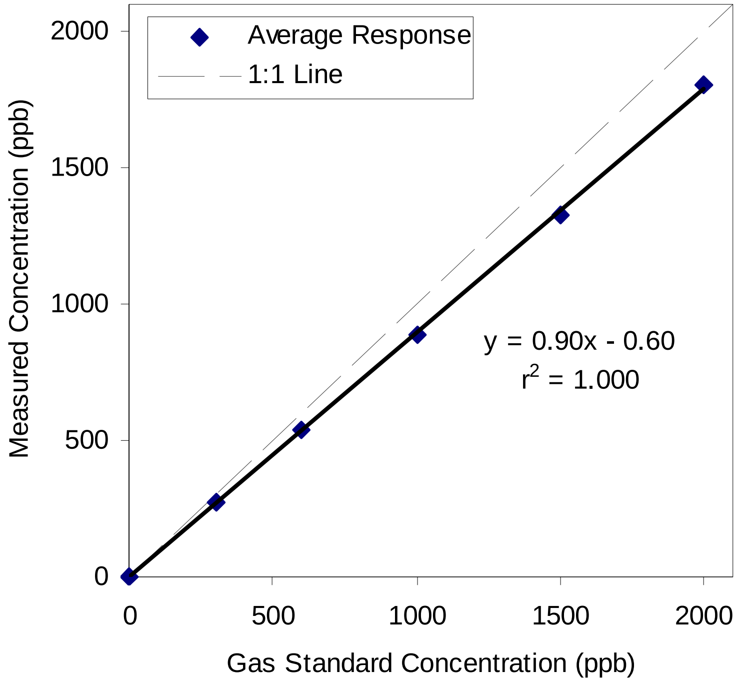

Figure 6-6. Results of Linearity Check of the Model 17C During Phase II

6.3 Precision

Table 6-2 presents the calculated precision of the Model 17C measured during the accuracy and linearity checks. During Phase I, the precision of the Model 17C readings varied from 0.2% to 0.5% RSD, with an average precision of 0.3%. During Phase II, the precision of the Model 17C readings ranged from 0.2% to 0.6% RSD at the five concentration levels measured in the accuracy/linearity checks, also with an average of 0.3%.

6.4 Response Time

Response time was determined during each phase from the amount of time required for the Model 17C to reach 95% of the change in the stable concentrations during the accuracy/linearity checks calculated from the change in NH_3 concentration. Table 6-3 presents a summary of the response time determinations for the Model 17C. Rise times ranged from 180 to 4,560 seconds, with fall times between 120 and 180 seconds during Phase I. The 300-ppb, 600-ppb, and 1,000-ppb nominal NH_3 standards were each delivered for 3 hours, during which time the signal rose slowly at a rate of approximately 7 to 28 ppb per hour. Thus, the "stable reading" for each standard began approximately 2 hours after the start of the standard delivery. This had a significant influence on the rise time calculations. During Phase II, rise times ranged from 600 to 900 seconds (calculated from 5-minute-averaged data), and the fall time from 1,000 ppb to zero was 1,200 seconds. The steady rise discussed above was not apparent during the Phase II checks.

Table 6-2. Calculated Precision of the Model 17C

	Phase I		Phase II	
NH_3 Gas Standard Concentration (ppb)	Average Measured Concentration (ppb)	RSD (%)	Average Measured Concentration (ppb)	RSD (%)
300	269	0.5	273	0.6
600	576	0.2	535	0.4
1,000	984	0.3	886	0.2
1,500	1,527	0.2	1,328	0.3
2,000	2,051	0.5	1,802	0.4
5,000	5,141	0.2	(a)	(a)
10,000	10,269	0.2	(a)	(a)
Average RSD		0.3		0.3

(a) The concentration levels and sequence of NH_3 concentrations supplied to the Model 17C were changed for the RA checks conducted during each phase; not all concentration changes were measured during both RA checks.

