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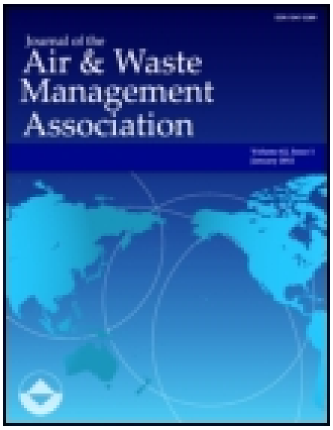

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Relative Accuracy Testing of an X-Ray Fluorescence-Based Mercury Monitor at Coal-Fired Boilers

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ABSTRACT

The relative accuracy (RA) of a newly developed mercury continuous emissions monitor, based on X-ray fluorescence, was determined by comparing analysis results at coal-fired plants with two certified reference methods (American Society for Testing and Materials [ASTM] Method D6784-02 and U.S. Environment Protection Agency [EPA] Method 29). During the first determination, the monitor had an RA of 25% compared with ASTM Method D6784-02 (Ontario Hydro Method). However, the Ontario Hydro Method performed poorly, because the mercury concentrations were near the detection limit of the reference method. The mercury in this exhaust stream was primarily elemental. The second test was performed at a U.S. Army boiler against EPA Reference Method 29. Mercury and arsenic were spiked because of expected low mercury concentrations. The monitor had an RA of 16% for arsenic and 17% for mercury, meeting RA requirements of EPA Performance Specification 12a. The results suggest that the sampling stream contained significant percentages of both elemental and oxidized mercury. The monitor was successful at measuring total mercury in particulate and vapor forms.

IMPLICATIONS

Currently available mercury continuous emission monitors are based on cold vapor atomic absorption or fluorescence spectroscopy, which only measure elemental mercury directly and require conversion for other forms. However, mercury speciation varies so that some sources may have a significant percentage in the oxidized and particulate forms. Whereas X-ray fluorescence is a reliable and accepted method for measuring metals, it has only recently been used for quantifying stack emissions from combustion sources on a continuous basis. An X-ray fluorescence–based continuous monitor can accurately measure total mercury under field conditions, regardless of the ionic state and phase of the mercury.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) is developing regulations for coal-fired boilers as part of Title III of the 1990 Clean Air Act Amendments in the form of a National Emission Standard for Hazardous Air Pollutants (NESHAP),[1] which will regulate mercury. In addition, the Clear Skies Bill[2] would allow mercury emissions trading if passed. Section 405 of this bill would require continuous emissions monitors (CEMs) for emissions accountability. Recently, EPA issued the Clean Air Mercury Rule (CAMR),[3] which regulates coal-fired boilers under Sections 110(a)(2)(D) and 111 of the Clean Air Act. The CAMR requires continuous monitoring but allows for sorbent sampling as an alternative. Previously, continuous monitoring has not been feasible, because available mercury CEM technologies lacked maturity. Because of recent technical improvements, CEMs may now become a preferred method, and OAQPS may also include requirements for the use of mercury CEMs as part of the NESHAP. Two additional drivers for CEMS are state agency requirements for 90% reduction from mercury in coal-fired power plants, and EPA consent decrees with several plants that are requiring that CEMS be installed. Implementation of these regulatory actions will require EPA to adopt CEM performance specifications.

EPA has finalized Performance Specification 12a (PS12a), "Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Monitoring System in Stationary Sources."[4] According to these specifications, an instrument is accurate if it performs with a relative accuracy (RA) of ≤20% relative to a standard method. RA is defined by these specifications as the absolute mean difference between the pollutant concentration(s) determined by the monitor and the value determined by the reference method plus the 2.5% error confidence coefficient of a series of tests divided by the mean of the reference method tests or the applicable emission limit. The equation for RA is as follows:

$$\mathrm{RA} = \frac{(|\bar{d}| + |CC|)}{RM} \times 100 \qquad (1)$$

where

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad (2)$$

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \qquad (3)$$

RM is the average reference method value, S_d is the standard deviation, and n is the number of datapoints.[4]

There has been limited success with multimetal monitors in meeting RA requirements of the previously proposed Performance Specification 10 (PS10).[5] Most multimetal monitors are based on laser-induced breakdown spectroscopy[6] or inductively coupled plasma (ICP).[7] Only one of these monitors, an ICP unit, has had success in field conditions.[7] However, that monitor was not tested for mercury. Currently available mercury continuous emission monitors are based on atomic fluorescence or cold vapor atomic absorption (CVAA) spectroscopy.[8] There are two significant disadvantages to these methods: they can only measure elemental mercury and are subject to interference from particulates and gases in flue gas streams. Recent tests have shown some success for these monitors during RA testing, but test data are limited, and further tests with oxidized forms of mercury are needed.[9–11] There has been wide variability in species distribution at coal-fired boilers,[12] and it is important to measure all forms of mercury.[8]

X-ray fluorescence (XRF) technology has been used since the 1960s and has proven to be a reliable method for metals quantification. The basic approach of the XRF monitor (Xact) is to draw a continuous representative sample of stack gas to a stilling chamber where a smaller metered sample is extracted and passed through a filter tape that collects metals in the particulate and vapor phases. After sampling, the sample filter is analyzed by an XRF analyzer where the masses of multiple metals can be measured with detection limits between 0.1 and 3 μg/dry standard cubic meter (dscm). The monitor operates in a batch mode where the sample is drawn over a specified time while the previous sample undergoes analysis. It meets the sampling and response time requirements for a batch CEM as proposed by PS10.[5] One of its advantages over other available methods is that the analysis is nondestructive so that the filter tape can be archived and independently verified by reanalysis at a later date. In addition to the nondestructive analysis, the mercury Xact offers other benefits, such as infrequent calibration with solid calibration rather than the use of gas-phase standards, minimal sensitivity to gas stream constituents, and minimal operator interactivity and training.

