July 2004

Environmental Technology Verification Report

OMNISENS
TGA310 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

July 2004

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Omnisens
TGA310 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.

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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	liters per minute
µg	microgram
µm	micrometer
mg	milligram
mL	milliliter
mm	millimeter
NIST	National Institute of Standards and Technology
NH_3	ammonia
NH_4^+	ammonium
PC	personal computer
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 Omnisens TGA300 Series Model TGA310 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 TGA310. The following is a description of the TGA310, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The TGA310 (Figure 2-1) is a trace gas analyzer that uses photoacoustic spectroscopy to measure ammonia concentrations in the atmosphere. In photoacoustic spectroscopy, absorbed infrared (IR) energy generates a temperature increase and an associated pressure increase, resulting in an acoustic wave that can be detected with a microphone. Sound intensity is directly proportional to the gas concentration. The amount of absorbed energy is determined by measuring the photoacoustic signal. In the TGA310, the light from a modulated carbon dioxide laser, with a wavelength coinciding with the wavelength of ammonia, travels through a photoacoustic sensing cell, through which ambient ammonia is continuously sampled.

The TGA310 has a 0.1-part-per-billion detection limit and allows real-time continuous detection. Monitoring is possible at air flow rates up to 5 liters per minute (Lpm). The TGA310 features a graphical user interface. A built-in personal computer (PC) incorporates a touch-screen display, and the measured ammonia concentration is highlighted on a real-time basis. The evolution of ammonia concentration is displayed on a chart and can be checked at any time for long-term trends analysis. The user gets an immediate view of the trend by checking the displayed concentration curves.

Figure 2-1. TGA310 Ammonia Analyzer

Measurement data are automatically stored in a designated file, allowing unattended measurements. Historical data can be retrieved remotely from the disk for data analysis. Calibration data are stored on the built-in disk drive, and default values can be retrieved at any time. Events such as run up and run down times, alarms, system messages, and setup modifications are stored in a log file.

The TGA310 requires 600 Watts of power from 110/230 volts alternating current. Its dimensions are 600 millimeters (mm) by 600 mm by 210 mm, excluding the PC, and it weighs less than 70 kilograms. The TGA310 costs $42,000.

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 TGA310'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 TGA310 was not available during Phase I of the verification test. However, during Phase II of the verification test, the TGA310 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 TGA310 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 TGA310 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 TGA310 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 TGA310 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

During Phase II, the TGA310 was installed by a vendor representative. Battelle and USDA staff worked with the vendor representative to establish procedures for operating the TGA310 during this verification test. The vendor representative trained Battelle and USDA staff to check several instrument parameters to verify the operation of the TGA310 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 during daily monitor checks. 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 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 the monitoring equipment and to provide a sheltered workspace. The TGA310 was installed in this instrument trailer with a Teflon sample line used to supply outside air to the inlet of the TGA310. Outside the trailer, the inlet of the sample line was positioned approximately 1.5 meters from ground level. The instrument trailer 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.

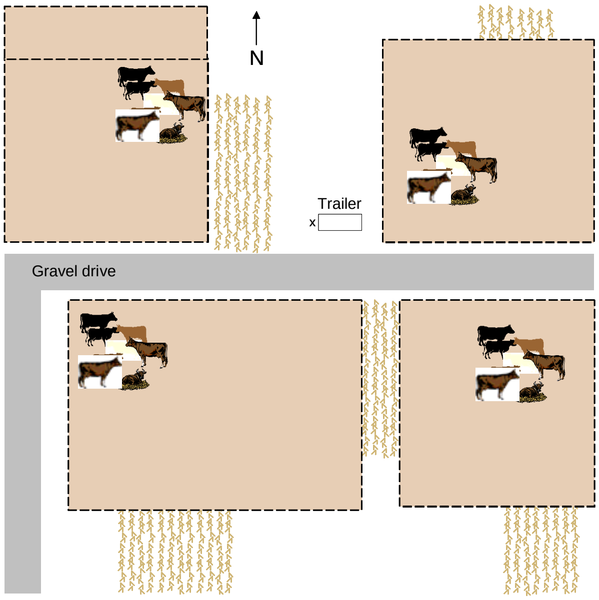

Figure 3-1. Phase II Test Site

3.3 Test Procedures

3.3.1 Accuracy, Linearity, Precision, and Response Time

During the first week of Phase II, the TGA310 was independently supplied with compressed NH_3 gas standards to achieve NH_3 concentrations over a range from 0 to 2,000 parts per billion (ppb) to simulate the approximate range expected in ambient air during Phase II. The gases delivered to the TGA310 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 TGA310 for approximately 30 minutes at each concentration level. Accuracy, linearity, and precision were established based on the continuous digital data set recorded by the TGA310 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 TGA310. These data were used to assess the response time of the TGA310.

3.3.2 Calibration and Zero Drift

On Tuesday, Wednesday, and Friday of the first week of testing, and Monday, Wednesday, and Friday of the last week of testing during Phase II, the TGA310 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 TGA310, respectively. Zero air and the 1,000-ppb NH_3 standard were each supplied to the TGA310 for approximately one hour, during which time the measured concentrations were recorded by the TGA310.

3.3.3 Interference Effects

Once during Phase II, the TGA310 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 TGA310 response. The interferent gases were supplied from diffusion tubes (VICI Metronics, Poulsbo, Washington) at concentrations of approximately 150 to 460 ppb in zero air and a 500-ppb NH_3 standard as carrier gases.

The process for supplying the interferent gases was as follows: zero air was supplied to the TGA310 until a stable reading was achieved. The interferent gas was added to the zero air flow and supplied to the TGA310 until a stable reading was observed (at least two minutes). The TGA310 was flushed for at least two 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 TGA310 until a stable reading was achieved. The interferent gas was added to the NH_3 standard for delivery to the TGA310, 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 TGA310 with a standard reference method was established by comparing the average TGA310 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 3-2 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.

