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Environmental Technology Verification Report

BRUKER DALTONICS, INC.
OPAG 22 OPEN-PATH GAS ANALYZER

Prepared by
Battelle

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The Business of Innovation

In collaboration with the
U.S. Department of Agriculture

Under a cooperative agreement with

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Bruker Daltonics, Inc.
OPAG 22 Open-Path Gas 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 permittees, 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>.

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List of Abbreviations

AFO	animal feeding operation
AMS	Advanced Monitoring Systems
CI	confidence interval
cm	centimeter
DL	detection limit
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FIA	flow injection analysis/analyzer
kg	kilogram
L	liter
Lpm	liters per minute
m	meter
µg	microgram
µm	micrometer
mg	milligram
mL	milliliter
mm	millimeter
min	minute
NIST	National Institute of Standards and Technology
NH ₃	ammonia
NH ₄ ⁺	ammonium
ppb	part per billion
ppm	part per million
%D	percent difference
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RPD	relative percent difference
RSD	relative 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 permittees; 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 Bruker Daltonics, Inc., OPAG 22 Open-Path Gas 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 OPAG 22. The following is a description of the OPAG 22, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The OPAG 22 (Figure 2-1) is a broadband, open-path, Fourier transform infrared spectrometer for remote sensing of hazardous atmospheric compounds. The detection limit for ammonia is 7 parts per billion (ppb) for a pathlength greater than 100 meters (m). The OPAG 22 allows real-time field screening analysis and includes an infrared radiation detector based on the Bruker ROCKSOLID™ interferometer. Internal calibration sources provide self-test and self-calibration for radiometric measurements.

The OPAG 22 detects the absorption of infrared radiation by chemical species. For maximum sensitivity, an active infrared source is positioned an optimal distance from the detector (active mode). Without the active source (passive mode), the OPAG 22 can detect chemical species with less sensitivity using infrared radiation from other sources, such as buildings or the ground, that are an optimal distance from the detector. The OPAG 22 was evaluated only in active mode during this verification test, although it was operated in passive mode during a portion of the



Figure 2-1. OPAG 22 Open-Path Gas Analyzer

test. The OPAG 22 consists of an infrared detector (interferometer module), which is connected to a portable personal computer and a power supply module. This allows the computer to be installed in a location separate from the detector. In the standard configuration, the detector is mounted on an adjustable tripod. The detector can operate for more than four hours before the batteries need to be charged. The active infrared source is mounted on a second tripod and requires a continuous power source.

The OPAG 22 dimensions are 400 millimeters (mm) by 370 mm by 250 mm, and weighs 18 kilograms (kg). It operates on a 12- to 36-volt, 30-Watt power supply. The active infrared source weighs 15 kg. The OPAG 22 (detector and active source) costs \$75,480, the data system (portable personal computer) costs \$13,520, the tripod for the detector

costs \$3,215, a 24-volt battery pack costs \$450, a battery charger costs \$558, and a 24-volt power supply costs \$300.

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 OPAG 22'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.

The active infrared source for the OPAG 22 was not available during Phase I of the verification test so verification data were not collected for Phase I. During Phase II of the verification test, the OPAG 22 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 OPAG 22 response time, the time to reach 95% of the stable signal, was also assessed during the delivery of the NH_3 standards. The OPAG 22 response to ambient air was also

evaluated during Phase II as the comparability to simultaneous determinations by an ambient NH_3 reference method (acid-coated denuders). Additionally, the ease of use of the OPAG 22 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 Description—Phase II

The OPAG 22 active source was not available during Phase I of the verification test and testing activities could not be performed on the OPAG 22 when operating in passive mode. During Phase II, the OPAG 22 was installed in the active mode configuration by a vendor representative and made NH_3 measurements approximately every five seconds during operation. Battelle and USDA staff worked with the vendor representative to establish procedures for operating the OPAG 22 during this verification test. The vendor representative trained Battelle and USDA staff to check several instrument parameters to verify the operation of the OPAG 22 and identify signs of malfunction, which was done on a daily basis. 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.

Figure 3-1 shows a schematic diagram of the cattle feedlot during Phase II of the verification test. A temperature-regulated instrument trailer was used to house some of the monitoring equipment and to provide a sheltered workspace. The OPAG 22 was installed outside in a harvested corn field surrounded on three sides by cow pens. The measurements reported by the OPAG 22 represent the average NH_3 concentration integrated over the space between the active source and detector in the path of the infrared radiation (pathlength). The initial pathlength for the OPAG 22 was 126 m, but was increased to 156 m on October 24, 2003, to include the Reference Method Sampling Site Number 1 in the path of the OPAG22. The active source and detector positions are shown in Figure 3-1 and the reference method sampling stations were at distances 4, 47, and 78 m from the OPAG 22 detector. 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.