The Xact monitor was originally developed as a multimetal continuous emission monitor[13] and first tested as an automatic online system at an Army demilitarization incinerator during two separate testing periods, May 2001 and May 2002.[14,15] During the first test, the monitor met the previously proposed PS10 RA requirements for cadmium (Cd), chromium (Cr), and nickel (Ni), but not mercury (Hg). Further analysis indicated that there was Hg lost in the transport line because of inadequate heat tracing. During the second test, the monitor met the RA requirements for lead (Pb), Cd, Cr, barium (Ba), and antimony (Sb). Again, it did not meet the requirements for Hg, but there was clear indication of Hg loss from reference method (M29) samples and analysis errors.[15,16] Since these tests were conducted, further development has yielded a chemically treated resin tape that is capable of capturing particulate and vapor-phase Hg,[17,18] and the Hg-specific monitor was developed by refining the Hg analysis, resulting in an improved detection limit of 0.1 μg/dscm. Because the Hg monitor analyzes the samples with one of three excitation conditions used by the multimetal monitor, it is also capable of measuring Pb, copper (Cu), zinc (Zn), arsenic (As), selenium (Se), bromine (Br), and Ni.

In November 2004, the multimetal Xact underwent comparison testing monitored by EPA against a quantitatively spiked aerosol. The aerosol containing Hg, Pb, Cd, Cr, and As was injected into the Xact under laboratory conditions at four concentration levels ranging from 20 to 120 μg/dscm. The Xact concentration measurements for all five metals, including Hg, were within 5% of the theoretical spiked concentrations. The test was then repeated in the field, in 2005, with the same metals spiked into a flue gas from a Hazardous Waste Combustor in Lafayette, IN. In this test, the Xact concentration measurements for all five metals were within 13% of the theoretical spiked concentration.[19]

In July 2003, the Hg Xact was tested against the EPA Ontario Hydro Method (OHM) during a test at a coal-fired power plant sponsored by the EPA Emissions Measurement Center.[9] The purpose of this test was to assess the performance of commercially available Hg CEMs at a coal-fired power plant. After this test, improvements were made to improve the transport and heat tracing. The improved Hg Xact was installed at the Iowa Army Ammunition Plant (IAAP) coal boiler and tested against EPA Reference Method 29 (RM29) during January 2005. The comparisons between the reference methods and the Xact for these two tests are presented.

MONITOR DESCRIPTION AND OPERATION

The Hg monitor has three integrated sections: sampling and analysis, flow measurement and control, and control/user interface. When sampling, the Hg monitor draws <1 standard L/min of gas from a sampling chamber or manifold through a heated transfer line. The gas sample then passes through the injector tube where it is quickly cooled to <90 °C and pulled through a sealed 10-mm-diameter spot on the treated filter tape. The gas sample then passes through an acid absorber cartridge and water trap before the flow rate is measured with a mass flow meter. The sample is taken for a specified period of time (10–30 min), and then the tape is advanced 50 mm to position the sample spot in the X-ray analysis region where analysis begins. Meanwhile, another sample is taken at a new spot on the filter tape. By design, the analysis time is equal in duration to the sampling time. Figure 1 shows a detailed sketch of the hardware in the sampling and analysis section.

Accurate measurement of the sample relies on quantitative trapping of all phases of metals on the filter tape. Because of the high vapor pressure of elemental and oxidized species of Hg, a conventional filter only traps the particulate phase. This filter tape has been treated with an oxidant and has demonstrated Hg trapping efficiencies in excess of 99% at conditions similar to that seen in coal-fired boilers.[17]