Table 6-3. Response Time Determinations

	Phase I(a)		Phase II(b)	
Change	Rise Time (seconds)	Fall Time (seconds)	Rise Time (seconds)	Fall Time (seconds)
0 – 300 ppb	4,560	—	900	—
300 – 600 ppb	2,520	—	600	—
600 – 1,000 ppb	420	—	600	—
1,000 – 1,500 ppb	(c)	—	600	—
1,500 – 2,000 ppb	(c)	—	600	—
1,000 – 10,000 ppb	180	—	(c)	—
10,000 – 5,000 ppb	—	180	—	(c)
5,000 – 2,000 ppb	—	120	—	(c)
2,000 – 1,500 ppb	—	120	—	(c)
1,500 – 0 ppb	—	180	—	(c)
1,000 – 0 ppb	—	(c)	—	1,200

(a) Only 1-minute averaged data were available for this check.

(b) Only 5-minute averaged data were available for this check.

(c) The concentration levels and sequence of NH_3 concentrations supplied to the Model 17C were changed for the RA checks conducted during each phase; not all concentration levels were measured during both RA checks.

However, the temporal resolution of the response time calculation was limited since the data used for the calculation were 5-minute average values. It should be noted that the minimum response time that can be calculated from 5-minute average values is 10 minutes. The measured response times include the time associated with the equilibration of NH_3 on the tubing and inlet surfaces during delivery of the gas standard.

6.5 Calibration and Zero Drift

The calibration/drift checks were conducted by supplying a 1,000-ppb NH_3 gas standard and zero air to the Model 17C for a period of one hour each on Monday, Wednesday, and Friday during the first and last week of each phase. The values reported in Tables 6-4 and 6-5 are based on the average readings during the calibration and zero checks when the readings of the Model 17C had stabilized. The results from the Phase I calibration and zero drift checks are presented in Table 6-4. Unfortunately, some data from the last week of Phase I were not recovered from the Model 17C and were not available for interpretation. No drift was observed in response to 1,000 ppb NH_3 or zero air during Phase II. The results of the Phase II calibration and drift checks are summarized in Table 6-5. No clear trend was observed for either the calibration or zero drift; however, the response to 1,000 ppb NH_3 increased by 34 ppb and 17 ppb during Weeks 1 and 4, respectively.

Table 6-4. Calibration and Zero Checks During Phase I

	Zero Check (ppb)					Calibration Check(a) (ppb)				
Check Number	Mean (ppb)	SD(b) (ppb)	Max-imum (ppb)	Min-imum (ppb)	Number of Data Points	Mean (ppb)	RSD (%)	Max-imum (ppb)	Min-imum (ppb)	Number of Data Points
Week 1 Monday	(c)					(c)				
Week 1 Wednesday	8	0.5	9	8	11	(c)				
Week 1 Friday	6	0.5	6	5	47	1,015	0.6	1,024	1,008	24
Week 4 Monday	4	0.4	4	3	13	3,554(d) 1,016(e)	0.2	3,567	3,547	21
Week 4 Wednesday	11	0.3	12	11	12	1,016	0.4	1,023	1,010	20
Week 4 Friday	(f)					(f)				

(a) 1,000-ppb NH_3 nominal concentration.
(b) SD reported for zero drift check since the RSD is not meaningful for near-zero values.
(c) Gas delivery too short to reach stable value.
(d) 3,500-ppb NH_3 nominal concentration.
(e) Equivalent response to a 1,000-ppb NH_3 nominal standard.
(f) Data for this check were lost due to download failure.

