

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Emission Monitor

APPLICATION: MEASURING ELEMENTAL AND OXIDIZED
MERCURY EMISSIONS

**TECHNOLOGY
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The U.S. Environmental Protection Agency (EPA) has created 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 substantially 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 that consist of buyers, vendor organizations, and permittees; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance 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 technology centers 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 used to measure mercury in flue gases. This verification statement provides a summary of the test results for the PS Analytical Ltd. Sir Galahad II (SG-II) mercury continuous emission monitor (CEM).

VERIFICATION TEST DESCRIPTION

The verification test was conducted over a three-week period in January 2001 at the Rotary Kiln Incinerator Simulator (RKIS) facility at EPA's Environmental Research Center, in Research Triangle Park, North Carolina. This mercury CEM verification test was conducted jointly by Battelle's AMS Center, EPA's Office of Research and Development, and the Massachusetts Department of Environmental Protection. A week of setup and trial runs was followed by two weeks of verification testing under different flue gas conditions. The daily test activities provided data for verification of the following performance parameters of the SG-II: relative accuracy in comparison to reference method results, correlation with the reference method, precision in sampling at stable flue gas conditions, calibration/zero drift from day to day, sampling system bias in transfer of mercury to the CEM's analyzer, interference effects of flue gas constituents on CEM response, response time to rising and falling mercury levels, response to low levels of mercury, data completeness over the course of the test, and setup and maintenance needs of the CEM. The Ontario Hydro (OH) draft American Society for Testing and Materials mercury speciation method was used as the reference method in this verification test. Paired OH trains were sampled at two locations in the RKIS duct to establish the precision of the OH method.

Quality assurance (QA) oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a data quality audit of 10% of the test data, a series of performance evaluation audits on several measurements at the RKIS, and both an internal and an external technical systems audit of the procedures used in this verification. EPA QA staff also conducted an independent technical systems audit at the RKIS.

TECHNOLOGY DESCRIPTION

The SG-II is an automated continuous emission monitor for elemental mercury and total vapor-phase mercury in combustion flue gases and other gas streams. The SG-II consists of a Model S235C400 mercury speciation module and an enclosed cabinet housing the SG-II amalgamation atomic fluorescence mercury detector (PSA 10.525), a stream selector module (PSA S235S100), personal computer, monitor, and keyboard, and a mercury calibration source (PSA 10.533). The speciation module converts oxidized mercury in the sample gas to elemental mercury by means of a proprietary aqueous reagent, allowing separate detection of elemental mercury and total mercury. The speciation module is approximately 75 cm wide x 45 cm deep x 90 cm high (30 in. wide x 18 in. deep x 36 in. high) and can be mounted on the stack being sampled or on a wall or supporting frame. The cabinet enclosing the other modules is approximately 75 cm wide x 75 cm deep x 180 cm high (30 in. wide x 30 in. deep x 72 in. high) and is mounted on wheels. A heated Teflon diaphragm pump draws a filtered sample flow of approximately 5 L/min from the gas source into the speciation module, which contacts the gas stream with the aqueous reagents in two bubblers. Two separate gas streams are thus produced, one of which has been scrubbed of oxidized mercury and therefore contains only elemental mercury. In the other gas stream, oxidized mercury is reduced to elemental mercury, producing an elemental mercury concentration equivalent to the original sum of oxidized and elemental mercury. These two gas streams flow to the stream selector module. Mercury in the selected gas stream is collected by passage through a preconcentration trap and subsequently thermally desorbed into the SG-II detector.

VERIFICATION OF PERFORMANCE

Relative accuracy: During the first week of verification testing, the SG-II provided an accuracy relative to the OH method of 20.6% for total mercury, at total mercury levels of about 7 to 8 $\mu\text{g}/\text{m}^3$. Testing showed relative accuracy of 22.8% for elemental mercury, and 27.2% for oxidized mercury at elemental mercury levels of approximately 6 to 7 $\mu\text{g}/\text{m}^3$ and oxidized mercury levels of approximately 1 to 1.5 $\mu\text{g}/\text{m}^3$. In the second week of verification testing, the SG-II provided a relative accuracy of 32.8% for total mercury, at total mercury levels of about 70 to 120 $\mu\text{g}/\text{m}^3$. Relative accuracy of 29.6% for elemental mercury, and 33.3% for oxidized mercury was found at elemental mercury levels ranging from about 5 to 25 $\mu\text{g}/\text{m}^3$ and oxidized mercury levels ranging from about 45 to 110 $\mu\text{g}/\text{m}^3$.

Correlation with the reference method: The coefficient of determination (r^2) of the SG-II and OH elemental mercury results was 0.853 based on data from both weeks combined. The corresponding r^2 value for oxidized mercury was 0.951, and for total mercury was 0.957.

Precision at stable flue gas conditions: Precision of the SG-II response was assessed in periods of stable mercury levels in the flue gas during the 15 OH sampling periods. The precision of the SG-II response for elemental mercury was within 10% relative standard deviation (RSD) in 13 of the 15 periods. For total mercury, precision was within 10% RSD in 11 of the 15 periods and within 15% in 14 of the periods.

Calibration/zero drift: Analysis of zero gas and elemental mercury standard gases in the first week of testing gave average zero gas responses of $0.001 (\pm 0.001) \mu\text{g}/\text{m}^3$ and standard gas responses of $15.1 (\pm 0.39) \mu\text{g}/\text{m}^3$. The standard gas results equate to a 2.6% RSD. Zero gas readings in the second week were $0.001 (\pm 0.006) \mu\text{g}/\text{m}^3$, and standard gas responses were $53.5 (\pm 1.34) \mu\text{g}/\text{m}^3$. These standard gas results equate to a 2.5% RSD.

Sampling system bias: The bias in transport of elemental mercury through the inlet system of the SG-II ranged from -0.3 to -4.9%.

Interference effects of flue gas constituents: Elevated levels of sulfur dioxide, nitrogen oxides, carbon monoxide, and hydrogen chloride had no significant effect on SG-II response to elemental or total mercury in flue gas. The presence of chlorine reduced elemental mercury readings to nearly zero, but caused no significant change in the total mercury readings. When these gases were all present at once in the flue gas, the SG-II readings for both elemental and total mercury were close to those seen with only mercury in the flue gas.

Response time to changing mercury levels: The SG-II operated with a 5- to 6-minute sampling/analysis cycle and achieved 95% or greater response to changes in mercury concentration within a single cycle.

Response to low levels of mercury: The SG-II produced a nearly quantitative response to as little as $0.57 \mu\text{g}/\text{m}^3$ of mercury in flue gas (the lowest concentration tested), and response at nominal levels of 0.57 to $4.5 \mu\text{g}/\text{m}^3$ of mercury was within about 10% of the nominal levels.

Data completeness: Data completeness for the SG-II was 100%.

Setup and maintenance needs: No significant repair or maintenance was needed. The SG-II uses 1 to 1.5 L/day of aqueous reagents to measure elemental and total mercury and consumes about 200 cubic feet of high-purity argon in a week of continuous operation

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