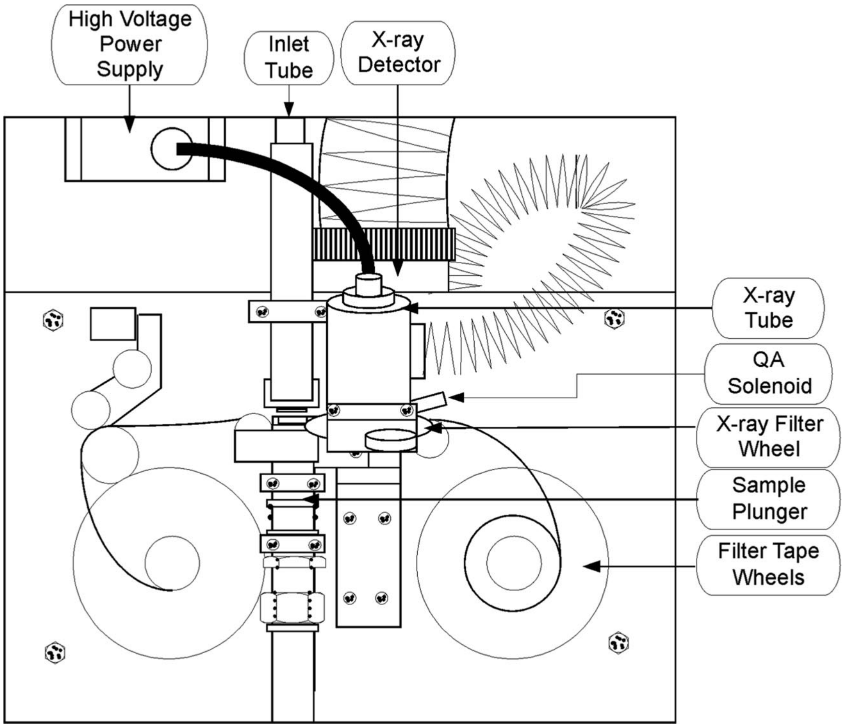

Figure 1. Sketch of Xact sampling/analysis equipment.

During analysis, the sample deposit is exposed to tube-generated X-rays, and the excited characteristic X-rays of Hg and other elements are detected by an energy-dispersive XRF analyzer. The analysis is controlled to sample one condition at 0–20 KeV. The measured X-ray intensity is proportional to the elemental mass in the sample. The overall concentration is determined by dividing the measured mass by the measured sample volume. The analysis is nondestructive so that the filter samples can be stored and reanalyzed for quality assurance or verification.

The Xact was calibrated in the laboratory before each field test. For the OHM test, it was calibrated against thin film standards and checked with a standard gas. For the RM29 test, it was calibrated against thin film standards and checked with a quantitative aerosol generator.[19] Once in the field, the calibration was checked with thin-film standards, and an energy alignment was conducted. The Xact detector receives a response across a broad range of energy levels and assigns all responses within a specified energy range to Hg. For this reason, it is critical that the range be correctly identified. Over time, this range can be shifted, and an energy alignment is needed. The energy alignment process is conducted by introducing a Cu standard to the detector. The Xact automatically determines the energy peak for the standard and evaluates whether this peak matches the theoretical energy location (8.046 kV). If a shift has occurred, then all of the peaks are realigned to match the peak of the Cu standard.

Operation is controlled by a single personal computer using custom-designed software. Most operating functions are automated, such as flow control, temperature control, detection analysis, and quality assurance functions. Data recorded includes flow rate, temperature, concentration, pressure, and potential error messages. The measurements are also shown on the monitor display screen during operation. A sample of Ni is fixed in the analysis area for a calibration check with each analysis. The mass flow controller data is automatically checked daily through comparison with a second onboard flow meter.

Modifications to the monitor were implemented during the period between the two reference method tests. The insulation and heat tracing was extended into the monitor as close as possible to the filter tape (10 cm). The flow control system was optimized, the embedded firmware and software were updated, and the method of chemically treating the filter tape was changed. The filter tape was originally pretreated with a proprietary oxidant and then placed in the monitor. The new method involves the addition of a dopant module that injects a very small amount of oxidant into the inlet tube just above the tape so that only the filter sample spot is treated.[18] A diagram of the layout of the monitor placed into a custom cabinet for use in the field as modified for the RM29 test is shown in Figure 2.

OHM COMPARISON TEST

Experimental

Reference method testing occurred at a nondisclosed commercial, coal-fired power plant during July 24–31, 2003. The plant was built in 2001 and has a 600-MW capacity with state-of-the-art pollution controls. These controls included ammonia injection and selective catalytic reduction for nitrogen oxides (NO_x), a lime spray dryer absorber for sulfur dioxide, and a fabric filter for particulates. The coal burned at this plant is from the Powder River Basin, Jacob's Ranch site. Five Hg CEMs, including the Xact, participated in this test. The other

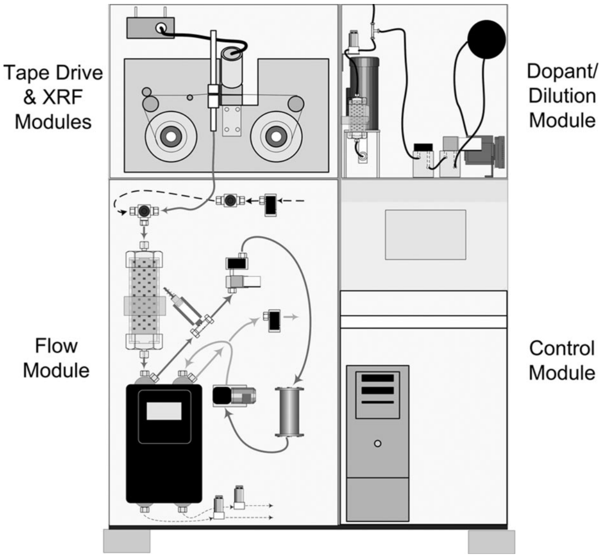

Figure 2. Schematic of Xact components placed in field cabinet.