Table 6-5. Calibration and Zero Checks During Phase II

	Zero Check (ppb)					Calibration Check[a] (ppb)				
Check Number	**Mean (ppb)**	**SD[b] (ppb)**	**Max-imum (ppb)**	**Min-imum (ppb)**	**Number of Data Points**	**Mean (ppb)**	**RSD (%)**	**Max-imum (ppb)**	**Min-imum (ppb)**	**Number of Data Points**
Week 1 Monday	4	0	4	4	22	830	1.4	848	817	16
Week 1 Wednesday	(c)					(c)				
Week 1 Friday	3	0.8	4	2	7	864	0.1	866	863	5
Week 4 Monday	7	2.2	12	5	24	859	0.3	862	855	8
Week 4 Wednesday	3	0.8	5	4	5	886	0.2	888	883	10
Week 4 Friday	(d)					876	0.2	880	872	35

(a) 1,000-ppb NH_3 nominal concentration.
(b) SD reported for zero drift check since the RSD is not meaningful for near-zero value.
(c) Data for this check were lost due to download failure.
(d) Zero air was not supplied 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 Model 17C was assessed by supplying the Model 17C with a series of four gases (hydrogen sulfide, nitrogen dioxide, 1,3-butadiene, diethylamine) in zero air and in a 500-ppb NH_3 standard. The response of the Model 17C during the introduction of these gases is summarized in Table 6-6. The interference gas concentrations carry an uncertainty of approximately ± 15%.

Table 6-6. Interference Effect Evaluation

		Interference Effect (%)	
Gas	**Interferent Gas Concentration (ppb)**	**Zero-Air Matrix**	**500-ppb NH_3 Matrix**
Hydrogen sulfide	285	0.5(a)	-0.2(a)
Nitrogen dioxide	95	-2.6	-5.9
1,3-Butadiene	95	0(a)	3.2(a)
Diethylamine	96	51.8	50.6

(a) Signal not significantly different from baseline without interferent gas.

The response of the Model 17C to hydrogen sulfide and 1,3-butadiene was negligible. The Model 17C showed small negative response to NO_2 in both zero air and a 500-ppb NH_3 standard. Diethylamine showed an interference effect of 51.8% in zero air and 50.6% in a 500-ppb NH_3 standard.

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 Model 17C for the reference sampling periods, during Phase I and Phase II, respectively. In general, the Model 17C appears 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 Model 17C data.

A linear regression of the Model 17C 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 1.20 (± 0.05), an intercept of 16 ppb (± 29), and an r^2 value of 0.984, where the numbers in parentheses represent the 95% CI. For Phase II, the linear regression results showed a slope of 0.86 (± 0.03), an intercept of -0.5 ppb (± 3.8), and an r^2 value of 0.990.

6.8 Ease of Use

The Model 17C was installed at the Phase I testing locations by two vendor representatives and at the Phase II testing site by one vendor representative. The Model 17C could be installed and operated by a user with minimal experience using instructions in the Model 17C manual. The Phase I installation involved an on-site calibration of the Model 17C with both NO and NH_3 standards, which were provided by the USDA and were independent of any gas standards used in the verification test. The installation took approximately one day, including time for the Model 17C to warm up before the calibration was performed. The vendor representative trained Battelle and USDA staff to perform two regular maintenance activities, which were conducted during both Phase I and Phase II. The Teflon filter at the end of the ambient inlet was changed once per week, and the desiccant was changed as needed, approximately every two weeks. Otherwise, no maintenance was performed on the Model 17C. A checklist was prepared by Battelle staff from information provided by the vendor representatives to establish whether the Model 17C was in proper working order. The checklist, shown in Appendix A, was completed when regular maintenance activities were performed, and the status of the instrument was checked daily by verifying that no alarms were showing on the Model 17C display.

The Model 17C stores a finite amount of data before they are overwritten. For the 5-minute data set, approximately 10 days of data were stored. Less than 24 hours of 1-minute averages were stored. As a result of these limits, the data were downloaded at least every 10 days and following testing activities whenever possible. Data were downloaded via a serial port connection between the Model 17C and a laptop computer provided by USDA with the software provided by the vendor. On several occasions, the data download was incomplete or failed due to software

