THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

TECHNOLOGY TYPE:	**CAVITY RING-DOWN SPECTROSCOPY**	
APPLICATION:	**MEASUREMENT OF AMMONIA SLIP IN STACK GAS**	
TECHNOLOGY NAME:	**Model G1103-c**	
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ETV Joint Verification Statement

The U.S. Environmental Protection Agency (EPA) has established 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 six verification centers under ETV, is operated by Battelle in cooperation with EPA's National Risk Management Research Laboratory. The AMS Center evaluated the performance of a cavity ring-down spectroscopy (CRDS) unit for the analysis of ammonia in stack gas. This verification statement provides a summary of the test results for the Picarro Model G1103-c ammonia analyzer.

VERIFICATION TEST DESCRIPTION

Testing was performed between July 24 and October 29, 2009 at a full-scale coal fired power plant owned and operated by the Tennessee Valley Authority. The power plant where testing was performed included multiple 200-megawatt boilers, each configured with selective non-catalytic reduction (SNCR) NO_x reduction capabilities that

involved the injection of an aqueous urea solution into each boiler. During testing, the Picarro Model G1103-c system was installed in an environmentally controlled instrument shelter and supplied with flue gas that was sampled from the superheat section of one boiler. The flue gas was drawn from the duct using a dilution probe (100:1 dilution) incorporating a particulate filter, and was delivered to the CRDS system through approximately 150-200 feet of heated Teflon sampling line. Reference ammonia measurement were performed according to a modified version of Conditional Test Method-027 (CTM-027), which includes non-isokinetic stack sampling and ion chromatographic analysis, to allow comparisons to the CRDS measurements. The relative percent difference (RPD) between the reference measurements and the CRDS measurements was calculated and used to determine the relative accuracy (RA) of the Model G1103-c. After completion of the field testing, the Picarro Model G1103-c was challenged under laboratory conditions by supplying zero air and an ammonia reference standard diluted over a range of target concentrations to assess precision, linearity, zero/calibration drift, and response time.

QA oversight of verification testing was provided by Battelle and EPA. Battelle technical staff conducted a performance evaluation audit and Battelle QA staff conducted a technical systems 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 Model G1103-c is based on information provided by the vendor. This technology description was not verified in this test.

The Model G1103-c is an analyzer designed to measure ammonia at the parts-per-billion level in the presence of carbon dioxide, water vapor, and other gas species present in flue gas streams. This analyzer is based on CRDS, which is a technique in which a gas sample is introduced into a high-finesse optical cavity and the optical absorbance of the sample is determined, thus providing concentration and/or isotopic ratio measurements of a particular gas species of interest.

The components which make up a basic CRDS instrument are a laser, a high-finesse optical cavity consisting of two or more mirrors, and a photo-detector. Operationally, light from a laser is injected into the cavity through one partially reflecting mirror. The light intensity inside the cavity then builds up over time and is monitored through a second partially reflecting mirror using a photo-detector located outside the cavity. The “ring-down” measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially with a time constant, τ, that depends on the losses due to the cavity mirrors and the absorption and scattering of the sample being measured. After shutting off the laser, most of the light remains trapped within the cavity for a relatively long period of time (i.e., microseconds [µsec]), producing an effective path length of tens of kilometers through the sample.

The analyzer continuously scans the laser over individual ammonia spectral features and records the absorption loss and wavelength at each spectral point. Each spectrum is comprised of absorption loss as a function of optical frequency. The concentration is proportional to the area under each measured spectral feature. Concentration measurements are provided approximately every second, corresponding to a total of 100 ring-down and wavelength monitor measurements, which provides sensitivity to approximately 0.3 ppb of ammonia in one second, or about 0.025 ppb with five of minutes of averaging. The Model G1103-c has an operational range of 0-10 ppm NH_3, with an optional extended range up to 50 ppm.

The Model G1103-c has dimensions of 43 cm x 25 cm x 59 cm (17” x 9.75” x 23”) including the base, and can be rack mounted or operated on a bench top. The approximate purchase price of the Model G1103-c is $55,000.

VERIFICATION OF PERFORMANCE

Table VS-1 provides a summary of selected verification test results for the Picarro Model G1103-c.

Table VS-1. Summary of Verification Results for the Picarro Model G1103-c

Performance Parameter	Method of Evaluation	Results
Linearity	Linear regression of multipoint calibration results	**Slope** / **Intercept** / **r^2** **Initial**: 0.998 (±0.02) / 19.5 (±41.0) / 0.997 **Final**: 1.03 (±0.009) / -12.3 (±13.3) / 1.000
Accuracy	Comparison to reference method results	**Laboratory Testing** / **Field Testing**[a] **Relative Std Dev (RSD)**: 4.3% / -25.2% **Relative Accuracy**: 4.6% / 31.9%
Precision	Evaluation of daily zero/span check results	**Zero Check** / **Span Check** **Mean**: 1.03 ppb / 1590 ppb **St. Dev.**: 0.77 ppb / 5.3 ppb **RSD**: 11.3% / 0.13% **% Diff. from Theory**: N/A / 4.3%
Zero/Span Drift	Evaluation of daily zero/span check results	• No apparent trend in changes between zero and span checks
Response Time	Calculated from daily zero/span check results	**Rise Time**: **0 sec** 02:26 (00:32); **30 sec** 02:40 (00:30); **2 min** 04:40 (00:20) **Fall Time**: **0 sec** 00:42 (00:11); **30 sec** 01:07 (00:11); **2 min** 02:26 (00:32) **Avg. Time** / **Mean** / **Std. Dev.**
Data Completeness	Ratio of number of data points collected to number of potential data points that could have been collected	• Completeness = 100%
Ease of use	Operator observations	• Initial installation was completed in ~45 minutes by vendor • Subsequent installations were performed by Battelle and on-site support staff in ~45 minutes • Operation is automated upon powering; requires no external intervention • Operated unattended for 3-month duration of the testing period • Daily space-delimited data files are generated automatically and stored in separate data files on an internal hard drive
Maintenance	Operator observations	• No routine maintenance activities were performed during testing • Non-routine maintenance included diagnostic tests performed after initial installation but prior to routine monitoring periods
Consumables/waste generated	Operator observations	• No consumables were used and no waste was generated during routine monitoring activities • Compressed gas standards were used for dynamic spiking tests; the waste gas stream from the dynamic spiking was combined with the excess flue gas

[a] These results are based on measurements from the entire field sampling system, including the dilution probe, the transfer line from the duct, and the Model G1103-c, compared with reference method measurements taken directly from the duct.

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