four were based on CVAA. Midwest Research Institute (MRI) conducted the OHM reference method testing.[9]

All of the sampling was conducted along a row of ports in a section of duct upstream of the stack and directly downstream of the exhaust fan. The flow was determined to be turbulent at the test location and ~82 °C. A heated sample line from one port was fed to a manifold that provided sampling for the Xact and two other CEMs. The OHM and CEM probes were the same length and positioned directly across from each other in the duct. The OHM was performed according to American Society for Testing and Materials (ASTM) D 6784-02.[20] Each sample was 2 hr in duration, and samples were stored at ~0 °C at the test site. The sample gas was drawn from the duct through a heated probe, a heated filter box, heated Teflon sample line, and to the manifold as shown in Figure 3.[9] The Xact pulled the sample gas from this manifold at a flow rate of ~0.2 L/min. The sample collection time set for this test was 30 min.

On initial installation and before testing, a series of seven blind elemental Hg standard gas tests were run with the Xact. The Xact-reported concentrations were within 1% of the certified standard concentration of 8 μg/m^3. Twelve OHM test runs were conducted over the testing period with the coal-fired plant operating under normal conditions. There was no spiking involved during the OHM tests, so that all of the Hg measured during the testing was emitted by the plant.

Results and Discussion

Typical measured concentrations for both the Xact and the OHM ranged from 1 to 3 μg/dscm. Overall, the RA of the instrument compared with the OHM is 25%, which is similar to the RAs of the other CEMs included in the test, which range from 15% to 40%.[9] Table 1 and Figure 4 show the Xact and OHM Hg concentration results.

Duplicate OHM trains were used for all 12 of the runs. On average, the OHM duplicate trains differ from each

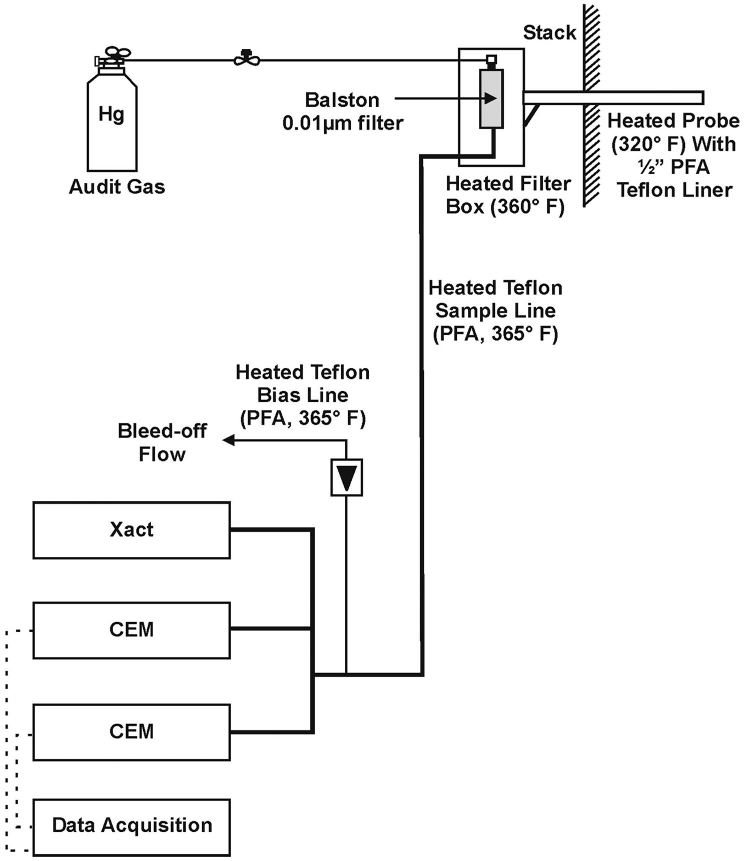

Figure 3. Stack gas delivery during OHM tests.

other by $\sim$25%, with three runs showing a difference of $>$50% (Figure 4). Concentrations for all but one OHM run are <3 μg/dscm. According to the standard method, the OHM precision is typically $\sim$34% when the Hg concentrations are <3 μg/dscm, so these precision results are typical or slightly better than historical OHM precision levels.[20] The magnitude of this imprecision, however, is on the same order as the desired RA. Thus, a large uncertainty exists in determining the RA at these low concentrations attributed in part to the imprecision of the OHM. For example, the RA of the OHM duplicate trains when compared with each other is 22%, only slightly better than the 25% obtained in comparison with the Xact. Figure 4 shows that the Xact data falls within the values for the two OHM trains in 4 of 10 runs. In addition, the mean Xact concentration was within 2% of the mean OHM concentration.

Table 1. Reported Xact and OHM concentration results (μg/dscm).