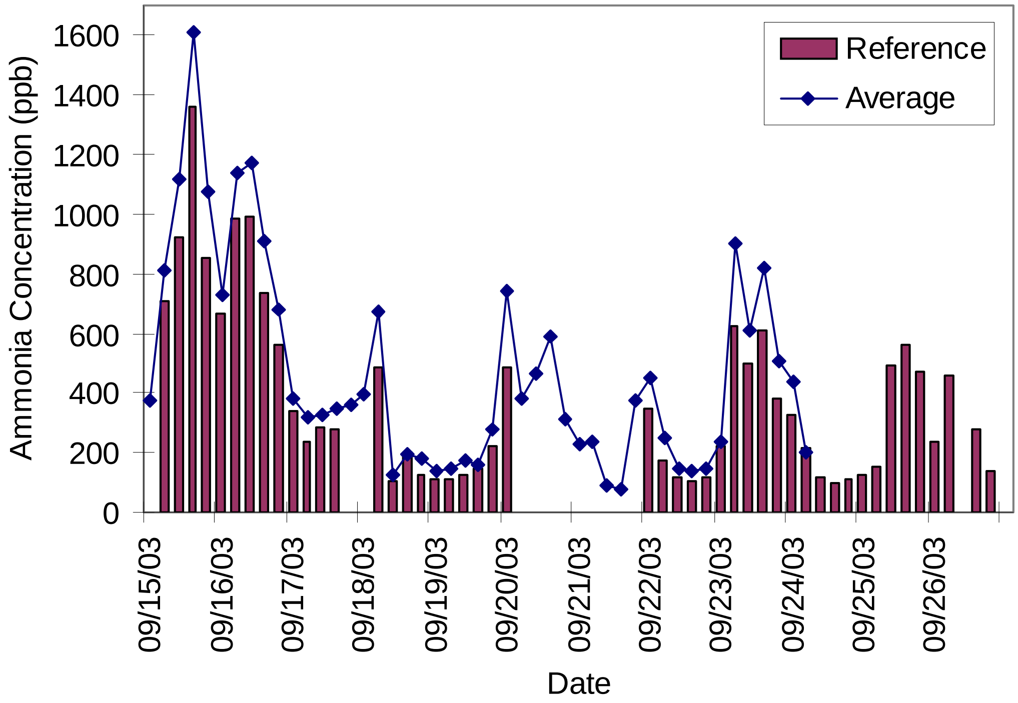

Figure 6-7. Comparison of Ambient Reference Measurements with Averages from the Model 17C During Phase I

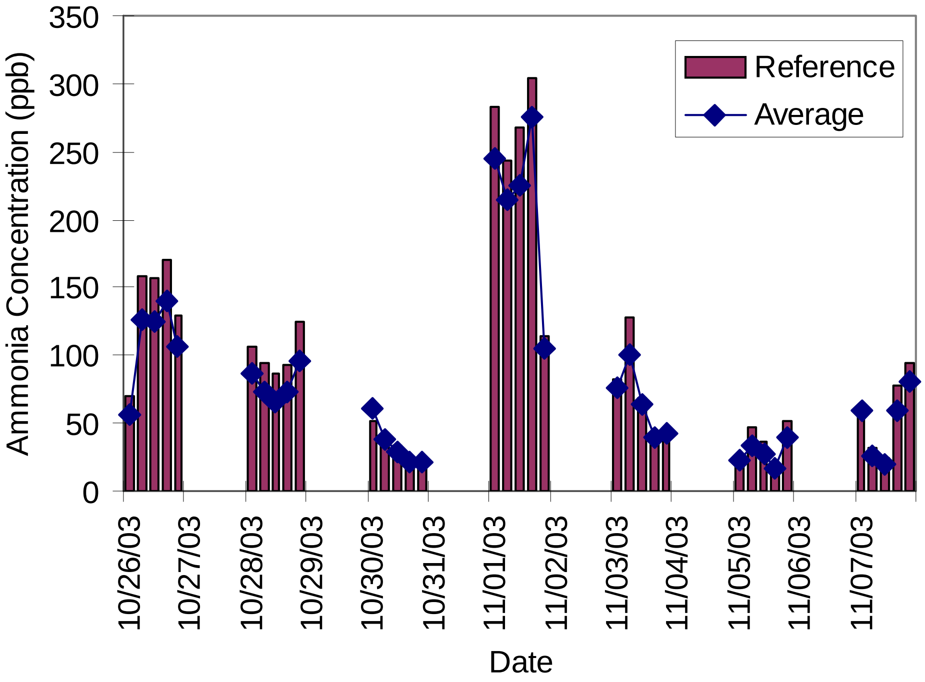

Figure 6-8. Comparison of Ambient Reference Measurements with Averages from the Model 17C During Phase II

