Mercury Continuous Emission Monitors (CEMs)

The U.S. EPA Environmental Technology Verification (ETV) Program's Advanced Monitoring Systems (AMS) Center, operated by Battelle under a cooperative agreement with EPA, has verified the performance of seven continuous emission monitors[1] (CEMs) for measuring mercury emissions (**Figure 1**). Four additional monitoring technologies are currently in testing with reports to be final in early 2007. To address the health effects caused by mercury emissions from coal-fired plants, EPA recently issued the Clean Air Mercury Rule (CAMR). This rule requires coal-fired power plants, the largest remaining unregulated source of human-generated mercury emissions in the U.S., to reduce mercury emissions. The rule also will require power plants to monitor their mercury emissions using technologies like those verified by the ETV Program.

One of the test locations for mercury CEM verification

Technology Description and Verification Testing

CEMs for mercury are a relatively new technology category. They offer an advantage over conventional laboratory techniques (e.g., the Ontario Hydro method) in that they can provide continuous or frequent results through sequential readings at intervals of several minutes, and thus, they avoid the delay, labor, and cost associated with laboratory methods.

The ETV-verified CEMs determine elemental mercury vapor concentrations by atomic absorption (AA), atomic fluorescence (AF), or plasma atomic emission (AE). The CEMs use aqueous reagents or heated catalysts to reduce oxidized forms of mercury to elemental mercury for detection, allowing measurement of total vapor-phase mercury. Although some CEMs only measure total vapor-phase mercury (i.e., the sum of elemental and oxidized mercury vapor), others allow separate measurement of the elemental and oxidized forms. **Table 1** summarizes some of the performance data for the verified technologies. Additional information on the verification of mercury CEMs can be found at http://www.epa.gov/etv/verifications/vcenter1-11.html.

The verification testing was conducted in two phases. In the first phase, four of the technologies were tested under conditions simulating a) coal-fired flue gas, and b) municipal incinerator flue gas. The tests took place at a pilot-scale incinerator in Research Triangle Park, North Carolina, over a three-week period. In the second phase, five technologies (including two of the technologies tested in the first phase) were evaluated at a full-scale hazardous waste incinerator in Oak Ridge, Tennessee. In addition, the ETV Program is currently conducting a third phase of testing at a coal-fired power plant. The box on the right identifies CEMs and sorbent-based sampling technologies included in this third phase.

Mercury and Its Regulatory Background at a Glance

Mercury is a toxic, persistent pollutant that, after deposition from the atmosphere and methylation bioaccumulates in the food chain, particularly in fish. Mercury can cause adverse neurological health effects, particularly in young children and the unborn children of mothers who eat food with significant quantities of mercury.

The Clean Air Mercury Rule (CAMR), which EPA issued on March 18, 2005, creates a market-based cap-and-trade program that will reduce nationwide utility emissions of mercury. Under a cap-and-trade program, coal-fired power plants that reduce emissions more than is required receive allowances. They can then trade these allowances to sources that are unable to meet the requirement, or bank them for future use.

A cap-and-trade program, like that under the CAMR, must include reliable monitoring of emissions to ensure that reductions occur, allow for tracking progress, and lend credibility to the trading component of the program. Therefore, the CAMR requires coal-fired utilities that emit more than 29 pounds of mercury per year to collect mercury emission data continuously. To collect these data, the utilities can use either CEMs, like those verified by the ETV Program, or another long-term mercury sampling method, a sorbent trap monitoring approach.

Mercury Monitoring Technologies Included in the Third Phase of ETV Verification

Tekran Instruments, Series 3300 Mercury CEM
Thermo Electron, Mercury Freedom System
Environmental Supply Company, HG-324 sorbent-based sampling system
Apex Instruments, mercury sorbent-based sampling system

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[1]The ETV Program operates largely as a public-private partnership through competitive cooperative agreements with non-profit research institutes. The program provides objective quality-assured data on the performance of commercial-ready technologies. Verification does not imply product approval or effectiveness. ETV does not endorse the purchase or sale of any products and services mentioned in this document.

Selected Outcomes of Verified Mercury CEM Technologies

- Contributed to advancing mercury monitoring technology and resulted in improvements in monitors by the participating vendors
- Helped inform the development of the CAMR and could assist in future rule refinements
- Helped small vendors compete in the marketplace
- Verification of the mercury CEMs involved significant collaboration with state agencies (e.g., Massachusetts and Connecticut), the Department of Energy and Illinois Clean Coal Institute. These collaborations resulted in the sharing of scientific expertise among the agencies and enabled smaller vendors to participate in the tests.