Run	OHM-A	OHM-B	OHM-Avg.	Xact
1	1.44	1.32	1.38	—
2	3.39	3.38	3.39	1.61
3	2.27	2.38	2.33	2.07
4	1.83	2.19	2.01	1.61
5	1.53	1.26	1.40	1.27
6	1.79	0.99	1.39	1.18
7	1.46	0.82	1.14	—
8	1.56	1.24	1.40	1.69
9	1.24	2.25	1.75	1.55
10	1.17	1.63	1.40	1.51
11	1.51	1.32	1.42	2.30
12	1.25	1.20	1.23	1.72
Average	1.70	1.67	1.68	1.65

Hg was present in the ionic form at an average of 2.1% by mass, with a maximum of 4.2%.[9] This low percentage of ionic Hg limits the applicability of these results for use at coal-fired boilers that emit a higher percentage of Hg in the oxidized form. This is an unfortunate result of this test, particularly for CVAA-based CEMs because of their inherent challenge to measure oxidized Hg.[10]

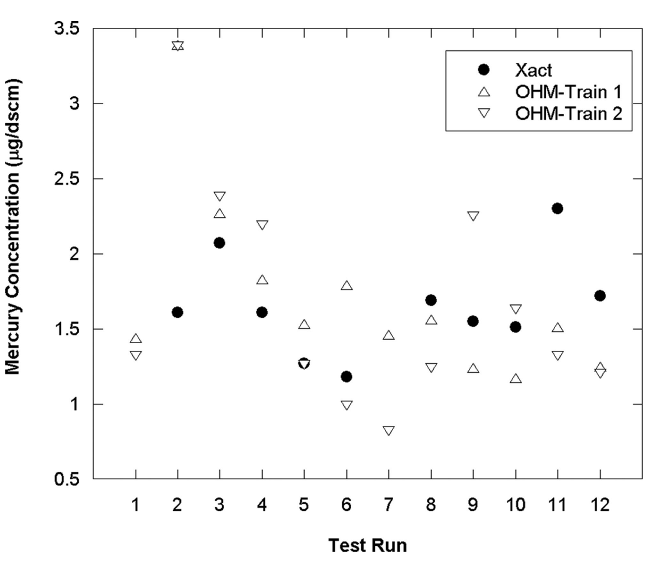

Figure 4. Comparison of Xact and OHM train results.

The Xact reported concentrations for 10 of the 12 OHM runs conducted. During run 1, the Xact experienced heater problems and developed a leak in the connection to the manifold, which was not repaired until the run was completed. During run 7, the instrument was accidentally turned off during the run. In addition to the leak in run 1, the instrument experienced problems with heat tracing throughout the tests. The inlet tube immediately before the tape was heat traced but not thoroughly insulated because of its close proximity to the X-ray tube. The water content of the stack was higher than expected, which led to periodic condensation in the tube with a resultant drop forming on the filter. Because the filter tape is hydrophilic, the droplet resulted in temporary severe pressure drops and flow control issues. However, it is not certain that the condensation impacted the tape collection efficiency, but the condensation on the walls could be a potential sink for oxidized Hg.

After OHM testing, the Xact was again injected with the calibration gas, but the Xact response was significantly lower than expected. It is suspected that the Xact may have experienced some problems with the calibration gas because of the heat-tracing problem. On occasion, the Xact also reported blank concentrations of ≤ 1 μg/dscm. The high blank values could not be duplicated by the instrument after it was removed from the test site. These results prompted the improvements in the heat tracing of the inlet tube as discussed earlier.

RM29 COMPARISON TEST

Experimental

Reference method testing occurred at IAAP from January 10 to January 12, 2005. The plant has two stoker boiler units, each with a power rating of 100 million British thermal units (MMBTU)/hr. The air pollution control system (APCS) consists of an electrostatic precipitator.

The coal burned at IAAP is from Eastern Kentucky. Two random samples from the 2003 coal used in this plant were tested for Hg content using XRF and CVAA for the analysis. The concentration was <0.02 ppm by weight, which is lower than the typical Hg concentration. In a report submitted to EPA, Hg concentrations from a wide selection of coal samples and based on data collected since 1993 range from 0.02 ppm to 0.3 ppm, with $>$75% having concentrations <0.1 ppm.[21] The nondetectable Hg content in these samples gave an indication that Hg emission levels may be close or even below M29 detection levels.[22] The imprecision and inaccuracy of M29 near the detection level can limit RA tests. Therefore, Hg and As were spiked into the stack gas during testing. Although the spiking was nonquantitative, it was able to consistently produce Hg concentrations between 20 and 40 μg/dscm and As concentrations of $\sim$20 μg/dscm. Spiking was conducted using a nebulizer to aerosolize a 5% nitric acid solution containing As nitrate and Hg nitrate at a rate of 0.2 mL/min.