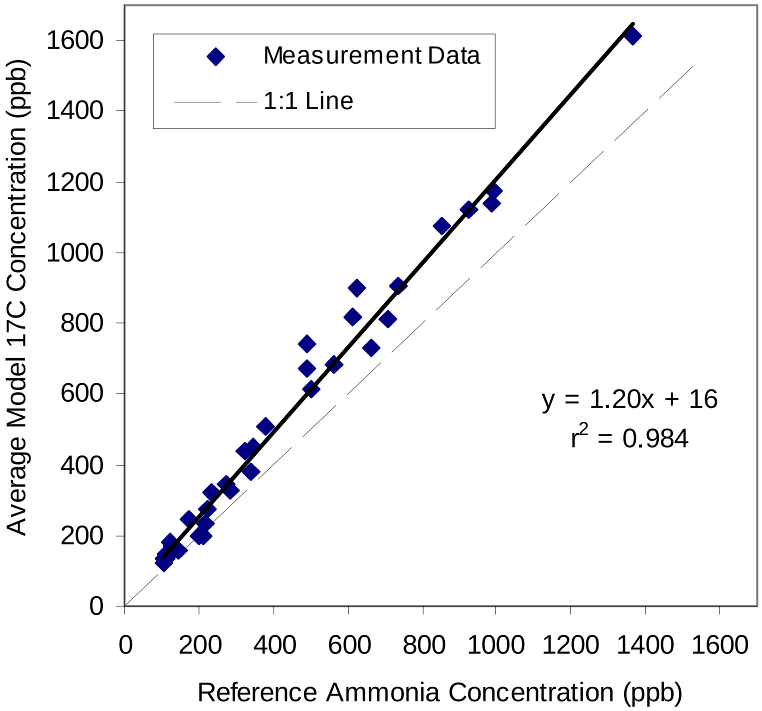

Figure 6-9. Scatter Plot of Model 17C Results versus Ambient Reference Measurements During Phase I

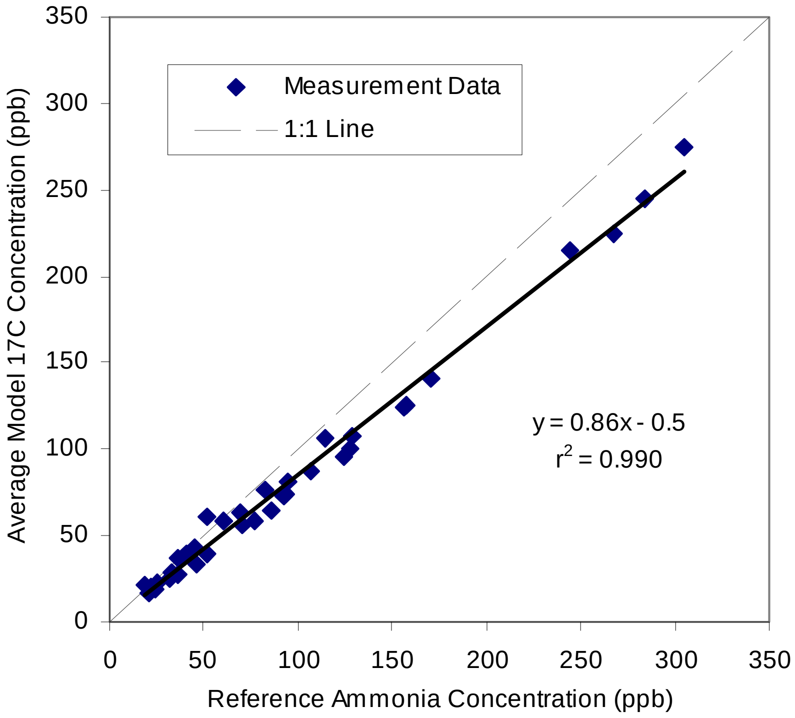

Figure 6-10. Scatter Plot of Model 17C Results versus Ambient Reference Measurements During Phase II