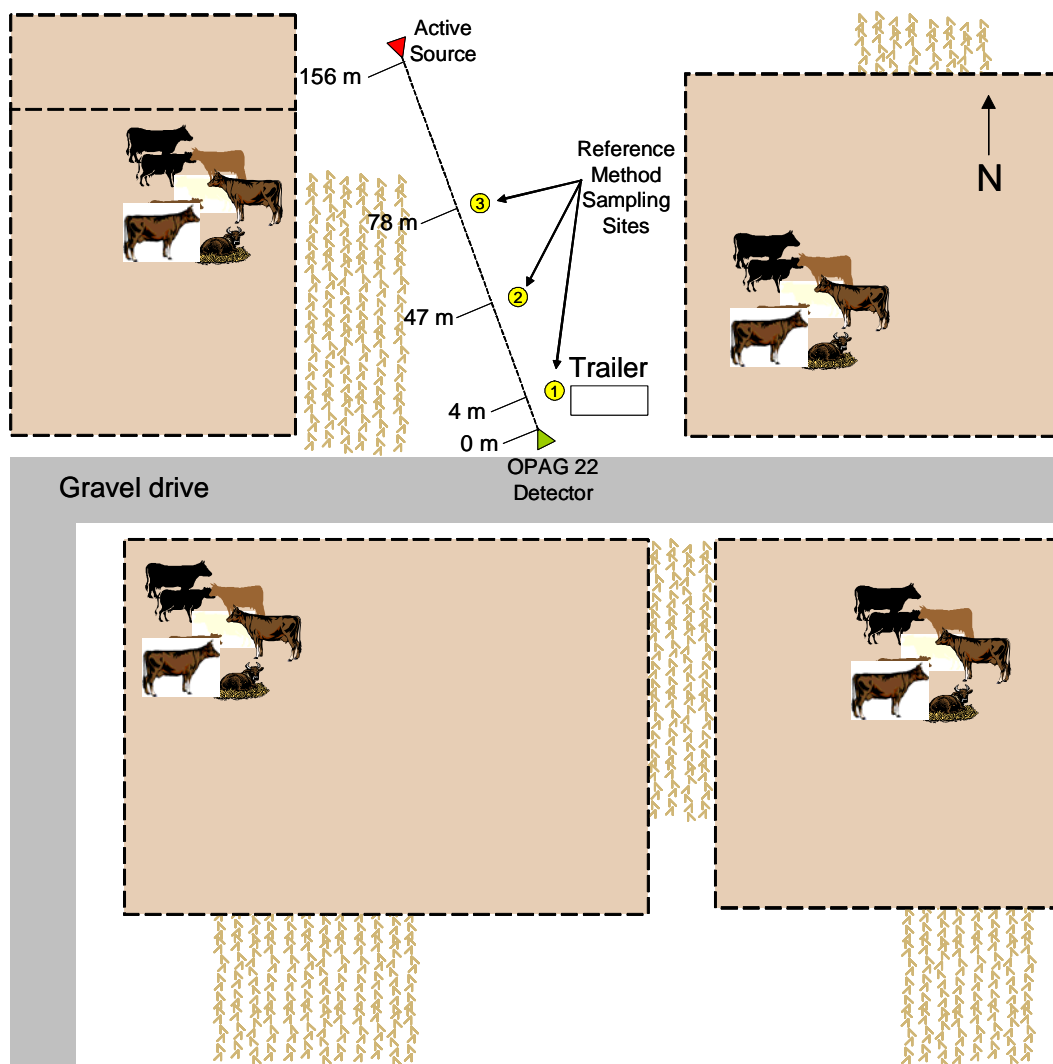


Figure 3-1. Phase II Test Site

3.3 Test Procedures

3.3.1 Accuracy, Linearity, Precision, and Response Time

During the first week of Phase II, the OPAG 22 was supplied with compressed NH_3 gas standards to achieve integrated NH_3 concentrations over a range from 733 to 9,761 ppb. The planned nominal NH_3 concentration range was 0 to 2,000 ppb, but due to several limitations described below, this range could not be achieved. The gases were delivered to the OPAG 22 by supplying high-concentration NH_3 standard gases (297, 479, or 5,000 parts per million [ppm]) directly into one of two polyvinyl chloride (PVC) gas cells (13 centimeters [cm] diameter, 0.227 and 0.303 m in length) that was capped on both ends with infrared transparent plastic film. The gas cell containing the NH_3 gas standard was positioned in front of the OPAG 22 detector and the NH_3 concentration reported by the OPAG 22 was recorded. This reported concentration represented the average NH_3 concentration over the full OPAG 22 pathlength, which included

the NH_3 standard in the gas cell in addition to the background NH_3 present in the ambient air in the remaining pathlength (i.e., between the gas cell and the active source). In order to accurately quantify the NH_3 concentration in the gas cell, its concentration must be sufficiently high that changes in the background NH_3 concentration during the check would be negligible. Thus, low integrated NH_3 concentrations (i.e., between 0 and approximately 300 ppb) could not be tested and constraints imposed by the gas cell pathlength and available gas standards limited the number of concentrations that could be tested. Attempts to use the two gas cells together in series were unsuccessful as the added length interfered with the transmission of the infrared beam to the detector. The 5,000 ppm gas standard could not be diluted to increase the number of delivered gas standard concentrations because of concerns that the high NH_3 level would contaminate USDA's dilution system that was available for use during the verification test.

The NH_3 gas was supplied to the OPAG 22 gas cell for approximately 10 minutes at each concentration level. The gas cell was moved in and out of the path of the OPAG 22 so that background NH_3 levels could also be quantified. The response time was assessed as the time to reach 95% of the stable reading for each gas standard concentration and background air. Accuracy, linearity, and precision were established based on the continuous digital data set recorded by the OPAG 22 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).

3.3.2 Calibration and Zero Drift

On Monday, Wednesday, and Friday of the first and last (fourth) week of testing during Phase II, the OPAG 22 was supplied with an NH_3 gas standard to check the calibration drift of the OPAG 22. Although the test/QA plan⁽²⁾ includes checks to evaluate zero drift, for the reasons explained above, the OPAG 22 response to zero air could not be tested. The NH_3 standards were each supplied to the OPAG 22 for approximately 10 minutes, during which the measured concentrations were recorded by the OPAG 22. The OPAG 22 average response to each gas standard concentration was normalized to 1,000 ppb NH_3 for ease in identifying potential calibration drift.

3.3.3 Interference Effects

The test/QA plan⁽²⁾ describes checks of the OPAG 22 response to a series of potential interference gases (hydrogen sulfide, nitrogen dioxide, 1,3-butadiene, and diethylamine). However, on the day that was scheduled for the interference check, the check could not be conducted because the OPAG 22 could only be operated in the passive mode after strong winds blew the active source over and the verification test staff were not able to realign the source and detector.

3.3.4 Comparability

The comparability of the OPAG 22 with a standard reference method was established by comparing the average OPAG 22 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* ($< 2.5 \mu\text{m}$).⁽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 3-2 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. 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 sampling systems that were pressure- and temperature-corrected.

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 Phase II. To capture diurnal variations in NH_3 concentrations, sampling was conducted on 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. The ChemComb sampling cartridges for a full day of sampling were installed in the Partisol speciation samplers before the first sampling period. The Partisol samplers automatically switched the ambient air flow to each cartridge according to the schedule defined above. As a result, the ChemComb samplers were exposed to the ambient environment for approximately 24 hours. After the final sampling period, all of the sampling media were retrieved and transported to the USDA laboratory for extraction and analysis. During Phase II, reference

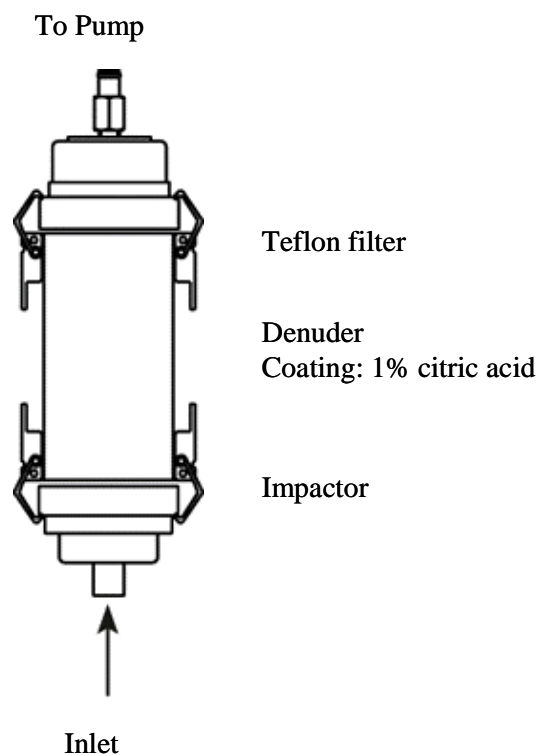


Figure 3-2. Reference Method Sampling Cartridge

sampling was conducted at three sampling sites, as shown in Figure 3.1. The first sampling site was located near the instrument trailer (4 m from the OPAG 22 detector); duplicate samples were also obtained at this site. Two additional sampling locations were positioned approximately 44 and 74 m from the OPAG 22 detector for use in the verification testing of the OPAG 22, but duplicate samples could not be obtained at these locations due to limitations of the Partisol samplers. The sampling schedule for Phase II deviated from the test/QA plan⁽²⁾ 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. The test/QA plan⁽²⁾ called for sampling every day, Monday through Friday, during the sampling period.

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⁽²⁾, 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 NH₃-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. The method involves heating the NH₃ sample with salicylate and hypochlorite in an alkaline phosphate buffer which produces an emerald green color proportional to the NH₃ 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 Phase II using a flow meter with a National Institute of Standards and Technology (NIST)-traceable calibration. 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 $\pm 5\%$ 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 NH₃ 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 NH₃ dilution system (Environics, Tolland, Connecticut) employs three heated mass flow controllers and valves dedicated for the dilution of compressed NH₃ 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⁽²⁾ 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 NH₃ mass corresponding to three times the standard deviation of the NH₃ mass collected on the field blanks. The reference method DL was more than six times higher than the equivalent FIA DL (0.6 microgram [μg] NH₃ per 20-mL sample).

The reference method DL, reported as an NH₃ mass, was used to determine the minimum detectable NH₃ concentrations for Phase II. Since the mass of NH₃ collected by the reference method is a function of the sampling time, flow rate, and the ambient NH₃ concentration, the minimum (time-integrated) ambient NH₃ 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 NH₃, the time-integrated ambient NH₃ concentration must be 20 ppb for a 12-hour sample and 120 ppb for a 2-hour sample. Accordingly, the minimum ambient NH₃ concentrations that could be detected from the collection of 2-, 4-, and 12-hour samples at a nominal flowrate of 10 Lpm were calculated from the reference method DL for Phase II.