The monitor was positioned in an enclosed temperature-controlled shed that was located $\sim$3 meters from the base of the stack and 10 meters below the sampling point. The sample was drawn from the horizontal rectangular section of ductwork that connects the APCS to the stack. The sampling was single-point nonisokinetic at a

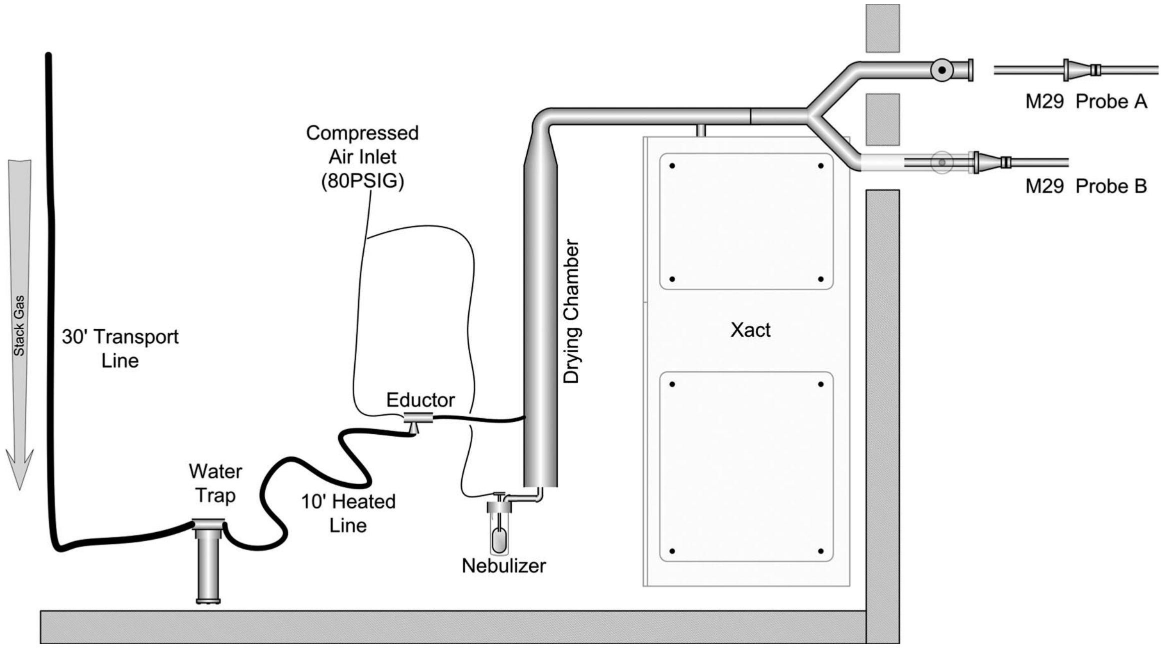

Figure 5. Test design for IAAP M29 testing.

rate of ~15 L/min. The sample was transported through heat-traced polytetrafluoroethylene (PTFE) tubing at ~40 °C to a water trap then through a heated line (82 °C) to an eductor, where it was combined with ~20 L/min of dry and filtered compressed air before it entered a heated drying chamber (140 °C). The nebulized spiking solution was injected into this chamber for a combined flow of ~40 lpm. The spiked, diluted, and heated sample then flowed into a custom manifold, where the majority was extracted by the Xact (0.7 L/min) and the two M29 sample trains (36 L/min). This setup, as shown in Figure 5, allowed for the best comparison of methods. The spiking setup and custom manifold were installed strictly for the reference method testing. The low temperature and water removal in the sample line during the testing were necessary, because the spiking solution needed to evaporate into the sample stream without condensation.

Twelve M29 runs were conducted during the 3-day test with 4, 5, and 3 runs completed on the first, second, and third days, respectively. The M29 sample train pairs used a custom glass-lined, heat-traced probe and a standard front and back half to sample a constant volume for each 2-hr test.[22] For these tests, the Xact sampling period was 30 min, and the M29 trains commenced sampling at the start of an Xact run and completed sampling at the end of the fourth Xact run. Because there has been evidence of Hg lost from M29 filters between sampling and analysis, the exposed M29 filters were kept refrigerated until analysis.[15,16] M29 trains were operated by the U.S. Army Center for Health Promotion and Preventive Medicine.

Results and Discussion

The Hg concentrations measured by M29 ranged from a low of 23 to a high of 43 μg/dscm. In this concentration range, the accuracy and precision is expected to be on the order of 10–15%.[23,24] In fact, the paired M29 train results were in excellent agreement, exhibiting an average difference of <4% for Hg and 3% for As, and their means differed by <1% for both elements. Because they generally agreed, the comparison with the Xact is more meaningful than the OHM comparison.

The condensation problems seen during the OHM comparison test seemed to have been corrected, and the Xact operated reliably for all 12 of the runs with no mechanical problems. In runs 1 and 2, however, the Xact energy alignment was not completed, and the results are not considered valid. Therefore, runs 3–12 were used for evaluating the Xact accuracy. This is acceptable, because PS12a specifies that the best nine runs at a minimum can be used to determine the accuracy of a candidate monitor.[4]

The M29 results were reported in two different ways: counting nondetects as the reporting limit value (RLV) and counting nondetects as zero concentration. Counting the nondetects as the RLV was selected as the chosen data set before comparison with the Xact data. The choice is potentially significant, because the concentration can be biased high when the nondetects are assumed at the RLV and low when they are assumed zero. For Hg and As, the difference between these concentration data sets is ≤1%, giving the chosen set a slightly greater RA result.

