THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE: **AMBIENT AMMONIA MONITOR**

APPLICATION: **MEASURING AMMONIA EMISSIONS AT ANIMAL FEEDING OPERATIONS**

TECHNOLOGY NAME: **QC-TILDAS**

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The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved 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. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with 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 Advanced Monitoring Systems (AMS) Center, one of seven technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. In collaboration with the U.S. Department of Agriculture, the AMS Center has recently evaluated the performance of ambient ammonia (NH_3) monitors to measure NH_3 emissions. This verification statement provides a summary of the test results for the Aerodyne Research, Inc. Quantum Cascade-Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS).

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the QC-TILDAS's performance in measuring gaseous NH_3 in ambient air at two animal feeding operations. The verification test was conducted in two phases, each at separate animal feeding operations. 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 and were expected to exhibit a wide range of NH_3 concentrations during the test periods. The verification test was designed to evaluate relative accuracy (RA), linearity, precision, response time, calibration and zero drift, interference effects, comparability, ease of use, and data completeness.

During Weeks 1 and 4 of each phase of the verification test, the QC-TILDAS response to a series of NH_3 gas standards of known concentration was used to quantify RA, linearity, precision, and calibration/zero drift. Ammonia gas standards ranging from 0 to 3,030 parts per billion (ppb) NH_3 and 0 to 2,000 ppb NH_3 were delivered during Phases I and II, respectively. The QC-TILDAS response time, the time to reach 95% of the change in the stable concentration, was also assessed during the delivery of the gas standards and reported in terms of seconds (s). During the second phase, interference effects were quantified from the QC-TILDAS response to various chemical species that may be present at animal feeding operations; the potential interferent gases were delivered both in the presence and absence of NH_3. The QC-TILDAS continuous response to ambient air also was evaluated during both phases as the comparability to simultaneous determinations by a time-integrated ambient NH_3 reference method (acid-coated denuders). Comparisons were made with reference samples that were collected on a five-per-day schedule for periods of between 2 to 12 hours for approximately 10 days during each phase, based on procedures in EPA Method IO-4.2.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the QC-TILDAS was provided by the vendor and does not represent verified information.

The QC-TILDAS is a tunable infrared laser spectrometer, based on pulsed quantum cascade laser technology. The QC-TILDAS uses an absolute spectroscopic analysis method that is inherently self-calibrating, making calibration gases unnecessary. The QC-TILDAS is optimized for NH_3, but it can be used for a variety of gases, depending on laser selection. Ambient NH_3 is continuously sampled in a multipass (56-meter path length, 0.5-liter volume) cell at reduced pressure (30 to 60 Torr). The glass surfaces are siloxyl-coated to minimize surface losses. The QC-TILDAS uses the unique infrared spectroscopic identification, or fingerprint, of NH_3 to quantify ambient NH_3 levels. The QC-TILDAS consists of an optical and an electronic subunit, mounted together. The optical system is on a temperature-stabilized 25-centimeter (cm) × 60-cm optical breadboard and contains a laser, multiple-pass absorption cell, and infrared detectors, coupled with all-reflective optics. The quantum cascade laser for NH_3 detection at a 10.3-micrometer wavelength is thermoelectrically cooled in a hermetically sealed housing and operates in the pulsed mode. The astigmatic Herriot multiple pass cell has two mirrors separated by 32 cm. Two infrared detectors, one for the sample cell and one for a reference cell are contained in one liquid nitrogen-cooled dewar. (Thermoelectrically cooled detector options are available with reduction in sensitivity.) The electronics subunit consists of laser temperature and current controllers, pressure and temperature probes, valve driver, and computerized data acquisition. The data acquisition rate is adjustable from 1 Hertz (Hz) to 20 Hz. The electronics are mounted in a standard 48.3-cm rack, 53.3 cm wide by 53.3 cm deep. The total height of QC-TILDAS is 61 cm. The combined weight of the electronics and optical modules is 77.3 kilograms. Several options for removal of particulate matter are available, including the inlet system used in this verification test that utilizes secondary air flow for inertial separation of particulate matter. A vacuum pump is required for continuous sampling at reduced pressure in the absorption cell. A temperature-controlled, closed-loop circulator provides the coolant for the laser housing and electronics. QC-TILDAS costs $118,000.