failure. This problem is recognized by Thermo Electron and is attributed to an incompatibity between the Model 17C and computers with clock speeds greater than 266 MHz. Representatives of Thermo Electron have indicated that an effort is underway to resolve this issue. During both phases of testing combined, 42 download attempts were documented. Of these attempts, 19 were successful, 17 were incomplete, and 6 failed; as a result, some data were not recovered. The time spent attempting data downloads was not documented, but is estimated to be approximately three hours for each phase. A summary of these and other activities involving the Model 17C during Phase I and Phase II are presented in Tables 6-7 and 6-8, respectively.

Table 6-7. Activities Performed During Phase I

Date	Time Offline (a) (minutes)	Down Time (b) (minutes)	Service Time (c) (minutes)	Activity
9/08/03	30			Supplied zero air and NH_3 standard(d)
9/10/03	1,595			Supplied zero air and NH_3 standard(d)
9/11/03	1,040			Supplied zero air and NH_3 standards(d)
9/12/03		120		Alarm: Cooler temperature high, caused by increased temperature of instrument trailer; reduction in trailer temperature eliminated error; no associated data loss
9/12/03			5	Changed Teflon inlet filter
9/13/03			5	Changed desiccant
9/17/03		120		Power loss: Instrument recovered without user intervention
9/25/03			5	Changed desiccant
9/26/03			5	Changed Teflon inlet filter
9/29/03	990			Supplied zero air and NH_3 standards; room air sampled for 12 hours overnight(d)
10/01/03	960			Supplied zero air and NH_3 standard(d)
10/03/03	120			Supplied zero air and NH_3 standard(d)
10/03/03		(12,300)(e)		Data download failure. 205 hours of data lost
Totals	4,735	240 (12,300)(e)	20	99% (66%)(e) data completeness(f) and 20-minute service time.

(a) Time Offline = time that the Model 17C 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 Model 17C 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) Data downloads were incomplete or failed, probably as a result of a software failure observed regularly during the verification test.

(f) Data completeness = the ratio of time that the Model 17C 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.

Table 6-8. Activities Performed During Phase II

Date	Time Offline [a] (minutes)	Down Time [b] (minutes)	Service Time [c] (minutes)	Activity
10/20/03		60		Alarm: Cooler temperature high, caused by increased temperature of instrument trailer; reduction in trailer temperature eliminated error; no associated data loss
10/20/03	170			Delivered zero air and NH_3 standards[d]
10/22/03	120			Delivered zero air and NH_3 standard[d]
10/20-10/23/03		3,300		Data lost; download failure[d]
10/23/03	150			Delivered zero air and NH_3 standards[d]
10/24/03	120			Delivered zero air and NH_3 standard[d]
10/26/03				Instrument time does not change for daylight savings
10/31/03			5	Changed Teflon inlet filter
11/7/03			5	Changed dessicant
11/9/03		1,440		Data lost; download failure[e]
11/10/03	75			Delivered zero air and NH_3 standard[d]
11/10/03			5	Changed Teflon inlet filter
11/12/03	120			Delivered zero air and NH_3 standard[d]
11/12/03	360			Delivered zero air and NH_3 standards[d]
11/13/03	480			Performed interference tests[d]
11/14/03	84			Delivered zero air and NH_3 standard[d]
Totals	1,679	60 (4,740)[e]	15	99% (86%)[e] data completeness[f] and 15-minute service time.

[a] Time Offline = time that the Model 17C 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 Model 17C 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 downloads were incomplete or failed, probably as a result of a software failure observed regularly during the verification test.

[f] Data completeness = the ratio of time that the Model 17C 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.