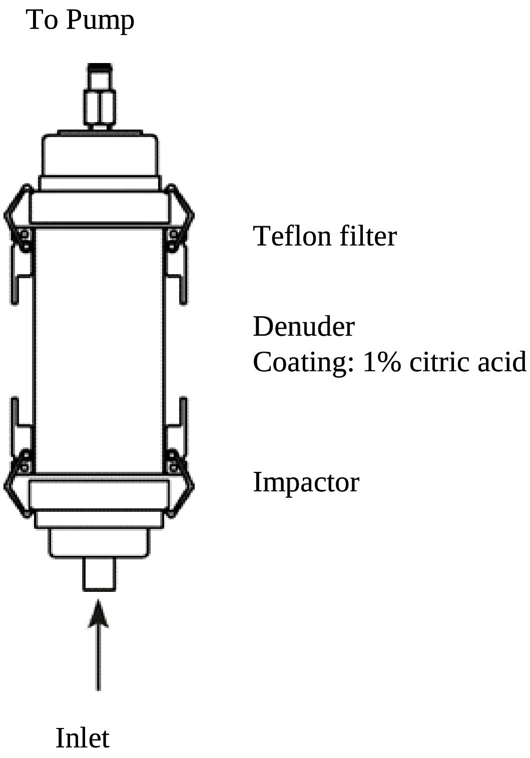

Figure 3-2. Reference Method Sampling Cartridge

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 (two-hour and four-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. 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. Two additional sampling locations were positioned approximately 44 and 74 meters from the instrument trailer for use in the verification testing of open-path monitors, 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 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 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, 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 thresholds 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 ± 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, (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. The reference method DL was more than six times higher than the equivalent FIA DL (0.6 microgram [µg] NH_3 per 20-mL sample).

The reference method DL, reported as an NH_3 mass, was used to determine the minimum detectable NH_3 concentrations for Phase II. 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 two-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 Phase II.

A total of 14 field blanks were collected in Phase II. The average NH_3 mass collected on these blanks was 2.5 µg NH_3, and the range was 0.5 to 4.6 µg NH_3. The mass collected on the field blanks ranged from 1.2% to 55.0% of the smallest reference sample mass collected on the same day, with an average of 19.2%. These percentages are not indicative of unusually high levels of contamination, but rather are a result of relatively low ambient NH_3 levels at the AFO. The impact of these blank levels on the results of this verification test may be manifested as a small positive bias of the reference method results relative to the readings of the technologies being verified. This bias would be most pronounced on days with low ambient NH_3 concentrations. The highest field blank percentages were measured on days when the integrated ambient NH_3 levels were as low as 6 ppb, which is approaching the 4.9-ppb minimum detectable ambient NH_3 concentration for a two-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 4-1. During Phase II, one measured NH_3 concentration in ambient air fell below the minimum detectable NH_3 concentration, as summarized in Table 4-1.

Table 4-1. 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

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. These backup denuders were used to check the degree of NH_3 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 NH_3

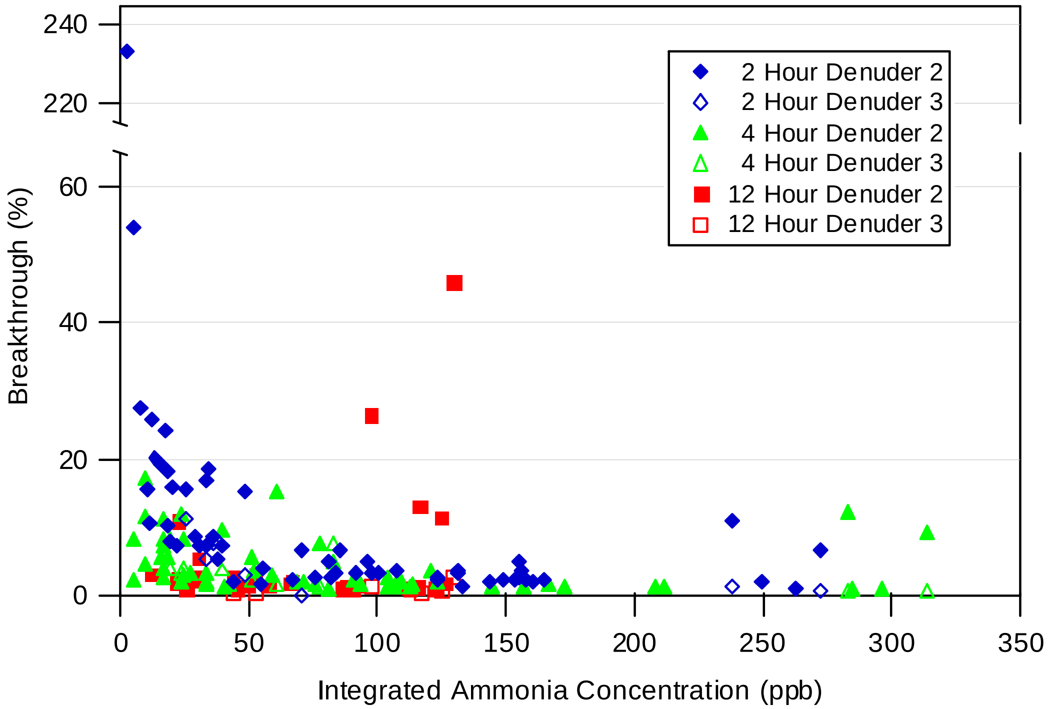

Figure 4-1. Denuder Breakthrough During Phase II as a Function of Integrated Ammonia Concentration

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.