Table 2 and Figures 6 and 7 compare M29 and Xact results for runs 3–12. In Figures 6 and 7, the four Xact concentration data reported for each M29 run are shown, and the M29 concentrations are shown as the average values between the two trains. The Xact and M29 concentrations are in good agreement for these runs, with the average Xact-to-M29 Hg concentration ratio within 9% and the average Xact-to-M29 As concentration ratio within 13%. RA for Hg and As is calculated as equal to 17% and 16%, respectively. Both of these values meet the PS12a and previously proposed PS10 RA requirements for multimetals CEMS.

Table 2. Comparison of M29 and Xact concentrations for valid runs (μg/dscm).

	Hg					As				
	M29 Train					M29 Train				
Run	A	B	Average	Xact	Xact/M29	A	B	Average	Xact	Xact/M29
3	33.6	33.0	33.3	27.4	0.82	27.3	28.5	27.9	20.6	0.74
4	38.4	39.4	38.9	30.5	0.78	25.7	25.3	25.5	20.1	0.79
5	29.2	26.7	28.0	26.1	0.93	20.7	21.4	21.1	18.6	0.88
6	40.9	42.8	41.8	39.0	0.93	24.5	24.2	24.4	22.3	0.92
7	37.5	37.7	37.6	36.4	0.97	19.5	19.4	19.4	16.7	0.86
8	31.1	31.8	31.5	34.7	1.10	19.2	18.8	19.0	17.2	0.91
9	39.0	38.8	38.9	32.7	0.84	19.2	17.1	18.2	16.5	0.90
10	26.9	25.0	25.9	24.4	0.94	21.8	21.1	21.5	18.8	0.87
11	32.5	33.3	32.9	27.1	0.82	21.5	20.6	21.0	19.0	0.90
12	25.0	23.4	24.2	22.2	0.92	18.7	17.9	18.3	16.3	0.89
Average	33.4	33.2	33.3	30.0	0.91	21.8	21.4	21.6	18.6	0.87

Although the Xact data met EPA-defined RA criteria, it is likely that the 9–13% difference between the two methods is attributable in part to the systematic bias in the Xact concentrations. In the case of M29, two separate trains were used with independently determined volumes, and two separate analytical procedures were used to determine elemental mass. As such, only a bias in M29 flow calibration could explain a systematic bias in both elemental measurements, which is unlikely. It is more likely that the Xact data are systematically biased because of either a volume bias or a biased XRF geometry factor used for both elemental determinations. The XRF geometry factor is a constant that reflects the distance for the triangle between the X-ray tube, filter tape, and detector. This factor reflects the impact of distance and angles on the detector response.

The consistency between the Xact-to-M29 ratios for Hg and As suggests that the Xact had 100% trapping efficiency for the vapor-phase Hg. M29 results indicate that ~95% of the Hg was in the impingers portion (back half) of the sample train (Table 3), suggesting that it was in vapor phase. In contrast, essentially all of the As was on the particulate filter (front half), which is only capable of capturing particulate-phase metals. The consistent ratios indicate that the Xact captured both metals equally and that there is no indication of loss because of filter trapping inefficiency for the vapor-phase Hg. This shows that the Xact is capable of capturing and measuring both the particulate- and vapor-phase metals, including elemental Hg.

It is generally accepted that most of the Hg captured in the permanganate impinger of the M29 train will be elemental and that in the nitric acid impinger will be oxidized.[25] It is also assumed that Hg captured as particulate in the front half is oxidized. This is not accepted as an exact speciation method but allows for a qualitative analysis. Table 3 suggests that significant quantities of both forms of Hg were present, where, on average, 20% of the total Hg was found in the front half and M29 nitric acid impingers combined and 74% in the permanganate impingers. The amount of presumed oxidized Hg is significant enough to claim its capture and detection. More importantly, the monitor was able to accurately measure the Hg concentration in the exhaust when both forms of Hg were present and significant.

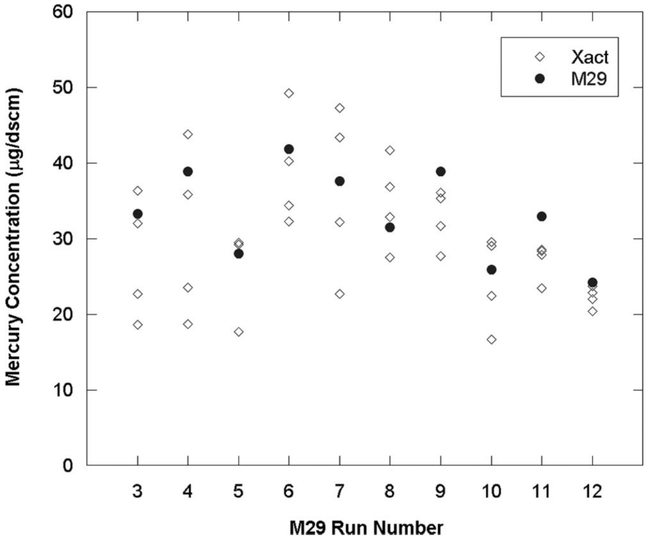

Figure 6. Comparison of Xact data and average M29 results for Hg.