A total of 14 field blanks were collected in Phase II. The average NH₃ mass collected on these blanks was 2.5 µg NH₃, and the range was 0.5 to 4.6 µg NH₃. 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 NH₃ 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 NH₃ concentrations. The highest field blank percentages were measured on days when the integrated ambient NH₃ levels were as low as 6 ppb, which is approaching the 4.9-ppb minimum detectable ambient NH₃ 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 NH₃ collected from field blanks for Phase II was 1.4 µg, which resulted in a 6.6 µg NH₃ Phase II reference method DL. The minimum detectable ambient NH₃ concentrations for 2-, 4-, and 12-hour samples (at a nominal flow rate of 10 Lpm) are shown in Table 4-1. During Phase II, one measured NH₃ concentration in ambient air fell below the minimum detectable NH₃ concentration, as summarized in Table 4-1.

Table 4-1. Minimum Detectable Ambient NH₃ 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

Use of backup denuders is called for in the test/QA plan⁽²⁾ during periods when breakthrough greater than 10% of the front denuder is observed or expected. These backup denuders were used to check the degree of NH₃ breakthrough. The breakthrough checks were conducted at each 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 NH₃

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). Data for all three Phase II sampling locations are included here.

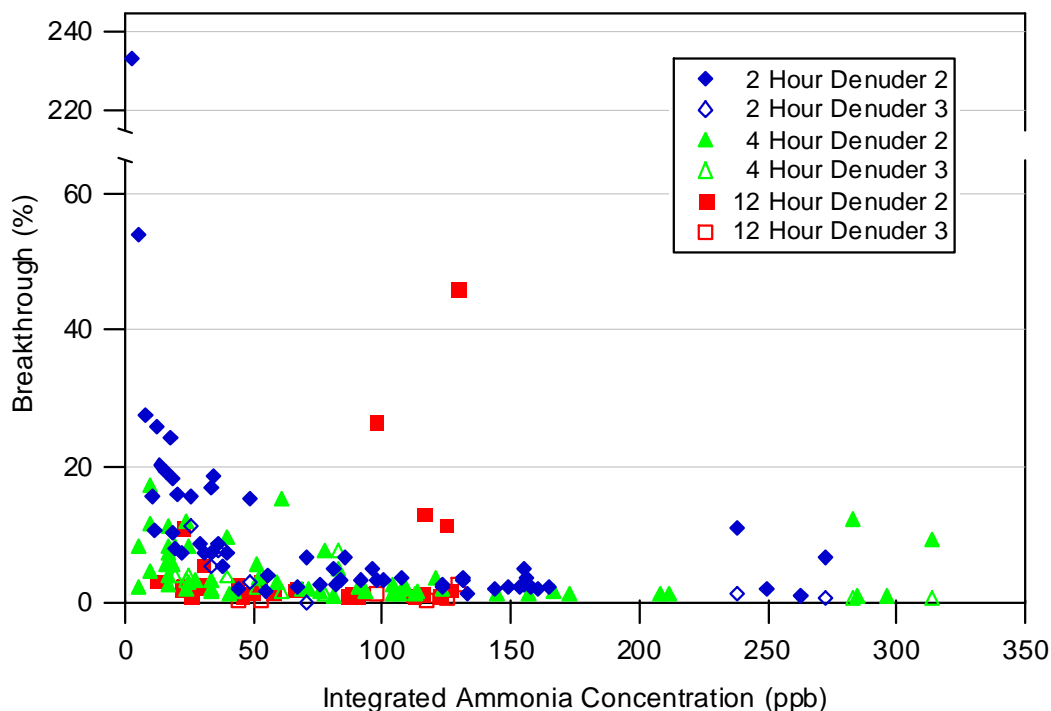


Figure 4-1. Denuder Breakthrough During Phase II as a Function of Integrated Ammonia Concentration

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 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 4-2 summarizes the results of the breakthrough checks for Phase II.

Table 4-2. 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 NH₃ concentration that was less than the minimum detectable NH₃ 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). 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 4-3 summarizes the results of the duplicate sampling for 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%. The absolute RPD for 7 of the duplicate samples exceeded the QA limit of 10% specified in the test/QA plan⁽²⁾. To verify the quality of the reference method, NH₃ 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.

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

Table 4-3. Duplicate Sampling During Phase II

	RPD (%)	Absolute Difference (ppb)
Average	7	5
Maximum	32	18
Minimum	0.7	0.6
Number of duplicate samples		35
Number with RPD >10%		7

blanks deviated from the test/QA plan⁽²⁾ 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. (Note: The test/QA plan⁽²⁾ 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. 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 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 4-2 shows the measured NH_3 captured by the sampling cartridges versus the NH_3 delivered during the dilution checks.

This 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 4-2. 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.

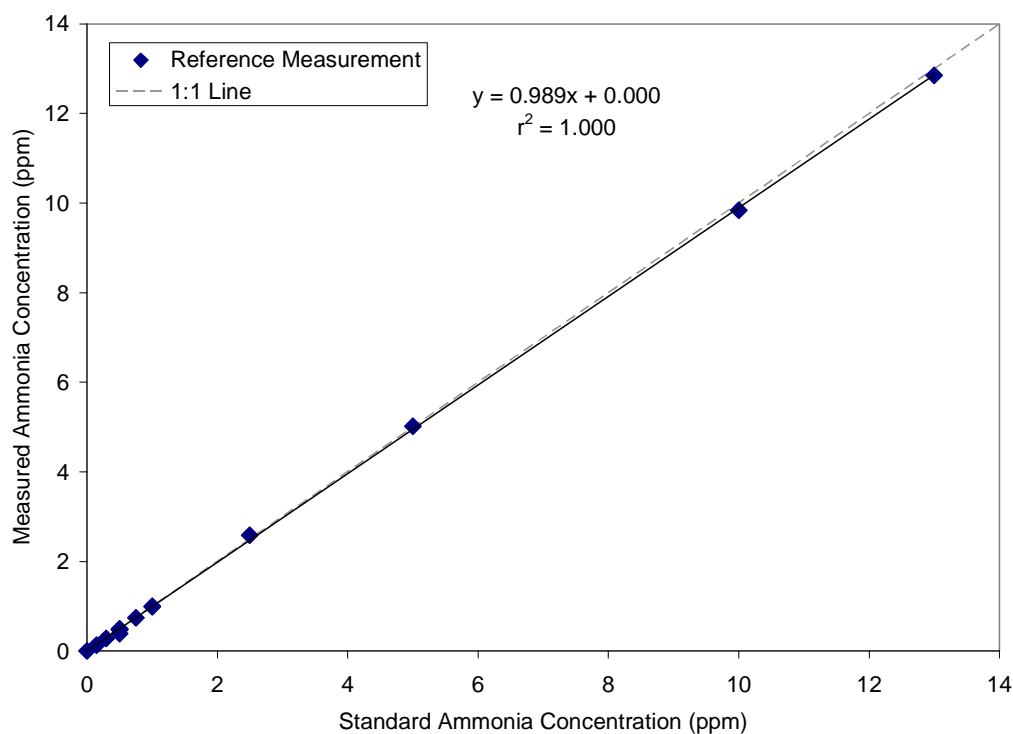


Figure 4-2. Analysis of Diluted Ammonia Standards Using the Denuder Reference Method

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 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 $\pm 10\%$ (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 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⁽²⁾, 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 4-4 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, the entries in the laboratory record books or on field data sheets were not reviewed within two weeks. A deviation report was filed to address this.

Table 4-4. 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. The OPAG 22 reports NH_3 concentration measurement data that represent the average NH_3 concentration integrated over the analyzer's pathlength. During checks that required the delivery of NH_3 gas standards using a gas cell, the OPAG 22 detected both the NH_3 present in the gas cell and the NH_3 present in the ambient air along the remaining pathlength. The ambient air concentration ($[\text{NH}_3]_a$) was measured by the OPAG 22 over the total pathlength before and during or after each NH_3 standard measurement. This made it possible to calculate the contribution of ambient air to the total OPAG 22 measured response during the delivery of an NH_3 gas standard. This assumes that $[\text{NH}_3]_a$ did not change during each check period. For all checks that required the delivery of NH_3 gas standards, Equation 1 was used to calculate the expected response ($[\text{NH}_3]_e$) of the OPAG 22 to a gas standard confined in the gas cell.

$$[\text{NH}_3]_e = \frac{([\text{NH}_3]_s \times d) + ([\text{NH}_3]_a \times (l - d))}{l} \quad (1)$$

where $[\text{NH}_3]_s$ is the NH_3 gas standard concentration, d is the pathlength of the gas cell, $[\text{NH}_3]_a$ is the average measured OPAG 22 ambient NH_3 concentration before and/or after delivery of the gas standard, and l is the total pathlength between the OPAG 22 active source and detector.