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 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). 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. 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%. The absolute RPD for 7 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.

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

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	

blind samples. (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. 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.

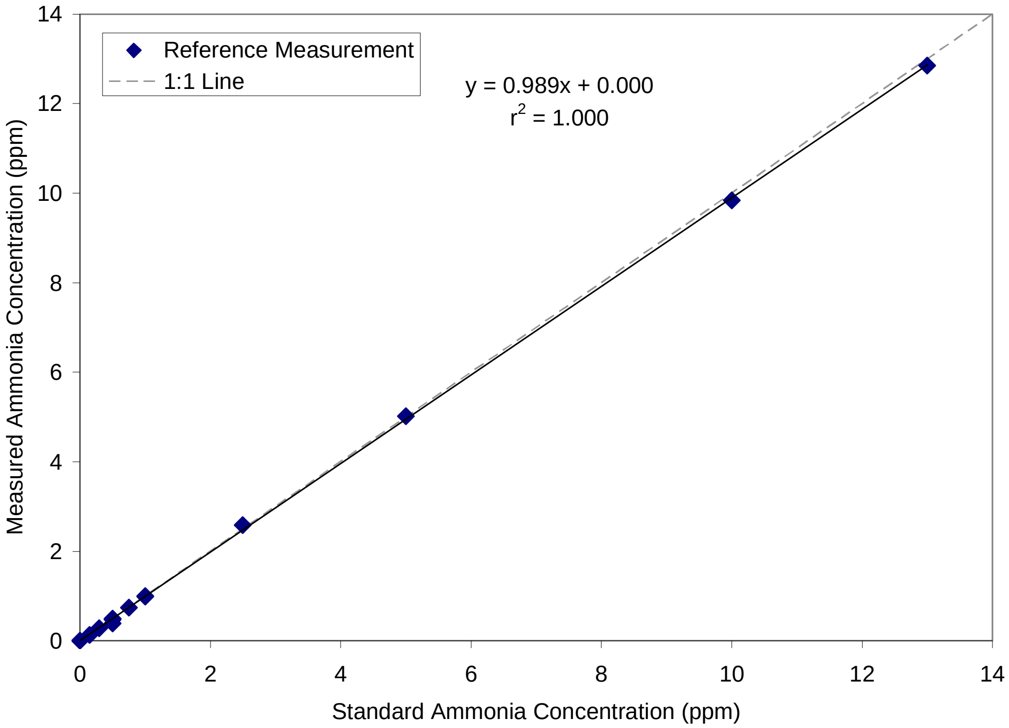

Figure 4-2. Analysis of Diluted Ammonia Standards Using the Denuder Reference Method

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 4-2. 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.

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 ± 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 RA 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, 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, 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, PC, 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 TGA310 response to each NH_3 gas standard was calculated according to Equation 1:

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

where $\bar{x}$ is the average TGA310 response to an NH_3 gas standard of nominal concentration x_n. During Phase II, the RA with respect to all of the gas standards (n) delivered to the TGA310 was calculated using Equation 2:

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

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 TGA310 as the dependent variable. 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 TGA310 measurements of several NH_3 gas standards. The mean and standard deviations of those readings were calculated. The RSD was then determined as:

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

where *SD* is the standard deviation of the TGA310 readings and $\bar{x}$ is the mean of the TGA310 readings.

5.4 Response Time

Response time was assessed in terms of both the rise and fall times of the TGA310 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 TGA310 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 TGA310 during 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 are reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the TGA310 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 during Phase II of testing so that up to six NH_3 standard and zero air readings (on Tuesday, Wednesday, and Friday of Week1 and Monday, Wednesday, and Friday of Week 4) were used for this calculation. This calculation, along with the range of the data, indicates 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 TGA310 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 TGA310, 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 TGA310 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 TGA310 as the dependent variable. Comparability was expressed in terms of slope, intercept, and r^2 and was calculated for Phase II of the verification test.

Chapter 6
Test Results

The results of the verification test of the TGA310 are presented in this section. During testing, the TGA310 was set to collect 3-second average readings. For data logging purposes, a parameter (deltaConc) can be set to optimize the number of points recorded in the database (optimize the database size). This parameter is a percentage of the difference between two recorded points and was set to 1% for this verification test. Therefore, if the difference was greater than "deltaConc," the value was recorded in the database; whereas, if the difference was lower than "deltaConc," the value was not recorded. The values presented here are based on the data recorded with these settings. The TGA310 was not available for testing during Phase I of the verification test. Therefore, the results presented are from Phase II only.

Meteorological conditions collected using the meteorological monitoring 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 NH_3 data set collected by the TGA310 (bottom panel). The shaded region shows the period during which NH_3 reference measurements were conducted. The TGA310 was installed and began recording data on the second day of Phase II, as shown in the figure. The two gaps in the TGA310 ambient data set were caused by computer-related failures and are discussed in Section 6.8. The TGA310 NH_3 measurements ranged from 3 to 1,648 ppb during Phase II and averaged 166 ppb.

6.1 Relative Accuracy

During the first week of Phase II, the TGA310 was supplied with compressed NH_3 gas standards at a variety of concentrations to assess RA. The compressed NH_3 gas standards were diluted in zero air and delivered to the inlet of the TGA310 at a flow rate of 1 Lpm. It should be noted that frequency and phase instability warnings and alarms sounded on the TGA310 during the delivery of gas standards from the NH_3 dilution system. The instabilities were probably caused by small fluctuations in the NH_3 dilution system output flow rate; alarms did not sound when zero air was delivered directly from the compressed gas cylinder, bypassing the dilution system. The alarms sounded during 16% of the gas standard delivery periods.

