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 OXIDIZED MERCURY EMISSIONS**		
TECHNOLOGY NAME:	**Model MS-1/DM-5**		
COMPANY:	**Nippon Instruments Corporation**		
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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 Nippon Instruments Corporation Model MS-1/DM-5 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 MS-1/DM-5 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 each of two different 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 MS-1/DM-5 is a continuous monitor for elemental and oxidized vapor-phase mercury. The monitor consists of one Nippon MS-1 mercury speciation unit and two Nippon DM-5 mercury detectors. The DM-5 units each detect elemental mercury continuously by cold vapor atomic absorption without a preconcentration step. The MS-1 unit separates elemental and oxidized mercury by means of a wet scrubbing and chemical reaction system fed by a peristaltic pump. In the MS-1, filtered flue gas is first contacted with deionized water, which collects all oxidized mercury while leaving elemental mercury in the vapor phase. The gas containing the elemental mercury is passed directly to one of the DM-5 units for detection. The collected oxidized mercury is reduced to elemental mercury in a continuous liquid flow system, using a proprietary reagent. The elemental mercury produced is then swept from solution into a clean air stream and sent to the second DM-5 monitor. The two DM-5 monitors thus provide separate and continuous measurements of elemental and oxidized mercury in a parallel two-channel mode of operation. Oxidized mercury readings have a time lag of about one minute relative to the elemental mercury readings, due to the delay in the liquid flow system. Each DM-5 unit has a digital display in $\mu g/m^3$ of mercury, along with RS-232 output for recording data by a laptop computer or data logger. No external gas supplies are required. The MS-1 is 43 cm wide x 23 cm deep x 59 cm high (17 in. W x 9 in. D x 23 in. H) and weighs 16 kg (35 lbs.). Each DM-5 is 43 cm W x 22 cm D x 55 cm H (17 in. W x 8.7 in. D x 21.7 in. H), and weighs 25 kg (55 lbs). These instruments operate on 100 to 110 V AC.

VERIFICATION OF PERFORMANCE

Relative accuracy: During the first week of verification testing, the MS-1/DM-5 accuracy relative to the OH method was 13.2% for total mercury, at total mercury levels of about 7 to 8 $\mu g/m^3$. Testing showed relative accuracy of 11.0% for elemental mercury, and 54.9% for oxidized mercury, at elemental mercury levels of approximately 6 to 7 $\mu g/m^3$ and oxidized mercury levels of approximately 1 to 1.5 $\mu g/m^3$. In the second week, the relative accuracy was 39.1% for total mercury, at total mercury levels of about 70 to 120 $\mu g/m^3$. Relative accuracy of 50.4% for elemental mercury, and 49.1% for oxidized mercury, was found at elemental mercury levels of about 5 to 25 $\mu g/m^3$ and oxidized levels of about 45 to 110 $\mu g/m^3$.

Correlation with the reference method: The coefficient of determination (r^2) of the MS-1/DM-5 and OH elemental mercury results was 0.417 based on data from both weeks combined. The corresponding r^2 value for oxidized mercury was 0.937, and for total mercury was 0.938.

Precision at stable flue gas conditions: The precision, as percent relative standard deviation (% RSD), of the MS-1/DM-5 response for elemental mercury was within 10% in 11 of the 15 OH periods and within 15% in 14 of the periods. For oxidized mercury, precision was never within 10% RSD, but nine of the 15 periods showed precision within 15% RSD. For total mercury, precision was within 10% RSD in 10 of the 15 OH periods and within 15% in 14 of the periods. These precision results include both variability in the test facility and in the MS-1/DM-5.

Calibration/zero drift: Analysis of zero gas and elemental mercury standard gas results for the MS-1/DM-5 showed a 2.9% RSD for each DM-5 detector in repeated analysis of standard gas during the first week. During the second week, the results showed a 0.5% RSD for one DM-5 detector and 0.6% RSD for the other.

Sampling system bias: The bias in transport of elemental mercury through the Nippon inlet system was approximately -7%.

Interference effects of flue gas constituents: Elevated levels of sulphur dioxide, nitric oxide, and carbon monoxide had no effect on MS-1/DM-5 response to elemental or oxidized mercury in flue gas. The presence of hydrogen chloride reduced elemental mercury readings by about 25%, without a corresponding increase in the oxidized mercury readings of the MS-1/DM-5. The presence of chlorine reduced elemental mercury readings by about the same amount as did hydrogen chloride, but also caused a large increase in oxidized mercury readings. When all these gases were present at once in the flue gas, the MS-1/DM-5 readings were close to those seen with only mercury in the flue gas, indicating no substantial interference from the combination of these gases.

Response time to changing mercury levels: The rise and fall times of the MS-1/DM-5 were about 50 and about 35 seconds, respectively.

Response to low levels of mercury: The MS-1/DM-5 responded to as little as 0.57 $\mu g/m^3$ of mercury in flue gas, but the response to concentrations of 0.57 to 4.5 $\mu g/m^3$ averaged only about 65% of the nominal total mercury concentration.

Data completeness: Data completeness for the MS-1/DM-5 was 100%.

Setup and maintenance needs: No repair or maintenance of the MS-1/DM-5 was needed during the verification test. The unit produces 2 to 3 L/day of aqueous waste solutions, in the form of the reagents used to separate elemental and oxidized mercury.

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