5.1 Relative Accuracy

The percent difference (%D) of the average OPAG 22 response to each NH_3 gas standard was calculated according to Equation 2:

$$\%D = \frac{\bar{x} - [\text{NH}_3]_e}{[\text{NH}_3]_e} \times 100 \quad (2)$$

where \bar{x} is the average OPAG 22 response to an NH_3 gas standard of integrated concentration $[\text{NH}_3]_e$. During Phase II, the average RA with respect to all of the gas standards (n) delivered to the OPAG 22 was calculated using Equation 3:

$$\text{Average RA} = \frac{1}{n} \left(\sum_{i=1}^n |\%D_i| \right) \times 100 \quad (3)$$

5.2 Linearity

Results from the addition of NH₃ gas standards to the OPAG 22 detection path during the RA checks were also used to assess linearity. A linear regression analysis of the data was performed using the NH₃ concentration of the compressed gas standards ([NH₃]_s) added to the OPAG 22 detection pathlength as the independent variable and the resulting change in the measured OPAG 22 concentration as the dependent variable. For periods when 0 ppb NH₃ was added (i.e., the OPAG was measuring ambient air), the dependent variable was equal to the standard deviation of the OPAG 22 measurements. The NH₃ added to the OPAG 22 detection path was expressed as the integrated NH₃ concentration across the OPAG 22 pathlength ([NH₃]_{SA}) as described by Equation 4.

$$[\text{NH}_3]_{\text{SA}} = \frac{[\text{NH}_3]_{\text{s}} \times d}{l} \quad (4)$$

Linearity was expressed in terms of slope, intercept, and r^2 value. 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 the OPAG 22 measurements of several NH₃ gas standards. The mean and standard deviations of those readings were calculated. The RSD was then determined as:

$$\text{RSD} = \frac{\text{SD}}{\bar{x}} \times 100 \quad (5)$$

where SD is the standard deviation of the OPAG 22 readings and \bar{x} is the mean of the OPAG 22 readings.

5.4 Response Time

Response time was assessed in terms of both the rise and fall times of the OPAG 22 when sampling NH₃ gas standards. Rise time (i.e., background to 95% response time for the change in NH₃ concentration) was determined from the OPAG 22 response when the gas cell containing an NH₃ standard was moved into the OPAG 22 detection path. Once a stable response was achieved with the gas standard, the fall time (i.e., the 100% to 5% background response time) was determined in a similar way, moving the gas cell out of the OPAG 22 detection path. Response times are reported in terms of seconds. It should be noted that response times include the time associated with equilibration on the surfaces of the gas cell.

5.5 Calibration and Zero Drift

Calibration drift is reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the OPAG 22 in the sampling of NH₃ gas standards over the duration of this verification test. The calibration drift was calculated during Phase II of testing so that up to six NH₃ standard readings (on Monday, Wednesday, and Friday of Week 1 and Week 4) were used for this calculation. The mean response for each calibration check was normalized to 1,000 ppb (i.e., the mean was multiplied by 1,000 and divided by the [NH₃]_c) to facilitate the comparison of the data. The results of these checks indicate the day-to-day variation in standard readings. As discussed in Section 3.3, zero drift was not evaluated for the OPAG 22.

5.6 Interference Effects

As discussed in Section 3.3.3, interference checks could not be performed on the OPAG 22.

5.7 Comparability

Comparability between the OPAG 22 results and the reference method results with respect to ambient air was assessed by calculation of the %D. The OPAG 22 measurement data were averaged over 2-, 4-, and 12-hour time intervals corresponding to the reference method sampling schedule. Reference method data from the three sampling sites were averaged for each sampling interval to represent the integrated NH₃ concentration across the detection path of the OPAG 22. Since the measured NH₃ concentrations from the available data did not vary by a factor of five during testing, comparability for that phase was calculated using Equation 2 and reported as a %D rather than in terms of a linear regression.

Chapter 6 Test Results

The results of the verification test of the OPAG 22 are presented in this section. The OPAG 22 infrared source for active mode operation was not available during Phase I of the verification test. The activities outlined in the test/QA plan⁽²⁾ for this verification test could not be completed on the OPAG 22 when operating in passive mode (i.e., without the active source). The OPAG 22 was operated in active mode during Phase II except for a brief period at the end of the phase when it was operated in passive mode. As such, the results presented here are from Phase II only. The values presented in this section are based on readings recorded by the OPAG 22 approximately every 4 seconds, or the minimum time required to scan the interferometer a pre-set number of times.

It should be noted that the OPAG 22 appeared to be malfunctioning during this verification test, as observed during installation by verification test staff and the vendor representative and supported by information provided by the vendor after completion of the test. The vendor representative spent several days troubleshooting the OPAG 22 in an effort to determine the source of sharp positive and negative peaks that were present in the measured spectral data. At this time, Battelle staff observed that the noise patterns were consistent with an unstable/failing interferometer reference laser (used as an internal reference to synchronize the interferometer mirror movement with the detector signal). Absorption anomalies resulting from interferometer reference laser instabilities, which are consistent with the anomalies observed in the OPAG 22 data, have been documented in the literature.⁽⁶⁾ The vendor indicated that the OPAG 22 used in this test failed the diagnostic self-test on its first use after test completion. Troubleshooting efforts by the vendor after completion of the test revealed that the OPAG 22 interferometer reference laser was faulty. The vendor also stated that failing reference lasers have previously caused intermittent operation, similar to that observed for the OPAG 22 as described in Section 6.8. Thus, the results presented in this report are for the verification of an OPAG 22 that was apparently not functioning properly. These problems resulted in the loss of a significant portion of the data during testing.

Meteorological conditions collected using the meteorological station during Phase II are presented in Figure 6-1. 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 6-1 shows the Phase II wind direction, wind speed, and ambient temperature data and the ambient NH₃ data set collected by the OPAG 22 (bottom panel). The shaded region shows the period during which NH₃ reference measurements were conducted. Data acquired in the active mode are shown in red (lower panel, left axis). During the last week of Phase II, the active source was blown over by strong winds, after which time measurements were conducted in passive mode (lower panel, right axis, shown in orange) because the verification test staff were not able to realign the source and detector. The gaps in the ambient NH₃ data set were caused by computer-related failures, which are discussed in Section 6.8. The reported OPAG 22 measurements ranged from 0 to 140 ppb during Phase II and averaged 32 ppb.

