ETV Joint Verification Statement

TECHNOLOGY TYPE: CONTINUOUS EMISSION MONITOR
APPLICATION: MEASURING MERCURY EMISSIONS
TECHNOLOGY NAME: Hg-200
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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.

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. The AMS Center has recently evaluated the performance of continuous emission monitors (CEMs) used to measure mercury emissions. This verification statement provides a summary of the test results for the Opsis AB Hg-200 CEM.
VERIFICATION TEST DESCRIPTION

The purpose of this verification test was to evaluate the performance of mercury CEMs at a full-scale field location, over a substantial duration of continuous operation. The CEMs were challenged by stack gases generated from the thermal treatment of a variety of actual wastes in the Toxic Substances Control Act Incinerator (TSCAI) at the East Tennessee Technology Park in Oak Ridge, Tennessee. CEM responses were compared with reference mercury measurements of total (Hg_T), oxidized (Hg_{Ox}), and elemental (Hg_e) mercury. Mercury standard gases were used to challenge the CEMs to assess stability in long-term operation, and the instruments were operated for several weeks by TSCAI staff to assess operational aspects of their use. The reference method for establishing the quantitative performance of the tested technologies was the Ontario Hydro (OH) method. For the Hg-200, relative accuracy (RA), correlation with the reference method, and precision (i.e., repeatability at stable test conditions) were assessed for total mercury in the stack gas emissions. Sampling system bias, calibration and zero drift, and response time were assessed for Hg_e only, using commercial compressed gas standards of Hg_e. The data completeness, reliability, and maintainability of the Hg-200 over the course of the verification test were assessed during several weeks of continuous operation.

QA oversight of verification testing was provided by Battelle. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

TECHNOLOGY DESCRIPTION

The following description of the Hg-200 was provided by the vendor and does not represent verified information.

The Hg-200 includes a dilution extraction sampling system that provides a stack sample to the mercury analyzer. The dilution system includes a dilution probe and a pump. Four ¼-inch Teflon lines and a power cable connect the probe to the CEM. One Teflon line carries dilution air to the dilution probe on the stack, another sends diluted sample from the dilution probe back to the analyzer, the third sends calibration gas from the analyzer location to the probe, and the fourth is a vacuum sensor line for verifying system operation. The sample is pulled from the stack through a 1-inch pipe insert extending from the dilution probe to the middle of the stack. The probe mounts on a standard 4-inch port. The dilution block of the probe, which includes the filters, is heated to 200°C (392°F). An internal dilution system consisting of two critical orifices mixes sample and dilution air to achieve a sample dilution of 1:100. This diluted sample is pulled by the pump down the sample line to the analyzer. Because the sample is diluted by a factor of 100, the potential for condensation in the sample line is low. Total flow in the sample line is two liters per minute. When Hg_T is analyzed, the sample passes through a thermocatalytic converter that forms Hg_e from any Hg_{Ox} compounds in the sample gas. The converter includes a quartz element heated to 350°C (662 °F). This function can be cycled on and off so that Hg_T and Hg_e can be differentiated. The cycle time is normally five minutes. (In this verification test the Hg-200 was used only in the Hg_T mode.)

The analyzer is a double-beam photometer that preconcentrates Hg_e on a gold trap. A personal computer data logger is connected to the Hg-200 through a serial RS232 line. The system cycles and measurement times are controlled by Windows software, which provides primary data storage before the results are exported to a data acquisition computer. Windows software also sets up the sequences that switch between measuring Hg_e and Hg_T.

The 115-volt system is 91.4 cm (36 inches) high, 76.2 cm (30 inches) wide, and 80.0 cm (32 inches) deep.

VERIFICATION OF PERFORMANCE

Relative Accuracy: To verify the RA of the Hg-200 for measuring total mercury, results were compared for 18 OH reference method sampling runs using dual trains at Hg_T levels from <1 to 200 micrograms per dry standard cubic meter of flue gas. The Hg-200 showed an RA for Hg_T of 76.3% overall. The RA was 63.1% with OH Run 16 excluded. (In OH Run 16 the TSCAI burned packets of solid waste at relatively high mercury content, with no liquid waste. The flue gas mercury content in that run was likely highly variable and, therefore, difficult to determine accurately with a batch analyzer such as the Hg-200.)
Correlation with Reference Method Results: Correlation of the Hg-200 readings with all 18 OH HgT results showed an overall $r^2$ of 0.935.

Precision: Precision of the Hg-200 was determined using two OH sampling periods having relatively stable introduction of mercury in aqueous waste into the TSCAI. The estimated maximum variability attributable to the Hg-200 was 43.4% and 12.5% relative standard deviation (RSD) for these two periods.

Sampling System Bias: Sampling system bias was not evaluated because the Hg-200 is designed to accept mercury standard gases only at the sampling system inlet.

Relative Calibration and Zero Drift: Calibration and zero drift of the Hg-200 was assessed by multiple analyses of mercury gas standards and zero gas. Sixteen zero gas analyses during the six-week field period resulted in a mean reading ($\pm$ standard deviation) of 0.72 ($\pm$ 0.36) $\mu$g/m$^3$. Fourteen analyses of an 11.6 $\mu$g/m$^3$ mercury gas standard over the same time period resulted in an RSD of 13.6%. Seven analyses of a 38.3 $\mu$g/m$^3$ mercury gas standard over 5 ½ weeks of the field period resulted in an RSD of 18.6%. Three analyses of a 46.2 $\mu$g/m$^3$ mercury gas standard on two days resulted in an RSD of 5.3%.

Response Time: Rise and fall times of the Hg-200 were determined at times of switching between zero and mercury standard gases. The Hg-200 achieved 95% rise and fall in approximately one five-minute measurement cycle.

Data Completeness: The Hg-200 data completeness rate was 65.8% over the entire six-week field period.

Operational Factors: Approximately two weeks of data were invalidated by a problem with the Hg-200 valve system, which proved troublesome throughout the entire six-week field period.

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