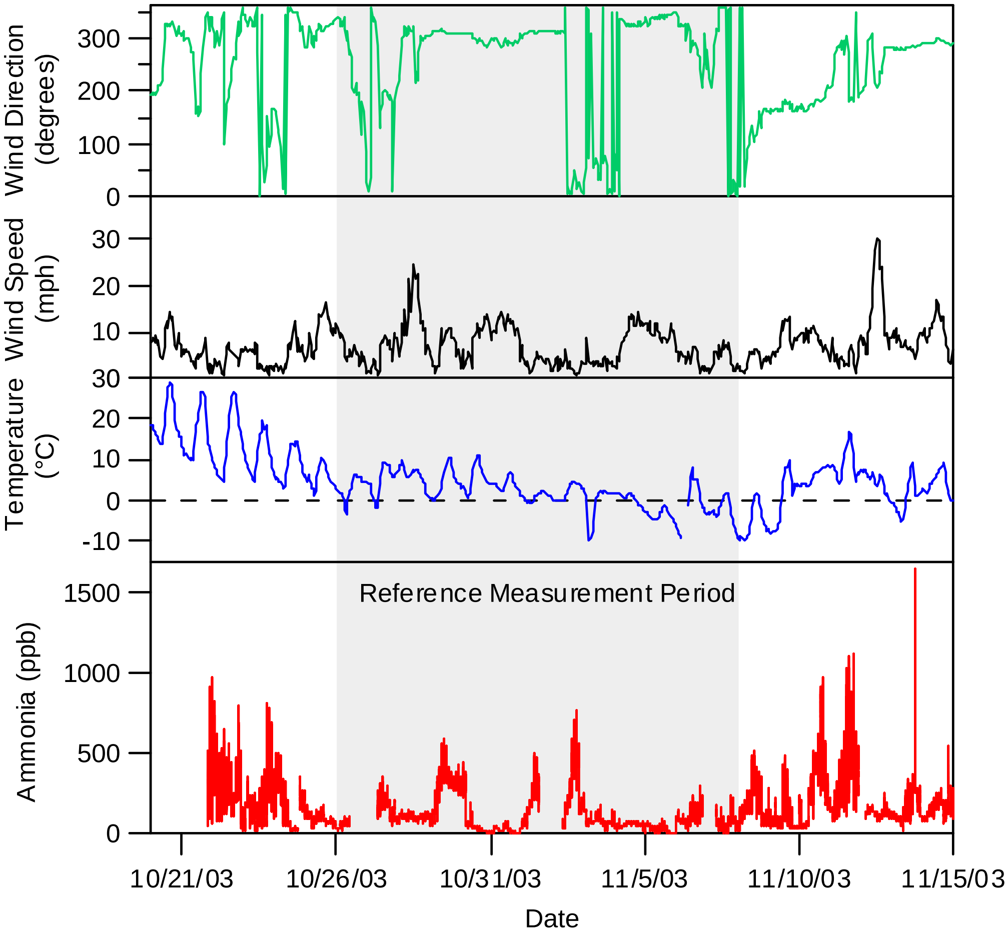

Figure 6-1. Phase II Meteorological Conditions and TGA310 Ambient NH_3 Measurements

Figure 6-2 presents the NH_3 concentrations recorded by the TGA310 during the RA checks, along with the nominal NH_3 concentration levels supplied to the TGA310. The TGA310 response to the 1,000-ppb NH_3 standard was unstable for approximately the first 15 minutes of the standard delivery; activities in the instrument trailer may have disrupted the TGA310 stability. As with the other gas standard concentrations, the RA calculation does not include data obtained when the TGA310 signal appeared to be unstable. The gap in the data between the 600-ppb and 2,000-ppb standards resulted from the loss of NH_3 during the delivery of these two standards. The supply of NH_3 ran out shortly after delivery of the 600-ppb standard; the NH_3 flow was reestablished and used for delivery of the 2,000-ppb standard. The averages of the

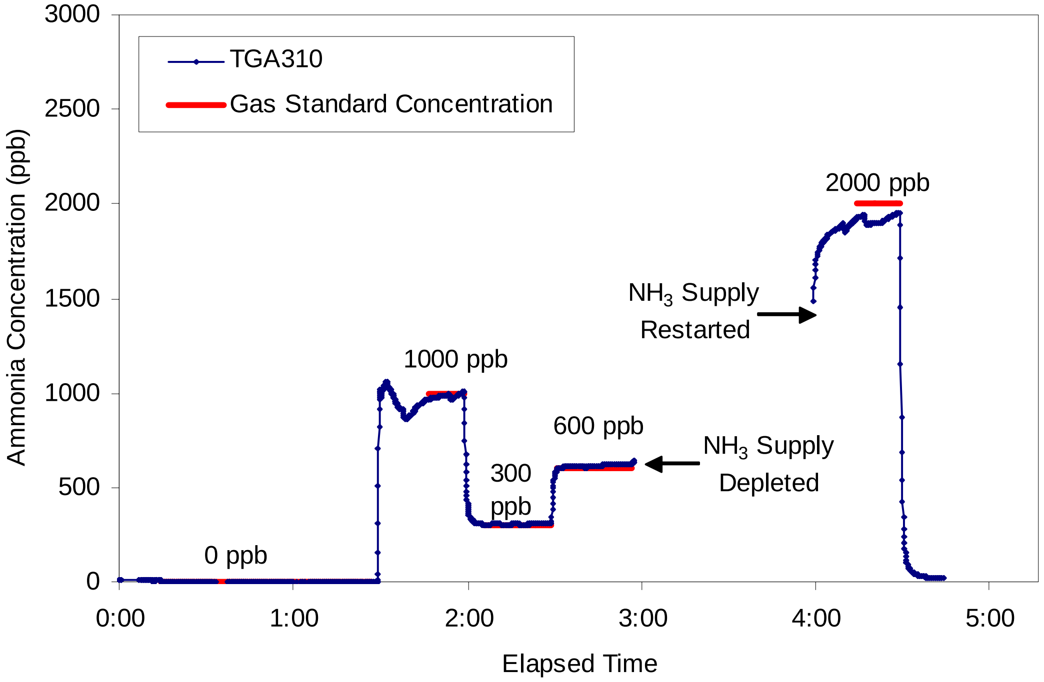

Figure 6-2. Phase II Accuracy Results for the TGA310

measurements at each nominal NH_3 concentration are presented in Table 6-1 along with the calculated %D and the number of data points used in the calculations. The %Ds of the TGA310 ranged from -2.9% to 2.5% over the four concentration levels measured, and the RA (i.e., the average of the absolute values of the %Ds) was 2.2%.