6.1 Relative Accuracy

During the first week of Phase II, the RA of the OPAG 22 was assessed using the method of standard additions. Compressed NH₃ gas standards in a gas cell were added to the OPAG 22 detection path at several concentrations while the OPAG 22 was continuously measuring the

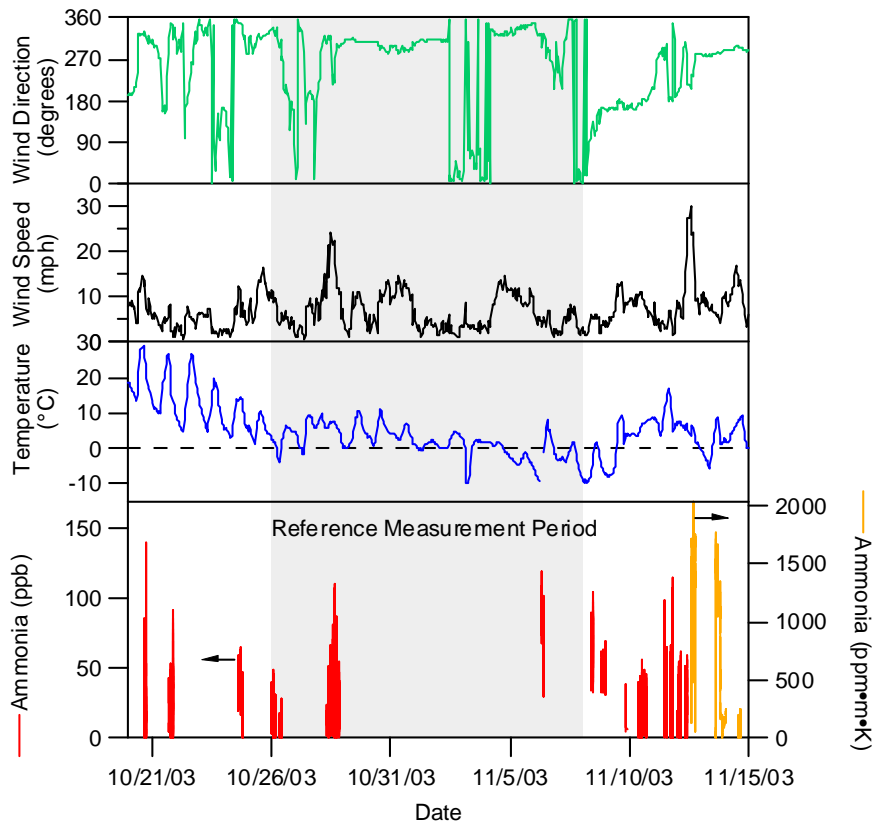


Figure 6-1. Phase II Meteorological Conditions and OPAG 22 Ambient NH₃ Measurements

ambient air NH_3 concentration across the remaining detection pathlength. The compressed NH_3 gas standards were delivered into a gas cell that abutted the OPAG 22 detector, positioned between the detector and the active source. In this configuration, the OPAG 22 detected NH_3 in the gas cell in addition to the ambient air across the measurement pathlength, which was either 126 or 156 meters. The contribution of the OPAG 22 response from the ambient air was accounted for using Equation 1, assuming that $[\text{NH}_3]_a$ did not vary during the check period. The contribution from ambient air was between 0.1% and 3.6%, with an average contribution of 1.6%. Two gas cells were constructed from 0.227-meter and 0.303-meter lengths of PVC pipe (13 cm in diameter) that were capped on both ends with plastic film provided by the vendor representative. The plastic film did not absorb significant infrared radiation in the NH_3 absorption region. The compressed gas standards at concentrations of 297 ppm, 479 ppm, and 5,000 ppm were delivered directly into one of the PVC pipes without further dilution. The use of two gas cells of different lengths and three NH_3 standard concentrations provided a series of six nominal NH_3 standard concentrations ($[\text{NH}_3]_e$). Unfortunately, difficulties encountered during testing prevented testing at all six nominal concentrations.

Figure 6-2 presents the NH_3 concentrations recorded by the OPAG 22 during the RA checks, along with the expected NH_3 response ($[\text{NH}_3]_e$) calculated for each gas standard concentration level supplied to the OPAG 22 gas cell. The data shown by asterisks represent the values that were hand-recorded during checks for which the data were lost due to computer-related problems, as described in Section 6.8. The input gas standard concentration ($[\text{NH}_3]_s$), gas cell pathlength (d), measured ambient NH_3 concentration ($[\text{NH}_3]_a$), and total pathlength (l) are also reported in Table 6-1, along with the averages of the measurements at each nominal NH_3 concentration ($[\text{NH}_3]_e$), the calculated %D, and the number of data points used in the calculations. During delivery of the 5,000 ppm NH_3 standards (integrated concentrations of 9,743 to 9,761 ppb), the OPAG 22 signal appeared to be saturated. These values were not used to calculate the RA, but are reported in Table 6-1 and Figure 6-2. The %Ds of the OPAG 22 ranged from -29 to -22 over the range of concentration levels measured (between 740 and 875 ppb), and the average RA (i.e., the average of the absolute values of the %Ds) was 26%.

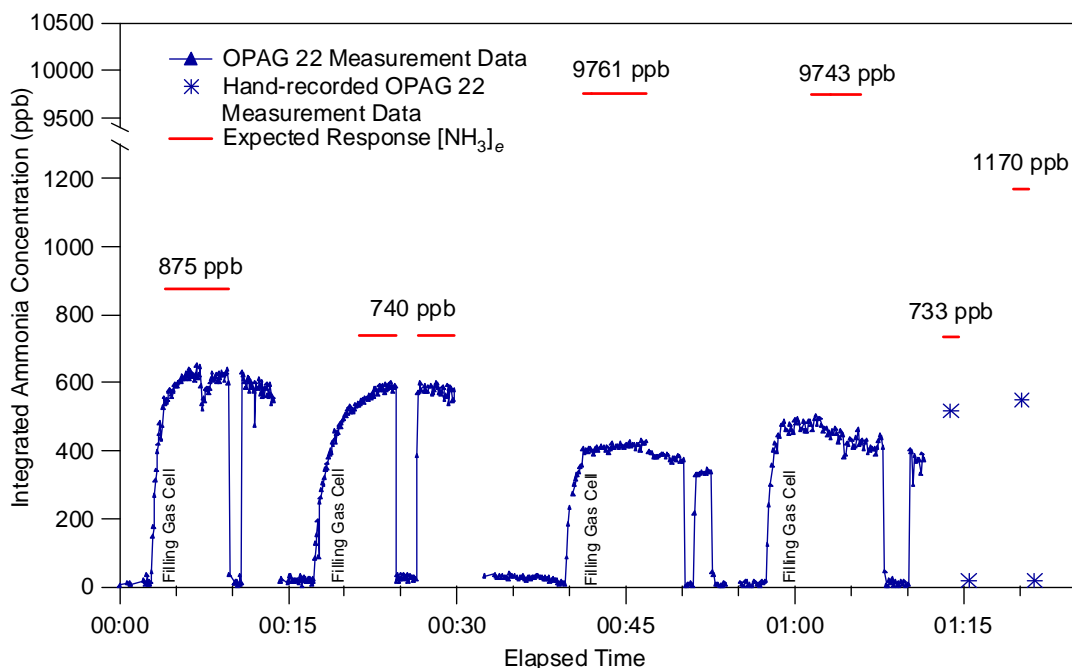


Figure 6-2. Phase II Accuracy Results for the OPAG 22

Table 6-1. Relative Accuracy Results

Gas Standard Concentration [NH ₃] _s (ppm)	Gas Cell Path-length <i>d</i> (m)	OPAG 22 Measured Ambient Concentration [NH ₃] _a (ppb)	Total Path-length <i>l</i> (m)	Expected Integrated Concentration [NH ₃] _e (ppb)	Average OPAG 22 Measured Integrated Concentration (ppb)	Number of Data Points	%D
297	0.303	26.1	126	740	580	24	-22
479	0.227	11.8	126	875	618	20	-29
297	0.303	18.5	126	733	518	1 ^(a)	(-29) ^(a)
479	0.303	18.5	126	1,170	550	1 ^(a)	(-53) ^(a)
5,000	0.303	27.3	156	9,761	417	18	(-96) ^(b)
5,000	0.303	9.2	156	9,742	478	22	(-95) ^(b)
Average RA							26%

^(a) The data from this RA check were lost due to a computer error (“DDE” error). One measured value was hand-recorded in the laboratory research notebook for [NH₃]_a and the OPAG 22 response to the NH₃ standard while the test was being conducted. Thus, the number of data points used in the calculations is equal to 1 for these checks. These values were not included in the average RA calculation.

^(b) RA checks conducted with the 5,000-ppm NH₃ gas cylinder standard appeared to saturate the NH₃ absorption peaks. These data were not included in the average RA calculation.