Fig 1. ETV-Verified CEMs for Mercury (First Two Phases of Testing)

Envimetrics, Argus-Hg 1000 Mercury CEM: Uses AE spectroscopy with a proprietary catalytic converter that reduces molecular forms of mercury to atomic mercury. Total mercury can be measured during automatic operation, or both total and elemental mercury can be measured when manually operated.

OPSIS AB, HG-200 Mercury CEM: Uses a double-beam photometer to measure total or elemental mercury with a thermo-catalytic converter that forms elemental mercury from any oxidized mercury compounds to measure total mercury.

Nippon Instruments Corporation, DM-6/DM-6P Mercury CEM: Uses cold vapor AA with a catalytic process to measure total mercury.

PS Analytical, Ltd., Sir Galahad II Mercury CEM (verified in both phases): Uses AF to provide separate and continuous measurement of elemental and total mercury with a proprietary aqueous reagent to convert oxidized mercury to elemental mercury for total mercury measurement.

Nippon Instruments Corporation, AM-2 Elemental Mercury CEM: Uses cold vapor AA, with a distilled water scrubbing trap for removal of any oxidized mercury species, to measure elemental mercury.

Nippon Instruments Corporation, MS-1/DM-5 Mercury CEM (verified in both phases): Uses cold vapor AA to provide separate and continuous measurements of elemental and oxidized mercury, which are separated using a wet scrubbing and chemical reaction system.

CEM: Uses cold vapor AA to provide separate and continuous measurements of elemental and total mercury, with catalytic pyrolysis to decompose oxidized mercury to elemental mercury for total mercury measurement.

The price of the monitors ranged from $30,000 to $70,000 at the time of testing.

Table 1. Selected Performance of Verified CEMs for Mercury

Technology[A]	Average Relative Accuracy, %	Relative Precision, %	Response Time (95%)	Bias, %	Correlation[B]			Data Completeness
					Slope	Intercept	r^2	
First Phase								
A	58.2 to 71% (total mercury)	2.5 to 27%	30 to 100 seconds	-44.5 to -20.5%	not reported	not reported	0.621	Not estimated
B	14 to 23% (elemental mercury)	3 to 40.3%	One 13-minute cycle	7%	0.885	-0.212	0.973	100%
C (Phase I)	20.6 to 32.8% (total mercury)	1.8 to 24.7%	One 5- to 6-minute cycle	-4.9 to -0.3%	0.681	2.492	0.978	100%
D (Phase I)	13.2 to 39.1% (total mercury)	3.7 to 23.9%	35 to 50 seconds	-7%	0.607	3.92	0.938	100%
Second Phase								
C (Phase II)	59.8% (total mercury)	8.9 to 15.9%	One 5- to 6-minute cycle	2.8 to 6.9%	0.4973	6.8904	0.875	88.3%
D (Phase II)	11.2% (total mercury)	9.2 to 17.3%	2 to 3 minutes	0.0 to 6.6%	0.899	2.4969	0.987	97.7%
E	76.5% (overall)	10.1 to 22.1%	One 7-minute cycle	0.3 to 14.6%	0.3404	9.4121	0.839	92.7%
F	20.3% (overall)	9.1 to 10.9%	2 minutes	0.0 to 13.6%	0.8347	3.5033	0.953	97.5%
G	76.3% (overall)	12.5 to 43.3%	One 5-minute cycle	Not evaluated	0.3559	8.1695	0.935	65.8%

[A] Because the ETV Program does not compare technologies, the performance results shown in this table do not identify the vendor associated with each result and are not in the same order as the list of technologies in Figure 1.
[B] Correlation data shown are for total mercury, except technology B, where results shown are for elemental mercury.

Note: In each phase of verification testing, the Ontario Hydro method was used as the reference method for establishing the performance of the tested technologies. The performance parameters verified included the following: accuracy relative to the Ontario Hydro method, correlation with that method, precision (i.e., repeatability), bias, calibration/zero drift, response time, interferences, data completeness, and other operational factors. The ETV Program found that the average relative accuracy for the monitors ranged from 11.2 to 76.5%. A result of 0% indicates perfect accuracy relative to the reference mercury concentration. The relative precision ranged from 1.8 to 43.3%. A result of 0% indicates perfect precision. A higher r^2 value indicates a higher correlation with the standard test method over the range of concentrations tested.

References

U.S. EPA, Mercury, http://www.epa.gov/mercury/ .

U.S. EPA, 2006. ETV Case Studies: Demonstrating Program Outcomes, Volume II . EPA/600/R-06/082. September 2006. (Primary source)

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