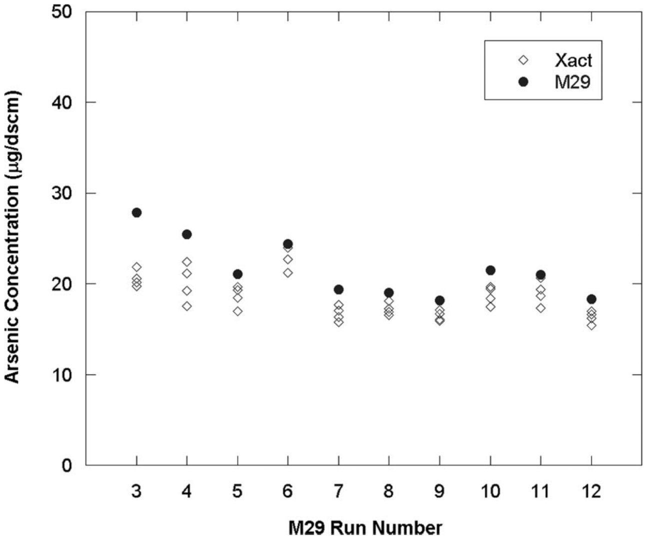

Figure 7. Comparison of Xact data and average M29 results for As.

Table 3. Percentage of total measured Hg in front half and solution impingers of M29 sample trains.

	%Hg in Front Half		%Hg in Nitric Acid/ Hydrogen Peroxide Impingers		%Hg in Potassium Permanganate/ Sulfuric Acid Impingers	
Run	**M29-A**	**M29-B**	**M29-A**	**M29-B**	**M29-A**	**M29-B**
3	1	1	16	14	77	77
4	1	1	14	15	83	82
5	2	2	28	28	65	66
6	1	1	16	20	74	71
7	1	1	13	16	80	77
8	1	1	17	17	70	72
9	1	1	9	8	84	85
10	18	16	16	13	59	64
11	12	14	8	7	77	77
12	13	16	11	12	73	71
Average	5	5	15	15	74	74

To evaluate precision and drift, Ni was analyzed with each run (Figure 8). The overall precision for the Ni is 1.2% with no observable outliers. The good precision of the Ni demonstrates that the instrument did not have significant problems with drift or precision. The upscale drift of the instrument was <0.5%, and the quality assurance precision was ~2% for daily zero and span checks. These results meet quality assurance requirements of PS12a and the previously proposed PS10.[4,5]

CONCLUSIONS

The Xact data reported in the OHM testing indicate an RA of 25% for Hg. The OHM precision for the test was ~22%. The limited accuracy and precision of OHM at low Hg concentrations was a problem for all of the candidate methods and provided an unreasonable basis for meeting the performance specification RA requirements. The Hg in this test was >96% in elemental form. Because many boilers have Hg in the oxidized form, these results were not representative of the entire source category. Therefore, this test did not validate the Xact performance when oxidized Hg is present. The Xact accurately measured the gas standard on initial installation and tracked changes in total Hg concentrations relative to the OHM throughout the test. However, the Xact developed cold spots because of inadequate heat tracing, which caused occasional water condensation and inconsistent results for some of the runs.

RA criteria for Hg and As were successfully met by the Xact during reference method testing at the IAAP coal-fired burner, with values of 17% and 16% for Hg and As, respectively. Changes made to the heat tracing of the monitor alleviated the condensation problems. Metals spiking was used to improve the M29 comparison by increasing M29 accuracy and precision. The Hg during this test contained significant portions of both elemental and oxidized Hg. These test results indicate that the Xact metals monitor can accurately measure total As and Hg in particulate and vapor forms in coal-fired boiler emissions by meeting the RA requirements of PS12a and the previously proposed PS10.

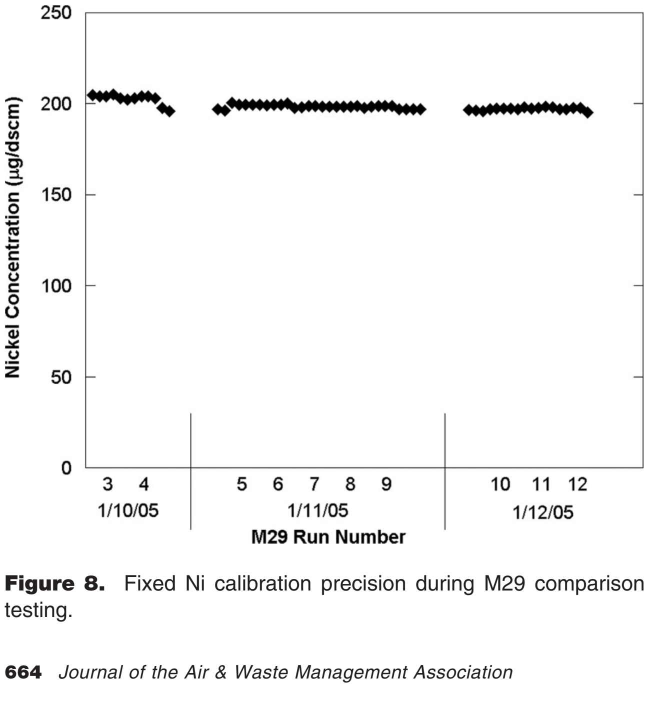

Figure 8. Fixed Ni calibration precision during M29 comparison testing.

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