6.2 Linearity

The detection of NH₃ gas standards by the OPAG 22 during the RA checks, which were conducted using the method of standard additions, was also used to assess linearity. Figure 6-3 shows the results of the linearity check for Phase II, where the independent variable is the integrated NH₃ concentration added to the OPAG 22 detection path, and the dependent variable is the average change in the measured OPAG 22 NH₃ concentration in response to the gas standard. Thus, when 0 ppb NH₃ was added to the detection path (i.e., the OPAG 22 was detecting only ambient air), the dependent variable was equal to the standard deviation of the ambient air OPAG 22 data points. The results of the NH₃ standard additions are presented in Table 6-2.

Table 6-2. Standard Addition Results for Linearity Check

Gas Standard Concentration [NH ₃] _s (ppm)	Gas Cell Pathlength <i>d</i> (m)	Total Pathlength <i>l</i> (m)	Integrated Standard Addition Concentration [NH ₃] _{SA} (ppb)	Change in Measured Concentration (ppb)	Number of Data Points
0	0.303	126	0	7	22
297	0.303	126	714	554	24
0	0.227	126	0	8	15
479	0.227	126	863	606	20
0	0.303	126	0	0	1 ^(a)
297	0.303	126	714	500	1 ^(a)
0	0.303	126	0	0	1 ^(a)
479	0.303	126	1,152	532	1 ^(a)
0	0.303	156	0	10	59
5,000	0.303	156	9,733	390	18
0	0.303	156	0	7	34
5,000	0.303	156	9,733	469	22

^(a) The data from this RA check were lost due to a computer error (“DDE” error). One measured value was hand-recorded in the laboratory research notebook for the OPAG 22 ambient concentration and response to the NH₃ standard addition while the test was being conducted. Thus, the number of data points used in the calculations is equal to 1 for these checks.

The range of concentrations used to test the OPAG 22 linearity was limited due to its configuration and the available NH₃ gas standards. Attempts to increase the pathlength of the gas cell for use with the 297- and 479-ppm standards were made, but the longer tubes could not be aligned in the OPAG 22 infrared beam to allow for quantification. Due to time and material constraints, shorter gas cells for use with the 5,000-ppm standard were not constructed at the time of testing. Dilution of the 5,000-ppm NH₃ standard was avoided because of concern about contamination

of the USDA dilution system. As a result, the range of concentrations delivered to the OPAG 22 was relatively narrow.

A linear regression of the change in OPAG 22 response versus the NH₃ concentration added to the OPAG 22 detection path, over the range from 0 to 9,733 ppb, showed a slope of 0.029 (± 0.047), an intercept of 201 (± 188) ppb, and a coefficient of determination (r^2) of 0.1624, where the numbers in parentheses represent the 95% CI. However, since the OPAG 22 response at the highest additions (9,733 ppb) appeared to be saturated, based on operator observations, the regression analysis was repeated excluding these data. The resulting r^2 value increased to 0.9144. The slope for this analysis was 0.583 (± 0.178), and the intercept was 24.9 (± 111). Both linear regression plots are shown in Figure 6-3, with the full data range shown in the inset.

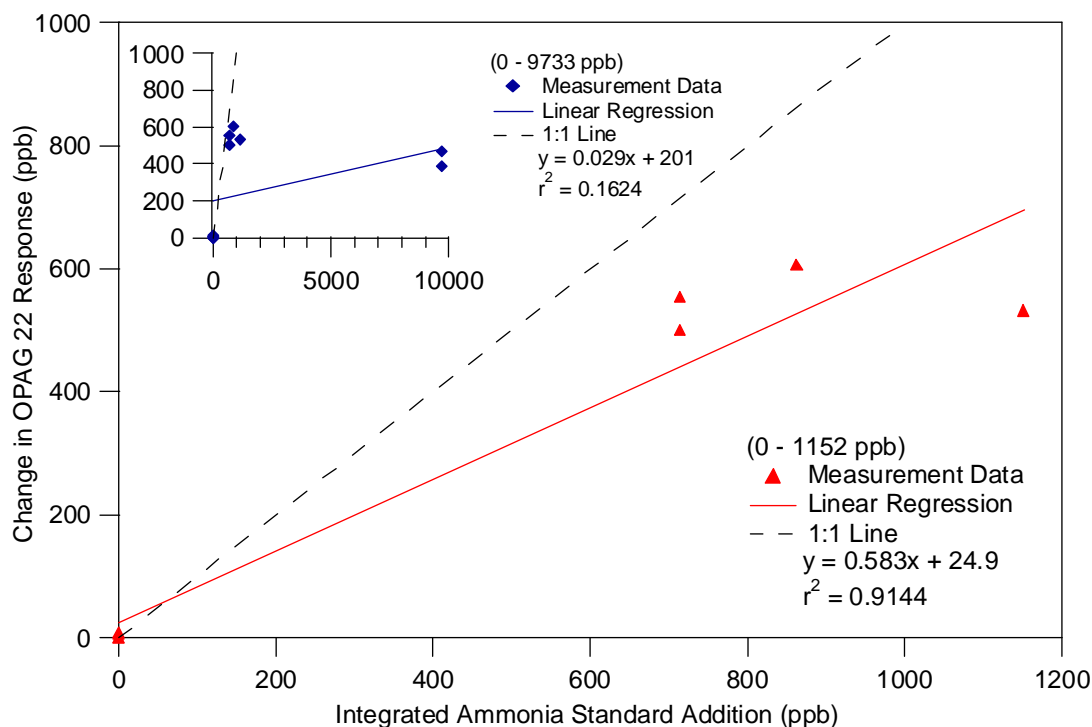


Figure 6-3. Results of Linearity Check of the OPAG 22 During Phase II

6.3 Precision

Table 6-3 presents the calculated precision of the OPAG 22 measured during the accuracy and linearity checks. The precision of the OPAG 22 readings was 1.8% at the NH₃ levels measured in the accuracy/linearity checks. Hand-recorded OPAG 22 responses ([NH₃]_e = 733 and 1,170 ppb from Table 6-1, n=1) were not included in this analysis.

Table 6-3. Calculated Precision of the OPAG 22

Compressed Gas Standard Concentration [NH ₃] _s (ppm)	Gas Cell Pathlength <i>d</i> (m)	Expected Integrated Concentration [NH ₃] _e (ppb)	Average OPAG 22 Measured Integrated Concentration (ppb)	Number of Data Points	RSD (%)
297	0.303	740	580	24	1.8
479	0.227	875	618	20	1.8
5,000	0.303	9,761	417	18	(1.7) ^(a)
5,000	0.303	9,743	478	22	(3.1) ^(a)
Average RSD					1.8

^(a) Checks conducted with the 5,000-ppm NH₃ gas cylinder standard appeared to saturate the NH₃ absorption peaks and were not included in this calculation.

6.4 Response Time

Response time was determined during Phase II from the amount of time required for the OPAG 22 to increase to 95% of the change in the stable concentrations during the accuracy/ linearity checks. This time represents the time for the OPAG 22 signal to change when the gas cell was moved in and out of the infrared beam. Table 6-4 presents a summary of the response time determinations for the OPAG 22. Measured rise times were between 4 and 14 seconds, and the fall times ranged from 5 to 9 seconds.

Table 6-4. Response Time Determinations

Change (ppb)	Measured Change (ppb)	Rise Time (seconds)	Fall Time (seconds)
ambient - 740	26 - 580	10	5
ambient - 875	12 - 618	5	9
ambient - 9,761	9 - 417 ^(a)	14	8
ambient - 9,743	27 - 478 ^(a)	4	8

^(a) Checks conducted with the 5,000-ppm NH₃ gas cylinder standard appeared to saturate the NH₃ absorption peaks, but the response times can still be reported.