6.9 Data Completeness

During Phase I, the Model 17C was operating and collecting data for more than 99% of the available time. However, because of difficulties associated with the data downloading procedure (described in Section 6.8), only 66% of the data were recovered. Similarly, in Phase II, the Model 17C was operating and collecting data for more than 99% of the available time, but only 86% of the data were recovered.

Chapter 7
Performance Summary

The performance of the Model 17C was evaluated in two phases in this verification test. Table 7-1 presents a summary of the performance of the Model 17C NH_3 analyzer during this verification test.

Table 7-1. Model 17C Performance Summary

Parameter	Results	
	Phase I	Phase II
Relative accuracy(a)	Average RA = 3.7% %D Range = −10.2% to 2.8%	Average RA = 10.5% %D Range = −11.5% to -8.9%
Linearity	Range = 0 to 10,000 ppb Slope = 1.03 (± 0.01) Intercept = −24 ppb (± 23) $r^2 = 1.000$	Range = 0 to 2,000 ppb Slope = 0.90 (± 0.02) Intercept = −0.6 ppb (± 20.3) $r^2 = 1.000$
Precision	Average RSD = 0.3% Range = 0.2% to 0.5%	Average RSD = 0.3% Range = 0.2% to 0.6%
Response time	Rise time = 180 to 4,560 seconds(b) Fall time = 120 to 180 seconds(b)	Rise time = 600 to 900 seconds(c) Fall time = 1,200 seconds(c)
Calibration/ zero drift	No apparent drift in response to zero air or a nominal 1,000-ppb NH_3 gas standard during Week 1 or Week 4.	No apparent drift in response to zero air or a nominal 1,000-ppb NH_3 gas standard during Week 1 or Week 4.
Interference effects(d)	Interference check conducted during Phase II.	• Hydrogen sulfide (285 ppb): no apparent effect • Nitrogen dioxide (95 ppb): a small negative response in zero air and 500 ppb NH_3 • 1,3-butadiene (95 ppb): no apparent effect • Diethylamine (96 ppb): ~50% response in both zero air and 500 ppb NH_3
Comparability	Slope = 1.20 (± 0.05) Intercept = 16 ppb (± 29) $r^2 = 0.984$	Slope = 0.86 (± 0.03) Intercept = −0.5 ppb (± 3.8) $r^2 = 0.990$
Ease of use	• Daily checks were simple and quick • Little skill required to operate • Minimal maintenance required • Regular data download necessary • Data download software unreliable	• Daily checks were simple and quick • Little skill required to operate • Minimal maintenance required • Regular data download necessary • Data download software unreliable
Data completeness	99% data collected, 66% data recovered(e)	99% data collected, 86% data recovered(e)

(a) Relative accuracy is expressed as an average absolute value of the percent difference from NH_3 gas standards.
(b) Only 1-minute averaged data available for this test. Standards for rise time calculation were delivered for three hours.
(c) Only 5-minute averaged data available for this test.
(d) Calculated as the change in signal divided by the interferent gas concentration, expressed as a percentage.
(e) Data loss due to incomplete/failed download attempts.

Chapter 8
References

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2. *Test/QA Plan for Verification of Ambient Ammonia Monitors at Animal Feeding Operations*, Battelle, Columbus, Ohio, September 2003.

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

Model 17C Checklist

ETV Verification of Ambient Ammonia Monitors
Thermo Electron 17C
Checklist

Vendor Representative Contact Information

- Change Teflon filter weekly   Date changed: _______________

- Data download
  Short records weekly   Date: _______________
  Long records after calibration tests   Date: _______________

- Check 17C and 17C Converter power is onCheck instrument display for time or alarm:
  (a) If alarm:
    1. Press menu
    2. Press down arrow to alarm
    3. Press enter
    4. Press down arrow and record alarms
    5. Notify vendor representative

- Check desiccant: Change when 3/4 of column turns pink. Date Changed: ____________

Signature: ____

Date: ____________________

Comments: ____
____
____
____