VERIFICATION OF PERFORMANCE

The performance of the QC-TILDAS was evaluated in two phases in this verification test. During both phases of the verification test, the QC-TILDAS was installed inside a temperature-regulated instrument trailer, and the Teflon QC-TILDAS inlet was used to sample the outside air. The following presents a summary of the performance of the QC-TILDAS during this verification test. The values presented in this table are based on 10-Hz data or 60-s averages as noted below. Values in parentheses are 95% confidence intervals.

Performance Summary of the QC-TILDAS

	Results					
	Phase I			Phase II		
Parameter		Week 1	Week 4		Week 1	Week 4
Relative accuracy(a)(b)	Average RA %D(c) Range	6.5% −15.0% to 6.5%	4.7% −11.4% to −2.2%	Average RA %D Range	10.0% −12.7% to −8.2%	Interference test conducted during Week 4
Linearity(a)	Range Slope Intercept r^2	0 to 3,030 ppb 0.840 (±0.032) 35 (± 42) 0.9989	0 to 2,326 ppb 0.962 (± 0.009) 1.5 (± 8.9) 0.9999	Range Slope Intercept r^2	0 to 2,000 ppb 0.919 (± 0.016) −8.8 (± 18.6) 0.9998	
Precision(a)	Average RSD(d) Range	2.4% 0.5% to 3.7%	2.5% 1.0% to 4.1%	Average RSD Range	1.9% 1.0% to 3.0%	
Response time(a) (95%)	Rise Time Fall Time	0.8 to 65.6 s (e)	1.4 to 15.0 s 5.5 s	Rise Time Fall Time	1.1 to 14.9 s (de	
Calibration/ zero drift	No apparent drift in response to zero air or to NH_3 standards during Week 4(f)			No apparent drift in response to zero air or in response to 1,000 ppb NH_3 during Week 1, a 34-ppb decrease observed for last check of Week 4.		
Interference effects(g)	Interference test conducted during Phase II			• Hydrogen sulfide (101 ppb): No apparent effect • Nitrogen dioxide (104 ppb): No apparent effect • 1,3-Butadiene (102 ppb): No apparent effect • Diethylamine (102 ppb): 19% increase in zero air, no apparent effect in 500 ppb NH_3(h)		
Comparability(i)	Slope = 1.09 (± 0.05) Intercept = 14.4 (±22.0) r^2 = 0.9822			Slope = 0.984 (± 0.026) Intercept = −9.52 (± 3.25) r^2 = 0.9943		
Ease of use	• Required liquid nitrogen fills every 12 hours; other daily checks were straightforward and quick • Technician experienced in instrumentation/spectroscopy required to operate; some spectra were refitted by vendor representative during periods when the operational parameters were not set properly • Testing activities completed in a short time • Operator required to restart after power loss • Delivery of gas standards required additional dilution because of 13-liters per minute inlet flow rate • Vendor representative conducted data processing to remove spurious data points resulting from automated zero air measurement for background subtraction					
Data completeness	92% data completeness, 90% data collected			100% data completeness, 98% data collected		

(a) 10-Hz data used for this analysis.
(b) Relative accuracy is expressed as an average absolute value of the percent difference from NH_3 gas standards.
(c) %D = percent difference.
(d) RSD = relative standard deviation.
(e) Fall time not measured/reported during this check.
(f) The first two calibration and zero checks during Phase I could not be analyzed because some ambient air was sampled along with the gas standards. Drift could not be assessed during Week 1 of Phase I.
(g) Calculated as the change in signal divided by the interferent gas concentration, expressed as a percentage.
(h) The presence of an NH_3 impurity in the diethylamine gas standard or the release of NH_3 from the sample lines during delivery could not be ruled out.
(i) 60-second averages used for this analysis.

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