Table 6-1. Relative Accuracy Results

NH_3 Gas Standard Concentration (ppb)	Average Measured Concentration (ppb)	Number of Data Points	Percent Difference (%)
0	0.7	227	NA
300	306	248	2.0
600	615	275	2.5
1,000	986	117	-1.4
2,000	1941	25	-2.9
Average RA			2.2%

NA = not applicable.

6.2 Linearity

Figure 6-3 shows the results of the linearity check for Phase II. A linear regression of the TGA310 response versus the gas standard concentration, over the range from 0 to 2,000 ppb, showed a slope of 0.966 (± 0.031), an intercept of 15.9 (± 31.9) ppb, and a coefficient of determination (r^2) of 1.000, where the numbers in parentheses represent the 95% CI.

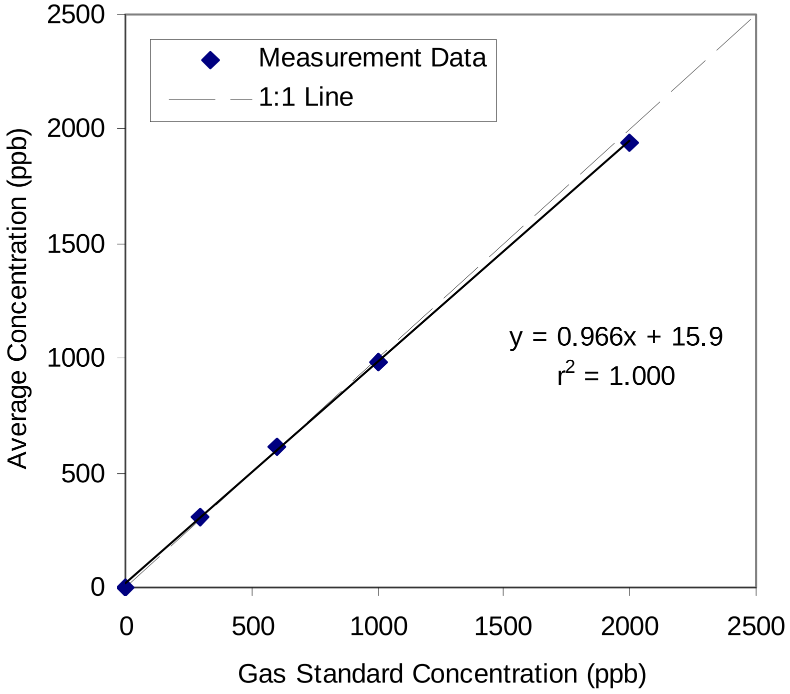

Figure 6-3. Results of Linearity Check of the TGA310 During Phase II

6.3 Precision

Table 6-2 presents the calculated precision of the TGA310 measured during the accuracy and linearity checks. The precision of the TGA310 readings varied from 0.4 to 1.2% RSD at the four NH_3 levels measured in the accuracy/linearity checks, with an average precision of 0.9%.

Table 6-2. Calculated Precision of the TGA310

NH_3 Gas Standard Concentration (ppb)	Average Measured Concentration (ppb)	Number of Data Points	RSD (%)
300	306	248	1.0
600	615	275	1.2
1,000	986	117	1.0
2,000	1,941	25	0.4
Average RSD			0.9

6.4 Response Time

Response time was determined during Phase II from the amount of time required for the TGA310 to rise to 95% of each of the expected concentrations or to fall by 95% of the stable readings during the accuracy/linearity checks. Table 6-3 presents a summary of the response time determinations for the TGA310. Measured rise times were 126 and 156 seconds (approximately two to two and a half minutes); the fall times were 124 and 169 seconds (approximately two to three minutes). The response times were measured with a sample flow rate of 1 Lpm. Response times are likely to be shorter for higher flow rates up to 5 Lpm, although this was not verified in this test.

Table 6-3. Response Time Determinations

Change (ppb)	Rise Time (seconds)	Fall Time (seconds)
0 - 1,000	126	–
1,000 - 300	–	124
300 - 600	156	–
2,000 - 0	–	169

6.5 Calibration and Zero Drift

The calibration/drift checks were conducted by supplying NH_3 gas and zero air to the TGA310 on Tuesday, Wednesday, and Friday during Week 1 and on Monday, Wednesday, and Friday during Week 4 of Phase II. The results of the Phase II calibration and drift checks are summarized in Table 6-4, including the number of measurements used for each calculation. The values reported in this table are based on the average readings during each calibration and zero check when the readings of the TGA310 had stabilized (i.e., the signal was neither visibly increasing nor decreasing); thus, the calculations for each check span somewhat different time periods that range from nine to 16 minutes. These results indicate no apparent drift in the response of the TGA310 to zero air, although the zero reading was slightly higher during Week 4. The TGA310 response to the 1,000-ppb NH_3 standard was higher at the end of the week than at the beginning of the week during both Week 1 (81 ppb higher) and Week 4 (55 ppb higher), although an overall drift over the 4-week phase was not apparent.

