

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION  
PROGRAM



## ETV Joint Verification Statement

**TECHNOLOGY TYPE: CONTINUOUS EMISSION MONITOR**

**APPLICATION: MEASURING MERCURY EMISSIONS**

**TECHNOLOGY NAME: MS-1/DM-5**

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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) used to measure mercury emissions. This verification statement provides a summary of the test results for the Nippon Instruments Corporation MS-1/DM-5 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 mercury ( $Hg^0$ ). 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 MS-1/DM-5, relative accuracy (RA) and correlation with the reference method were evaluated for  $Hg_T$ ,  $Hg_{OX}$ , and  $Hg^0$ . Precision (i.e., repeatability at stable test conditions) was assessed for  $Hg_T$ . 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 MS-1/DM-5 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 MS-1/DM-5 was provided by the vendor and does not represent verified information.

The MS-1/DM-5 monitors  $Hg^0$  and  $Hg_{OX}$  continuously in stack gas. This continuous mercury speciation analyzer consists of the MS-1 speciation unit and two DM-5 cold vapor atomic absorption detectors, one for  $Hg^0$ , the other for  $Hg_{OX}$ . The DM-5 detectors are connected to the MS-1 by a linking cable and a 6-millimeter (mm) (0.24-inch) Teflon tube. To measure  $Hg^0$ , sample gas and potassium chloride solution are mixed in a reaction tube to remove water-soluble  $Hg_{OX}$  and water-soluble organic mercury. Then, the gas and solution are separated in a gas/liquid-separating tube. After the gas is washed with a potassium hydroxide solution and dehumidified, the mercury is guided to the detector where gaseous  $Hg^0$  is measured. To measure  $Hg_{OX}$ , the solution containing  $Hg_{OX}$  and water-soluble organic mercury is guided to the lower part of the reaction tube to be mixed with a reducing solution of tin chloride. There,  $Hg_{OX}$  and the water-soluble organic mercury in the solution are reduced to gaseous  $Hg^0$ . The gas is washed by potassium hydroxide solution and dehumidified in an electronic cooler. The mercury then is guided to the detector for measurement.

The MS-1/DM-5 reports mass concentration in micrograms per cubic meter. It requires manual calibration and chemical reagents. Control keys are used to change sequence times, and a liquid crystal display shows the times. The MS-1/DM-5 operates on 100-volt AC power. The MS-1 is 480 mm (19 inches) wide, 230 mm (9 inches) deep, and 620 mm (24 inches) high and weighs 16 kilograms (35 pounds). Each DM-5 is 430 mm (17 inches) wide, 220 mm (nine inches) deep, and 550 mm (22 inches) high and weighs 16 kilograms (25 pounds).

## VERIFICATION OF PERFORMANCE

**Relative Accuracy:** The accuracy of the MS-1/DM-5 for measuring total vapor-phase mercury was verified by comparison to the results of 18 sampling runs using dual trains at  $Hg_T$  levels from <1 to 200 micrograms per dry standard cubic meter of flue gas. When all 18 OH runs were included in the comparison, an overall RA of 11.2% was found for  $Hg_T$ , and an overall RA of 10.1% for  $Hg^0$ .

**Correlation with Reference Method Results:** Correlation of the MS-1/DM-5  $Hg_T$  results with the OH results showed an  $r^2$  value of 0.987 when all 18 OH results were included. The  $r^2$  values for  $Hg^0$  and  $Hg_{OX}$  were 0.989 and 0.985, respectively.

**Precision:** Precision of the MS-1/DM-5 was estimated using two OH sampling periods having relatively stable introduction of mercury in aqueous waste into the TSCAI. The maximum variability attributable to the MS-1/DM-5 was 9.2% and 17.3% relative standard deviation (RSD) for these two periods.

**Sampling System Bias:** The bias introduced by the MS-1/DM-5 sampling system was evaluated by introducing Hg<sup>0</sup> standard gas both at the CEM analyzer and at the inlet to the sampling system. Sampling system bias results of 0.0 to 6.6% were found, at Hg<sup>0</sup> levels of about 7 to 45 µg/m<sup>3</sup>.

**Relative Calibration and Zero Drift:** Repeated analysis of zero gas and Hg<sup>0</sup> standards was used to assess the zero and calibration drift of the MS-1/DM-5 over the six-week field period. Analyses of zero gas produced a mean reading (± standard deviation) of 0.0 (± 0.1) µg/m<sup>3</sup>. Twenty-four analyses of an approximately 5.5 µg/m<sup>3</sup> Hg<sup>0</sup> standard over six weeks resulted in an RSD of 10.6%. Seven analyses of an approximately 36.5 µg/m<sup>3</sup> Hg<sup>0</sup> standard over three days resulted in an RSD of 2.4%. Eleven readings of an approximately 43.9 µg/m<sup>3</sup> Hg<sup>0</sup> standard over four weeks resulted in an RSD of 8.1% .

**Response Time:** Rise and fall times of the MS-1/DM-5 were determined at times of switching between zero and mercury standard gases. The 95% rise time was two minutes and the 95% fall time was approximately three minutes.

**Data Completeness:** The MS-1/DM-5 data completeness was 97.7% over the entire six-week field period.

**Operational Factors:** The MS-1/DM-5 operated reliably throughout the verification period. The most common maintenance needed was to prepare the chemical reagent solutions. The longest period of down time occurred due to a malfunction of the laptop data logger.

signed by Gabor J. Kovacs                      9/4/03  
Gabor J. Kovacs                                      Date  
Vice President  
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Battelle

signed by Gary J. Foley                                      9/30/03  
Gary J. Foley    Date  
Director  
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