6.5 Calibration and Zero Drift

The calibration drift checks were conducted by supplying NH₃ gas to the OPAG 22 for approximately 10 minutes each on Monday, Wednesday, and Friday during Weeks 1 and 4 of Phase II. Due to the nature of the open-path system, drift in the response to zero air could not be tested. The results of the Phase II calibration checks are summarized in Table 6-5, providing the mean response, RSD, and minimum and maximum values for each check. The values reported in this table are based on the average readings during each calibration and zero check when the readings of the OPAG 22 had stabilized (i.e., the signal was neither visibly increasing nor decreasing). The response to the NH₃ gas standards was normalized to 1,000 ppb, as described in Section 5.5, and included in the table for ease of comparison. The normalized response to the higher concentration (integrated) standards (i.e., greater than 1,000 ppb) also indicates that the OPAG 22 was not linear in that range and that even the 1,170-ppb integrated NH₃ gas standard may have saturated the OPAG 22 signal. The data collected for gas standard concentrations that did not appear to saturate the OPAG 22 signal (733, 740, and 875 ppb) are not sufficient to assess whether calibration drift occurred.

Table 6-5. Calibration Checks During Phase II

Check Number	Expected Integrated Concentration [NH ₃] _e (ppb)	Average OPAG 22 Measured Integrated Concentration (ppb)	Normalized OPAG 22 Measured Concentration (ppb) ^(a)	RSD (%)	Minimum (ppb)	Maximum (ppb)	n
Week 1 ^(b) Monday	740 875	580 618	783 706	1.8 1.8	564 601	599 639	24 20
Week 1 ^(b) Wednesday	733 1,170	518 550	707 470	(c)	(c)	(c)	1 ^(c) 1 ^(c)
Week 1 Friday	9,761 ^(d)	417	43	1.7	400	430	18
Week 4 Monday	9,743 ^(d)	478	49	3.1	454	504	22
Week 4 Wednesday	(e)						
Week 4 Friday	(f)						

^(a) Equivalent OPAG 22 response to a 1,000-ppb standard.

^(b) Checks were repeated using two different compressed NH₃ standards. The results from both checks are included here.

^(c) Data from these checks were lost due to a “DDE” error. Values reported here are based on approximate values recorded in the laboratory research notebook while the test was being conducted. Thus, the RSD and minimum and maximum values could not be reported.

^(d) Checks conducted with the 5,000-ppm NH₃ gas cylinder standard appeared to saturate the NH₃ absorption peaks. The lower-concentration NH₃ cylinders were consumed during the first two calibration checks.

^(e) The 5,000-ppm NH₃ compressed gas standard was not available for use during this check.

^(f) The OPAG 22 was operating in passive mode, and therefore a calibration check could not be conducted.

6.6 Interference Effects

The effect of potential interferent gases on the response of the OPAG 22 could not be assessed. The OPAG 22 could only be operated in the passive mode on the day that had been scheduled for the interference check; the active source was blown over by strong winds and could not be realigned by verification test staff.

6.7 Comparability

Figure 6-4 shows the NH₃ concentrations measured using the reference method along with the corresponding average readings of the OPAG 22 for the reference sampling periods during Phase II. The reference method value used for the comparison was the average NH₃ concentration measured at the three sampling locations using the reference method. Due to software errors discussed in Section 6.8, OPAG 22 data from only four of 35 reference sampling periods were

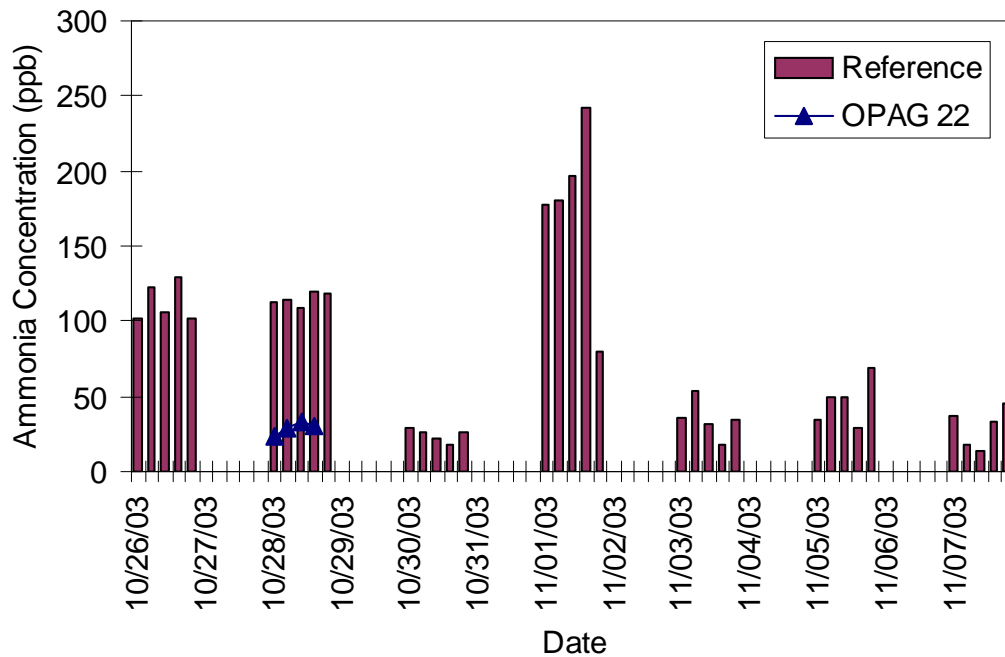


Figure 6-4. Comparison of Ambient Reference Measurements with Averages from the OPAG 22 During Phase II

recorded even though the OPAG 22 was operational. Although the verification test operators restarted the OPAG 22 on each sampling day and data collection was initiated, errors occurred during the first measurement period or files were overwritten by the software. During the periods when OPAG 22 data were collected, the measured NH_3 concentrations varied by less than a factor of five. Because of the limited concentration range, comparability is reported as the average absolute %D rather than in terms of the linear regression results. The %D values of the average reference method values and OPAG 22 measurement data are reported in Table 6-6. The %D values ranged from -79.7% to -69.9%. The average absolute %D was 74.8%.

Table 6-6. Comparability of Ambient Reference Measurements with Averages from the OPAG 22 During Phase II

Start Time	Reference Method Measurement (ppb)	Average Integrated OPAG 22 Measurement (ppb)	%D (%)
10/28/03 8:00	112.6	22.8	-79.7
10/28/03 12:00	113.7	28.4	-75.2
10/28/03 14:00	108.1	32.6	-69.9
10/28/03 16:00	117.7	30.5	-74.6
Average Absolute %D			74.8%

6.8 Ease of Use

Throughout the verification test, the IRIS NT software that controlled the OPAG 22 repeatedly experienced “DDE” errors after periods of between one and 12 hours of continuous operation, requiring frequent attention by the operators. Battelle and USDA operators restarted the software as soon as it was observed that an error occurred. This problem was brought to the attention of the vendor, but no apparent cause or solution to the problem was provided by the vendor. After completion of this verification test, the vendor indicated that a failing interferometer reference laser may have caused the intermittent operation. As a result of these errors, large portions of the potential data set were measured by the OPAG 22, but not stored by the computer. Additional data were lost because, as it was discovered during the verification test, the data files that were collected before the “DDE” errors occurred were overwritten when the IRIS NT software was restarted. Once this problem was discovered by the verification test staff, every effort was made to rename the appropriate file before restarting the software. The data files obtained in active mode contained concentration data (in ppb) for NH₃ as well as water, carbon dioxide, carbon monoxide, nitric oxide, nitrous oxide, nitrogen dioxide, nitric acid, methane, ethanol, and sulfur hexafluoride. Only measurements of NH₃ were verified in this test. The data files also reported several input parameters. The data files were output as tab-delimited text and were ~500 kilobytes in size for approximately 3 hours of continuous data reported every ~5 seconds. In passive mode, data were reported in units of ppm × meter × temperature (Kelvin), and the data files were approximately twice as large.