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

	Zero Check					Calibration Check[(a)]				
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 Tuesday	0.7	0.3	1.4	0.2	224	986	1.0	1,003	963	117
Week 1 Wednesday	1.7	0.1	2.0	1.4	128	981	1.1	997	964	109
Week 1 Friday	1.2	0.0	1.2	1.1	113	1,067	0.7	1,083	1,057	84
Week 4 Monday	4.9	0.8	6.7	3.7	101	1,004	0.9	1,024	987	86
Week 4 Wednesday	2.2	0.6	3.4	1.2	92	1,054	0.7	1,070	1,041	71
Week 4 Friday	2.9	0.1	3.1	2.7	99	1,059	2.0	1,185	1,043	95

(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.

6.6 Interference Effects

The effect of potential interferent gases on the response of the TGA310 was assessed by supplying the TGA310 with a series of four gases (hydrogen sulfide, nitrogen dioxide, 1,3 butadiene, diethylamine) in zero air and a 500-ppb NH_3 standard. The response of the TGA310 during the introduction of these gases is summarized in Table 6-5. The interference gas concentrations carry an uncertainty of approximately ± 15% (as reported by the manufacturer for uncertified permeation tubes). The response of the TGA310 to both hydrogen sulfide and nitrogen dioxide was negligible; however, the response of the TGA310 to 1,3-butadiene and diethylamine showed an increase between 20% and 28% in both a zero air matrix and an NH_3 matrix. Independent tests have indicated the presence of NH_3 in the diethylamine gas standard that may be present as an impurity or as a result of displacement from tubing walls during the delivery of the diethylamine standard. Thus, the measured interference may be at least partially due to this NH_3 impurity.

Table 6-5. Interference Effect Evaluation

Gas	Interferent Gas Concentration (ppb)	Interference Effect (%) Zero-Air Matrix	Interference Effect (%) 500-ppb NH_3 Matrix
Hydrogen sulfide	461	-0.1[a]	-0.3[a]
Nitrogen dioxide	154	-0.2[a]	0.5[a]
1,3-Butadiene	154	24	22
Diethylamine	155	28	20

[a] Signal not significantly different from baseline without interferent gas.

6.7 Comparability

Figure 6-4 shows the NH_3 concentrations measured using the reference method, along with the corresponding average readings of the TGA310 for the reference sampling periods during Phase II. In general, the TGA310 appeared to track changes in NH_3 concentrations measured with the reference method. These data are also presented in Figure 6-5 as a scatter plot to illustrate the correlation between the reference and TGA310 data. A linear regression of the TGA310 response versus the reference method concentration showed a slope of 1.15 (± 0.04), an intercept of -4.1 (± 3.6) ppb, and an r^2 of 0.994, where the numbers in parentheses represent the 95% CI.

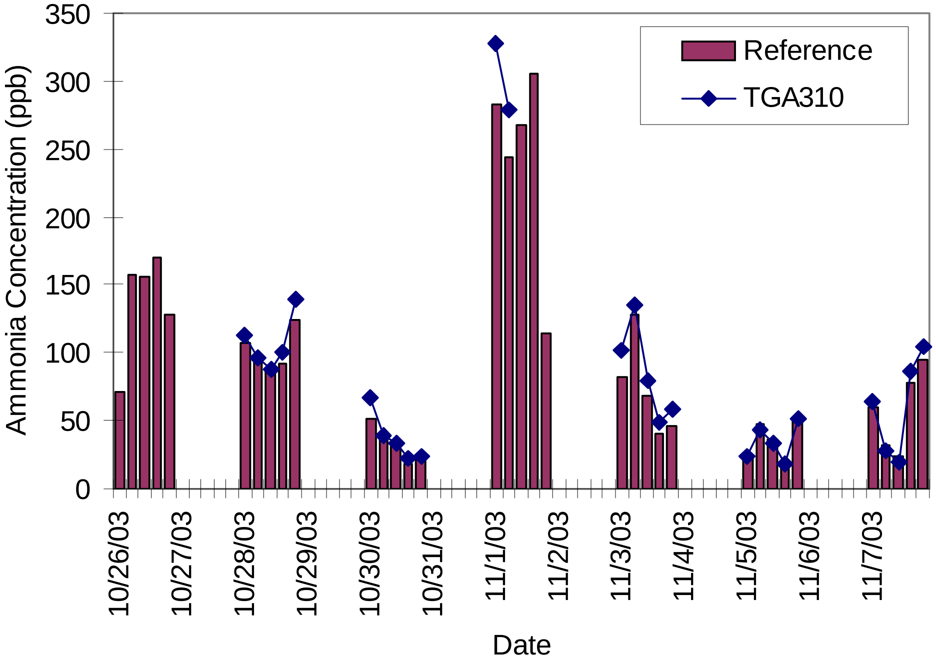

Figure 6-4. Comparison of Ambient Reference Measurements with Averages from the TGA310 During Phase II

