

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Emission Monitor

APPLICATION: MEASURING MULTIPLE METALS IN STACK GAS

TECHNOLOGY NAME: XCEM Multi-Metals Continuous Emission Monitor

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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 permittees; 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 (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 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 the Cooper Environmental Services X-ray based continuous emission monitor (XCEM). This verification statement provides a summary of these test results.

VERIFICATION TEST DESCRIPTION

The objective of the verification test was to quantitatively evaluate the performance of the XCEM under real-world conditions. Verification testing took place at the Tooele Army Depot (TEAD) Building 1320 deactivation incinerator. The XCEM was tested for its ability to measure five elements found in the feedstream—antimony (Sb), barium (Ba), cadmium (Cd), chromium (Cr), and lead (Pb), as well as arsenic (As), mercury (Hg), nickel (Ni), and zinc (Zn). Except for Pb, the stack gas levels of these target metals were prepared by spiking metal solutions into the stack gas at the base of the stack. Stack gas metal concentrations were simultaneously determined by the XCEM and by two EPA Method 29 (M29) sampling trains. The M29 trains sampled for two hours, while XCEM data, which are recorded every 20 minutes, were averaged over each M29 run. A total of 13 dual M29 runs were performed by the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) Air Quality Surveillance Program. In all cases, when reference method data were being taken, the spiking of the indicated metals was held constant throughout the entire sampling period to allow comparisons of XCEM data to reference method data under constant conditions. CHPPM's Directorate of Laboratory Services conducted laboratory analysis of the M29 sampling trains. The test activities provided data for verifying the relative accuracy (RA); correlation with reference method; precision; span, zero, and internal standard drift; bias; and response time. RA was determined by comparing M29 results to simultaneous XCEM results averaged over the M29 sampling periods. The RA of the XCEM with respect to M29 was assessed by

$$RA = \frac{|\bar{d}| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\%$$

Where d refers to the difference between corresponding M29 and XCEM results, n is the number of runs, and \bar{x} is the average M29 result. S_d denotes the sample standard deviation of the differences, while t_{n-1}^{α} is the t value for the $100(1-\alpha)^{\text{th}}$ percentile of the distribution with $n-1$ degrees of freedom. The RA was determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). Correlation of XCEM and M29 results was calculated using the same data used to calculate RA. Precision of the XCEM was calculated in terms of the percent relative standard deviation (RSD) of successive XCEM readings during periods of stable metal concentrations.

Drift was checked by automated daily XCEM span and zero QA measurements. Bias relative to M29 was identified using EPA Method 301 (M301) protocols. Response time was determined as the time between the start of one XCEM sampling period and the beginning of the next sampling period.

Battelle and EPA provided QA oversight of verification testing. Battelle QA staff conducted a data quality audit of 10% of the test data, and Battelle's Quality Manager performed an internal technical systems audit of the verification test during testing at the TEAD incinerator. Battelle, with the assistance of CHPPM staff, performed a series of performance evaluation audits to check the quality of reference measurements made in the verification test. A technical systems audit report was submitted to EPA Quality Management staff.

TECHNOLOGY DESCRIPTION

The XCEM extracts a sample of stack gas and concentrates the metals of interest on a chemically treated filter tape. Following collection, the filter tape advances, moving the sample spot to an analysis area where a laboratory-grade X-ray fluorescence (XRF) instrument is used to determine metal mass. The system is automated and can produce concentration data every 10 to 20 minutes for 19 elements of interest. The XCEM components include the extraction system, the sampling and analysis system, and the control system. The XCEM extraction system collects a representative stack gas sample from the stack and transports the sample to the filter tape. Upon entrance into the XCEM housing, the stack gas passes through a heat-traced stilling chamber that expands the tubing diameter and slows the gas velocity. An eductor, located downstream of the stilling chamber, is used to pull the stack gas through the extraction system. Of the two to three standard cubic feet per minute that pass through the stilling chamber, a sub-sample of approximately 0.8 liter per minute is extracted and directed through a filter tape, concentrating the metals sample for analysis. Following filtration, the stack gas is subsequently transported to the XCEM chassis

where drying and volume determination take place. The excess (i.e., unfiltered) stack gas is transported out of the stilling chamber through a flowmeter and is vented or returned to the stack. The sampling cassette holds a four-week supply of filter tape on a reel-to-reel system that is automated to accurately move the tape from the sampling to the analysis position. Sampling and analysis occur simultaneously, resulting in a continuous monitoring system that produces metal concentration values every 10 to 20 minutes. Metal mass on the filter is determined using a modified ThermoNoran QuanX energy dispersive XRF analyzer. The XCEM has an automated check for internal standard drift that measures a palladium (Pd) standard with each XCEM analysis.

The XCEM is controlled by a personal computer using a custom WonderWare software interface. All day-to-day functions of the XCEM are automated, including flow and temperature control, concentration determination, and QA routines. Flow, temperature, concentration, pressure, and error messages are automatically recorded in a secure database. The data can be imported into Excel or an equivalent program for subsequent analysis. Flows, temperatures, concentrations, and pressure are logged in real time on the screen computer monitor.

VERIFICATION OF PERFORMANCE

Relative Accuracy: The XCEM relative accuracy for Cd, Cr, and Ni was less than 26% (less than 20% calculated for nine runs). The remaining metals (As, Ba, Hg, Pb, Sb, and Zn) had RA values between 37 and 67%. The RA for Pb was 36.7% calculated for nine runs. The reported XCEM concentrations were uniformly high for As. The XCEM was consistently low for Zn, Ba, and Sb. XCEM Hg readings were very low at the start of each test day, rising gradually until they stabilized. The best agreement of XCEM and M29 Hg results (within about 20%) was found with M29 runs conducted late in the test day, when XCEM readings had stabilized.

Correlation with Reference Method: Correlation of XCEM and M29 results was calculated for five elements that varied enough during the test to justify this comparison. For Ni, Pb, Sb, and Zn, r^2 values exceeding 0.95 were found, although the r^2 value for Pb decreased to 0.75 when the high Pb levels in Runs 1 and 2 were excluded. For Hg, an r^2 value of 0.39 was found.

Precision: The XCEM's precision ranged from 6 to 21% over the nine target metals. This precision includes variability in the metals injection and the test facility, as well as in the XCEM itself.

Span, Zero, and Internal Standard Drift: XCEM span and zero drift were assessed over the four test days. Daily span readings of Cd, Cr, Hg, and Pb exhibited RSD values of 0.47 to 2.33% and no significant trends over time. Zero readings for all four elements were near or below the respective detection limits on all test days. The RSD of the XCEM's Pd internal standard was approximately 2.5%.

Bias: The XCEM results showed statistically significant positive or negative bias relative to M29 results for all the target metals, based on M301 procedures.

Response Time and Other Parameters: The XCEM functioned in an automated manner and automatically recorded concentrations, temperatures, flow rates, and QA data. It exhibited no mechanical problems, had an effective up time of 100%, and a response time of 20 minutes.

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