

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: CONTINUOUS EMISSION MONITOR

APPLICATION: MEASURING MERCURY EMISSIONS

TECHNOLOGY NAME: Sir Galahad II

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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 permittees), 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) to measure mercury emissions. This verification statement provides a summary of the test results for the PS Analytical, Ltd., Sir Galahad II (SG-II) 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^0) 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 SG-II, relative accuracy (RA), correlation with the reference method, and precision (i.e., repeatability at stable test conditions) were assessed for total and elemental mercury in the stack gas emissions. Sampling system bias, calibration and zero drift, and response time were assessed for Hg^0 only, using commercial compressed gas standards of Hg^0 . The data completeness, reliability, and maintainability of the SG-II 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 SG-II was provided by the vendor and does not represent verified information.

The SG-II is an automated CEM for Hg^0 and Hg_T in combustion flue gases and other gas streams. The SG-II consists of a Model S235C400 mercury speciation module; an enclosed cabinet housing the SG-II amalgamation atomic fluorescence mercury detector (PSA 10.525); a stream selector module (PSA S235S100); a personal computer, monitor, and keyboard; and a mercury calibration source (PSA 10.533). The speciation module converts oxidized mercury in the sample gas to Hg^0 by means of a proprietary aqueous reagent, allowing separate detection of Hg^0 and Hg_T . The speciation module is approximately 75 centimeters (cm) wide x 45 cm deep x 90 cm high (30 inches wide x 18 inches deep x 36 inches 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 inches wide x 30 inches deep x 72 inches high) and is mounted on wheels.

A heated Teflon diaphragm pump draws a filtered sample flow of approximately five liters per minute 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 Hg_{OX} and therefore contains only Hg^0 . In the other gas stream, Hg_{OX} is reduced to Hg^0 , producing an Hg^0 concentration equivalent to the original sum of Hg_{OX} and Hg^0 . 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, which has a detection limit of as little as 0.1 picograms of mercury. In this verification test, a sample flow of 0.5 liter/minute was passed through the preconcentration trap for 1 to 2 minutes. The overall cycle time of sampling, preconcentration, and analysis was approximately five minutes. The resulting detection limit for vapor-phase mercury is approximately 0.001 microgram per cubic meter ($\mu g/m^3$), with a linear dynamic range of up to 2,500 $\mu g/m^3$. The PSA 10.533 mercury source provides a calibration gas and blank stream that can be substituted for the sample stream on a scheduled or as-needed basis. This allows system bias checking for the entire sampling system.

The SG-II uses Windows[®]-based operating software for calibrating and operating the instrument and recording and displaying data. The duration, flow rate, and sequencing of the Hg^0 and Hg_T measurements are controlled by the software, as are the operation of the SG-II detector, the graphical display of data, and the scheduling of internal calibration checks. The software checks for alarm outputs from the various modules and can warn of any malfunctions.

VERIFICATION OF PERFORMANCE

Relative Accuracy: The accuracy of the SG-II for measuring Hg_T and Hg^o was verified by comparison with the results of 18 OH sampling runs at an Hg_T level from <1 to 200 micrograms per dry standard cubic meter of flue gas. The overall RA results were 54.7% and 59.8% for Hg^o and Hg_T , respectively. The RA for Hg_T is 42.8% if OH Run 16 is excluded from the calculation. (In OH Run 16 the TSCAI burned packets of solid waste of 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 SG-II.)

Correlation with Reference Method Results: Correlation of the SG-II Hg^o and Hg_T results with the OH results showed r^2 values of 0.948 and 0.875, respectively, when all 18 OH results were included.

Precision: Precision of the SG-II was estimated using two OH sampling periods having relatively stable introduction of mercury in aqueous waste into the TSCAI. The estimated maximum variability attributable to the SG-II was 8.9% and 15.9% relative standard deviation (RSD) for these two periods.

Sampling System Bias: The bias introduced by the SG-II sampling system was evaluated by introducing Hg^o standard gas both at the SG-II and at the inlet to the sampling system. Sampling system bias was 2.8% to 6.9% in the Hg^o measurement channel and 0.0% to 6.9% in the Hg_T measurement channel of the SG-II.

Relative Calibration and Zero Drift: Zero gas and mercury gas standards were used to assess the drift of the SG-II throughout the verification test. Zero gas readings over the six-week field period averaged $-0.05 (\pm 0.10) \mu g/m^3$, indicating minimal drift of the SG-II zero readings. Eighteen analyses of an approximately $14.9 \mu g/m^3 Hg^o$ standard over six weeks resulted in an RSD of 11.9%. Twelve analyses of an approximately $35.6 \mu g/m^3$ standard over five weeks resulted in an RSD of 10.2%. Four analyses of an approximately $39.3 \mu g/m^3 Hg^o$ standard over four days resulted in an RSD of 8.7%.

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

Data Completeness: The SG-II data completeness was 88.3% over the entire six-week field period.

Operational Factors: The most common maintenance needed was replacement of chemical reagent solutions and argon cylinders, which was done every few days. The most common operational problems were in the liquid flow system of the mercury speciation module, including problems in maintaining liquid reagent flows and levels in the impingers, in mass flow control of sample gas flows, and in moisture carryover from the impingers..

signed by Gabor J. Kovacs 9/4/03
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