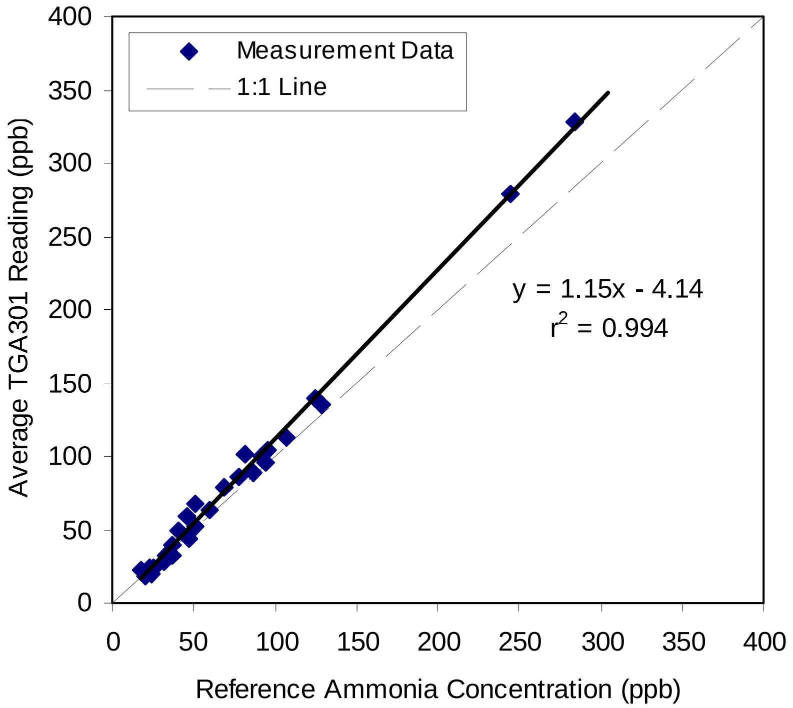

Figure 6-5. Scatter Plot of the TGA301 Results versus Ambient Reference Measurements During Phase II

6.8 Ease of Use

The TGA310 was installed on the second day of Phase II by a vendor representative, who completed the installation in several hours. The installation could be completed by an operator with minimal experience and the TGA310 manual. The vendor was on-site for less than one day, which allowed enough time to complete the installation and train Battelle and USDA staff to use the TGA310 and check its performance. Checklists, shown in Appendix A, were completed daily by Battelle/USDA staff. The checks were quick and straightforward and could be completed by an inexperienced user, although some instruction was necessary to download data and navigate the various menus in the TGA310 software. During Phase II of testing, no maintenance was performed on the TGA310. Table 6-6 presents a summary of activities involving the TGA310 during Phase II. Several TGA310 internal warnings and alarms sounded during this verification test, as discussed previously and summarized in Table 6-6. In general, the alarms were caused by temperature changes in the instrument trailer and small fluctuations in the output flow rate of the NH_3 dilution system (alarms observed during delivery of gas standards to the TGA310). The potential consequence of the conditions that caused the warnings and alarms is added noise in the TGA310 measurements. The TGA310 did not produce any waste during the test.

Table 6-6. Activities Performed and Power Outages During Phase II

Date	Time Offline(a) (minutes)	Down Time(b) (minutes)	Service Time(c) (minutes)	Activity
10/21/03	305			Delivered zero air and NH_3 standard(d)
10/21/03		(20)(e)		—Alarm: Frequency Noisy
10/21/03		(5)(e)		—Warning: Frequency Stabilizing
10/22/03	125			Delivered zero air and NH_3 standard(d)
10/22/03		(10)(e)		—Alarm: Frequency Noisy
		(20)(e)		—Warning: Frequency Stabilizing
		(1)(e)		—Warning: Phase Stabilizing
10/24/03	105			Delivered zero air and NH_3 standard(d)
		(1)(e)		—Alarm: Frequency Noisy
10/26/03		1,295	5	Data loss: computer time changed automatically for daylight savings, with user prompt.
11/2/03		1,080	5	Data loss: computer power shut down overnight. User restart.
11/7/03		660	5	Data loss: TGA310 program stopped running overnight. User restart.
11/10/03	60			Delivered zero air and NH_3 standard(d)
11/10/03		(50)(e)		—Warning: Frequency Stabilizing
11/11/03	310			Performed interference test(d)
		(5)(e)		—Alarm: Frequency Noisy
		(2)(e)		—Warning: Frequency Stabilizing
11/12/03	100			Delivered zero air and NH_3 standard(d)
		(10)(e)		—Alarm: Frequency Noisy
		(40)(e)		—Warning: Frequency Stabilizing
		(5)(e)		—Warning: Phase Stabilizing
11/14/03		(390)(e)		Alarm: System Overheat
11/14/03	110			Delivered zero air and NH_3 standard(d)
		(5)(e)		—Alarm: Frequency Noisy
		(1)(e)		—Warning: Frequency Stabilizing
10/21 - 11/14/03		(14,615)(e)		Warning: Temperature Fluctuation
Totals	1,115	3,035 (15,180)(e)	15	91% (87%)(f) data completeness(g) and 15-minute service time.

(a) Time Offline = time that the TGA310 was taken offline for zero or standard gas measurements. The period over which time offline was evaluated began at 2:00 p.m. on 10/21/03 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 TGA310 was not operating or was operating but not reporting reliable measurements. The period over which down time was evaluated began at 2:00 p.m. on 10/21/03 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 for times greater than 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 2:00 p.m. on 10/21/03 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 continued to be measured and recorded during periods when TGA310 alarms and warnings sounded. These times were not included in the data completeness calculation.

(f) The TGA310 was installed on the second day of Phase II, missing 30 hours of time during which data could have been collected. If this time is considered in the data completeness calculation, the TGA310 experienced 90% data completeness during Phase II.

(g) Data Completeness = the ratio of time that the TGA310 was not experiencing down time to the total time available for monitoring ambient NH_3 mixing ratios from the start of testing on 10/21/03 to the end of testing on 11/14/03. The total time that was available for monitoring during Phase II was 34,741 minutes or 579 hours.

