THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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Massachusetts Department of Environmental Protection

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Continuous Emission Monitor**
APPLICATION:	**MEASURING ELEMENTAL AND TOTAL MERCURY EMISSIONS**
TECHNOLOGY NAME:	**Lumex Mercury CEM**
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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 permitters; 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 Lumex Ltd. 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 Lumex CEM: 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, and a 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 Lumex CEM is a real-time continuous monitor for elemental and total mercury. The Lumex CEM is based on the analytical approach of cold vapor atomic absorption spectroscopy for detection of elemental mercury, with Zeeman high-frequency polarization background correction. The multipath optical cell and the Zeeman reduction of background interferences are designed to provide high sensitivity with minimal interferences from the combustion gas matrix. The sensitivity of this approach allows continuous real-time operation with no preconcentration and desorption steps. The CEM uses catalytic pyrolysis to decompose oxidized mercury to elemental mercury for detection, and thus uses no wet chemical reagents and no external gas supplies. The Lumex CEM is a two-channel instrument, in which one mercury detector operates with the catalytic pyrolyzer and one without, thereby providing simultaneous and continuous readings of total and elemental mercury, respectively. The Lumex CEM is microprocessor controlled by an RS-232 communications link. Software includes Windows-based data acquisition and processing. Readings can be reported at intervals from 1 second to 3 minutes; in this verification, data from both channels of the CEM were recorded at 1-second intervals. The Lumex CEM is a new device; during this verification test, modifications were made by Lumex staff that may have affected verification results. In addition, the Lumex CEM suffered accidental damage during the verification test that required substituting two external mercury detectors for the internal detectors in the CEM. Those external detectors were Lumex RA 915+ portable mercury detectors, designed for sensitive, fast-response measurements of elemental mercury. RA 915+ Serial No. 167 was used for detection of elemental mercury and RA 915+ Serial No. 164 was used for detection of total mercury by connection downstream of the catalytic pyrolyzer in the Lumex CEM. The RA 915+ units use the same detection approach as the CEM's internal detectors, and thus were a reasonable substitute that allowed verification to continue. The period when the RA 915+ detectors were used instead of the CEM's detectors is clearly indicated in this report.

VERIFICATION OF PERFORMANCE

Relative accuracy: During the first week of verification testing, the Lumex CEM provided accuracy relative to the OH method of 58.2% for total mercury, at levels of about 7 to 8 $\mu g/m^3$. Testing showed relative accuracy of 50.2% for elemental mercury, and 99% for oxidized mercury, at elemental mercury levels of about 6 to 7 $\mu g/m^3$ and oxidized mercury levels of about 1 to 1.5 $\mu g/m^3$. In the second week of verification, the Lumex instruments provided relative accuracy of 71% for total mercury, at total mercury levels of approximately 70 to 120 $\mu g/m^3$. Relative accuracy of 107% for elemental mercury, and 69.4% for oxidized mercury, was found at elemental mercury levels ranging from about 5 to 25 $\mu g/m^3$ and oxidized mercury levels ranging from about 45 to

110 µg/m^3. These RA results were caused primarily by a consistent underestimation of all mercury concentrations by the Lumex CEM, that may have been due to both losses of mercury in the inlet systems, and low pyrolyzer temperatures for much of the test.

Correlation with the reference method: The coefficient of determination (r^2) of the Lumex and OH elemental mercury results was 0.052, based on the data from both weeks of verification. The corresponding r^2 values for oxidized mercury and total mercury were 0.631 and 0.621, respectively.

Precision at stable flue gas conditions: Precision of the Lumex response was assessed in periods of stable mercury levels in the flue gas, during the 15 OH sampling periods. The precision (as percent RSD) of the Lumex response for elemental mercury was within 10% in five of the 15 periods, and within 15% in eight of the periods. For total mercury, precision was within 10% RSD in eight of the 15 periods and within 15% in 11 of the periods. These precision results include both variability in the test facility and in the Lumex instruments.

Calibration/zero drift: Calibration and zero drift were determined by repeated analysis of zero gas and elemental mercury standard gases. The failure of the Lumex CEM and subsequent substitution of the RA 915+ detectors interrupted the continuity of this portion of the test. Both the Lumex CEM and the RA 915+ detectors gave consistent readings on zero gas in both weeks of testing. Six analyses of a mercury standard gas with the Lumex CEM in the first week of verification gave average responses of 15.7 (± 7.9) and 14.7 (± 6.9) µg/m^3 for elemental and total mercury, respectively. These values equate to percent RSD's of 50.3 and 46.7%, respectively. Three analyses of the same standard with the RA 915+ detectors in the first week gave 13.2 (± 0.35) and 11.7 (± 3.0) µg/m^3, respectively, for percent RSD values of 2.7% and 25.4%. Seven analyses of a different standard by the RA 915+ detectors in the second week of verification gave readings of 55.3 (± 2.98) and 58.3 (± 3.55) µg/m^3 for elemental and total mercury, respectively. These standard gas results equate to percent RSD values of 5.4% and 6.1%, respectively.

Sampling system bias: Sampling system bias of the inlet systems used with the Lumex CEM and RA 915+ detectors was determined using elemental mercury gas standards. The bias in transport of elemental mercury through the entire inlet systems ranged from -20.5 to -44.5%.

Interference effects of flue gas constituents: Elevated levels of sulfur dioxide, nitrogen oxides, and carbon monoxide had little effect on Lumex CEM response to elemental or oxidized mercury in flue gas. However, the presence of hydrogen chloride or chlorine reduced elemental mercury readings from about 5 µg/m^3 to less than 1 µg/m^3, and the total mercury readings were also reduced by half or more in the presence of these species. When these gases were all present at once in the flue gas, the Lumex elemental mercury readings remained below 1 µg/m^3, and the total mercury readings were only about 60% of those with the same mercury level but no interferants present.

Response time to changing mercury levels: The Lumex CEM exhibited rise and fall times that varied substantially, usually ranging between about 30 seconds and 100 seconds.

Response to low levels of mercury: The Lumex CEM (with RA 915+ detectors in place) responded to as little as 0.57 µg/m^3 of mercury in flue gas, but the response to concentrations of 0.57 to 4.5 µg/m^3 averaged only about 55% of the nominal mercury concentration. Loss of mercury in the CEM's inlet system is one possible cause for the low response at low mercury levels.

Data completeness: Data completeness cannot be estimated well because of the changes in detectors used and the modifications made to Lumex inlet systems and the pyrolysis unit during the test.

Setup and maintenance needs: The setup and operation of the Lumex instruments was relatively simple, and the pyrolysis approach requires no chemical reagents or solutions and no external gas supplies. Routine maintenance

was limited to that required for the ice bath condensers in the sampling inlets. However, failure of the Lumex CEM early in the verification test required substitution of the RA 915+ detectors to continue the verification.

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