The OPAG 22 was installed by a vendor representative, who completed the installation in several days. The OPAG 22 was not functioning as expected by the vendor representative, who spent a significant amount of time troubleshooting the instrument and eventually was able to obtain what appeared to be reasonable data. The vendor representative trained Battelle and USDA staff to use the OPAG 22. Instructions, shown in Appendix A, were provided by the vendor representative to operate the OPAG 22 in passive mode. A few changes were necessary for operation in active mode. The only daily maintenance of the OPAG 22 included verifying

that the instrument was running and the computer was collecting data. If the active source and detector lost their alignment, verification test staff realigned the equipment. This task was best performed by two people: one to stand near the detector/computer and the other to adjust the active source, which was 126 or 156 m away from the detector. Because the OPAG 22 is an open-path technology, two additional reference samples were obtained during each sampling period along the OPAG 22 pathlength for use in the ambient reference method comparability checks. The OPAG 22 did not produce any waste during the test. Table 6-7 presents a summary of activities involving the OPAG 22 during Phase II.

Table 6-7. Activities Performed During Phase II

Date	Time Offline ^(a) (minutes)	Down Time ^(b) (minutes)	Service Time ^(c) (minutes)	Activity
10/20/03	65			Delivered NH ₃ standards ^(d)
10/22/03	35			Delivered NH ₃ standards ^(d)
10/24/03			30	Moved OPAG 22 detector to include reference method sampling location near the instrument trailer, realigned source and detector
10/24/03	40			Delivered NH ₃ standards ^(d)
11/4/03			10	No available file space on Drive C: emptied recycle bin and restart computer
11/10/03	20			Delivered NH ₃ standards ^(d)
11/12/03			20	Active source blew over in wind, could not realign so secured source and started passive mode sampling; missed interference check
10/20 - 11/14/03		31,850 ^(e)		OPAG 22 not collecting data due to “DDE” error (software) ^(e)
10/20 - 11/14/03			260	Reset OPAG 22 software due to “DDE” error
Totals	160	31,850	320	13% data collected, ^(e) and 320 min service time.

^(a) Time Offline = time that the OPAG 22 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 OPAG 22 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 verification test staff.

^(e) Although the OPAG 22 was operating during 100% of Phase II of the verification test, the software that ran the OPAG 22 (IRIS NT) experienced a “DDE” error after running continuously for between one and 12 hours. The software was restarted as soon as an error was discovered by the verification test staff, but it was determined during the test that the data files were overwritten when the IRIS NT software was reopened. Thus, data were lost between the periods when the “DDE” errors occurred and the subsequent periods when the software was restarted, but additional data were collected and subsequently lost when files were overwritten.

6.9 Data Completeness

During Phase II, 13% of the possible OPAG 22 data were collected, although the OPAG 22 was operating and conducting measurements during 100% of Phase II. The data loss of 87% was caused by software-related failures, as described in Section 6.8. The OPAG 22 operated in active mode during most of Phase II, but in passive mode during the last 9% of the verification test.

Chapter 7

Performance Summary

The performance of the OPAG 22 was evaluated only in Phase II of this verification test. Table 7-1 presents a summary of the performance of the OPAG 22 during Phase II of this verification test.

Table 7-1. Performance Summary of the OPAG 22

Parameter	Phase I	Phase II		
Relative accuracy	The OPAG 22 active source was not available in Phase I	Average RA = 26% (range = 740 - 875 ppb) %D range = -29 to -22 %		
Linearity		Range ^(a)	0 to 9,733 ppb	0 to 1,152 ppb
		Slope	0.029 (± 0.047)	0.583 (± 0.178)
		Intercept	201 (± 188)	24.9 (± 111)
		r ²	0.1624	0.9144
Precision		Average RSD = 1.8% (range = 740 to 875 ppb) Range = 1.8%		
Response time		Rise time = 4 to 14 seconds Fall time = 5 to 9 seconds		
Calibration/ zero drift		<ul style="list-style-type: none"> • Zero drift could not be tested^(b) • Available data were insufficient to evaluate calibration drift^(c) 		
Interference effects		Interference checks could not be conducted on the OPAG 22 ^(d)		
Comparability		%D range = -79.7% to -69.9% Average Absolute %D = 74.8% Number of Observations = 4		
Ease of use	<ul style="list-style-type: none"> • Software errors caused significant loss of data^(e) • Two operators needed for alignment and gas standard delivery • Gas standard delivery procedure required high concentration standards for delivery to the relatively short pathlength gas cell • No maintenance was necessary • Malfunction of OPAG 22 interferometer reference laser suspected during test.^(f) 			
Data completeness	13% data collected ^(e)			

^(a) The OPAG 22 signal appeared to be saturated for the higher integrated NH₃ concentrations tested; the linearity was calculated for the full range and also excluding the concentrations greater than 1,152 ppb.

^(b) Using the method of standard additions employed to deliver gas standards to the OPAG 22, a small pathlength of zero air could not be detected over the NH₃ in the ambient air present in the ~150 meter detection pathlength.

^(c) The large volume of NH₃ gas standard needed to fill the OPAG 22 gas cell depleted the available 297 ppm and 479 ppm NH₃ gas standards during the first week of Phase II. Delivery of the 5,000-ppm gas standard appeared to saturate the OPAG 22 signal; the low response to this standard is not likely indicative of calibration drift.

^(d) The active source for the OPAG 22 blew over during strong winds the evening before the interference check was scheduled for the OPAG 22. Verification test staff were not able to realign the active source.

^(e) The OPAG 22 software experienced “DDE” errors frequently throughout this verification test. Significant quantities of data were not collected as a result, even though the OPAG 22 was operating throughout the entire test. The “DDE” errors were probably caused by a failing interferometer reference laser in the OPAG 22.

^(f) Verification test staff observations and information provided by the vendor are consistent with a failing interferometer reference laser.

Chapter 8 References

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Appendix A
OPAG 22 Standard Operation

OPAG 22 STANDARD OPERATION

HARDWARE SETUP

1. Connect the power supplies for PC and OPAG to. Connect RS232 cable from OPAG 22 to PC.



- A: On/off rocker switch
B: Connection to the Notebook / PC Connection to the Acquisition Processor in the PC
C: Power supply connection, 10 - 36 V DC Power receptacle for power cable

2. Turn on OPAG 22 by pressing button A.

PC / WINDOWS NT INITIALIZATION

1. Turn on PC.
2. Follow login instruction for Windows NT. There is no password for login. Select OK with Administrator as the user name.
3. Select CANCEL when prompted with Restoring Network Connections window.

OPAG 22 INITIALIZATION

OPUS / IRIS NT SOFTWARE INITIALIZATION

1. Ensure the OPAG 22 is on.
2. Select the Windows NT START icon. Select OPUS icon
3. Enter OPUS in capitals as the password when prompted with the OPUS login window.
4. OPUS control software will initialize. Minimize the OPUS control software window.
5. Select IRIS NT icon from the desktop. IRIS NT software will initialize. OPAG 22 calibration, parameter settings and measurements are controlled through IRIS NT.

PASSIVE SAMPLE MEASUREMENTS WITH OPAG 22

OPAG 22 SAMPLE MODE PARAMETERS AND DATA FILE PATH.

1. Select SETTINGS from the IRIS NT menu. Select OPERATION MODE. Select GAS ANALYSIS (Passive). Select OK.
2. Select MEASUREMENT from the IRIS NT menu. Select SINGLE MEASUREMENT. A SINGLE MEASUREMENT WILL BE MADE. This measurement is required to access further parameter settings.
3. Select FILE. Select SAVE PROTOCOL. Set save file path to: C: \OPAGLOG\.. Choose appropriate filename ie. MMDDYYYY.

BLACKBODY CALIBRATION

1. Select SETTINGS from the IRIS NT menu. Select CALIBRATION. Select START from the calibration window. When the blackbody calibration is complete, select the FILE FOLDER icon, name and save the calibration file. The calibration file will automatically be used for following measurements.

CONTINUOUS MODE SAMPLING

1. Select MEASUREMENT from the IRIS NT menu. Select START ONLINE. The OPAG 22 will display and record chemical detection and ppmK concentration. Select OPAGLOG from desktop to review collected data.