The TGA310 software was quite flexible, which made it easy for the operator to archive data from specific time periods into separate files. The computer for the TGA310 stored the complete data set for Phase II and did not need to be downloaded during the test. However, data could be downloaded at any time by copying files onto an external disk drive (e.g., a “thumb” drive). The data archive files could be exported as text or Excel files using the TGA310 Viewer software that was provided by the vendor. Data were automatically archived every four hours, resulting in archive files of approximately 500 kilobytes each. The archive files produced for Phase II consumed approximately 60 megabytes of disk space. Operator input was required to respond to the PC prompt to change the time for daylight savings, and some data were lost as a result. On two occasions, the operator found that the computer for the TGA310 had shut down or that the TGA310 program had stopped running at some point overnight. The cause of these events (e.g., power failure/interruption, software glitch) is not known, and some loss of data resulted. Based on information from the vendor that was not verified as part of this test, the TGA310 now includes an automatic restart that is expected to resolve this problem.

6.9 Data Completeness

During Phase II, data completeness for the TGA310 was 91%. The data loss of 9% was caused by computer-related failures, as described in Section 6.8.

Chapter 7
Performance Summary

The performance of the TGA310 was evaluated only in Phase II of this verification test. Table 7-1 presents a summary of the performance of the TGA310 during Phase II of this verification test.

Table 7-1. Performance Summary of the TGA310

Parameter	Phase I	Phase II
Relative accuracy(a)	The TGA310 was not available in Phase I	Average RA = 2.2% Percent difference range = -2.9 to 2.5%
Linearity(a)(b)		Range = 0 to 2,000 ppb NH_3 Slope = 0.966 (± 0.031) Intercept = 15.9 ppb (± 31.9) r^2 = 1.000
Precision(a)		Average RSD = 0.9% Range = 0.4 to 1.2%
Response time(a)		Rise time = 126 to 156 seconds (1 Lpm flow rate) Fall time = 124 to 169 seconds (1 Lpm flow rate)
Calibration/ zero drift(a)		• No apparent drift in response to zero air. • Response to 1,000-ppb NH_3 gas standard increased by 81 ppb between Tuesday and Friday of Week 1. An increase of 55 ppb was observed between Monday and Friday of Week 4.
Interference effects(a)(c)		• Hydrogen sulfide (461 ppb): no apparent effect • Nitrogen dioxide (154 ppb): no apparent effect • 1,3-Butadiene (154 ppb): increase of 24% in zero air and 22% in 500 ppb NH_3 • Diethylamine (155 ppb): increase of 28% in zero air and 20% in 500 ppb NH_3(d)
Comparability		Slope = 1.15 (± 0.04) Intercept = -4.1 ppb (± 3.6) r^2 = 0.994
Ease of use		• Daily checks were simple and quick • Little skill required to operate • No data download necessary • No maintenance required • Loss of approximately 29 hours of data resulting from apparent computer-related failures
Data completeness		91%(e) (87%)(f)

(a) Frequency and phase instability warnings and alarms sounded on the TGA310 during 16% of the gas standard delivery periods when gas standards were supplied by the NH_3 dilution system. Warnings were probably caused by small fluctuations in the gas standard flow rate.

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

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

(d) Independent tests indicate that the diethylamine gas standard contained some NH_3 as an impurity in the gas standard or as a result of displacement from the tubing walls. Thus, the measured interference was at least partially due to the NH_3 impurity.

(e) Data loss of 51 hours attributable to computer-related failures.

(f) The TGA310 was installed 30 hours after the start of Phase II. If this time is considered, the TGA310 experienced 87% data completeness.

Chapter 8
References

1. *National Air Pollutant Trends, 1900-1998*. EPA-454/R-00-02, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 27711.

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

TGA310 Checklist

TGA300Series – Ammonia Trace Gas Analyzer

omnisens

Operation Checklist

Purpose of the document:

The present document provides some guideline information intended to check the operation of the instrument on a regular basis. The document refers to the "Installation checklist" report, filled by the person in charge of the installation, and provides the parameters and measured raw data at the time of the first installation.

General information :

- Measuring unit S/N : ……………………………………… - Location : ………………………………………
- Flow control S/N : ……………………………………… - Date : ………………………………………

Operation Checklist :

1.	Log In	In the main panel of the Graphical User Interface, log in as "Maintenance", log off and log in if necessary		
2.	Check the *Diagnostic* panel	Go to Menu and select *Diagnostic*		
3.	Check the status & diagnostic	• Are the indicators status in the Diagnostic panel OK (they all should be green (ideal) except "temperature" during the warming up time)?	☐ Yes	☐ No
4.	Record Raw Data values	•Record instrument the values displayed in the diagnostic panel:		

Raw Data:

- Frequency [Hz] : ………………………………………………
- Normalized signal [mV] : ………………………………………………
- Ref. Amplitude [mV] : ………………………………………………
- Phase [rad] : ………………………………………………
- Temperature [°C] : ………………………………………………
- Relative Humidity [%] : ………………………………………………
- Speaker [mV] : ………………………………………………

5.	Check *Ref* value	• Is the *Ref* value is within 30% margin around the value recorded at the time of the installation ?	☐ Yes	☐ No

6. Log OFF	Go back to the main panel and log OFF			
7. Check the recorded archives	Select *"Archive Viewer"* on the main panel menu			
	● Are recorded archives accessible with the *"Archive viewer"*?	☐ Yes	☐ No	
8. Sampling pump & air flow	● Is the air flow rate adjusted to the proper value (between 1.5 and 4 liter/min.)?	☐ Yes	☐ No	

Operator's name : ……………………………………………………… Signature : ………………………………………………………

In case of problem or if the answer to one the above question was NO, contact and fax or email the present document to:

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PSE-C
CH1015 Lausanne
Switzerland

Phone: +41 21 693 84 86
Fax: +41 1 274 20 31
Email: support@omnisens.ch

Important Note :

For debugging purposes, it is very helpful if the archived data is made available. Therefore in case of problem, zip the archive folder *Arch* (C://Omnisens/Data/Arch) and email it to support@omnisens.ch.