Testing of a Continuous Sampling Mercury CEM at the EPA-Rotary Kiln Incinerator Simulator Facility

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Introduction

This report has been prepared to document the performance of the continuous sampling mercury monitoring system developed by Ames Laboratory for use as a continuous emission monitor (CEM). This work was funded by the U.S. Department of Energy, Office of Environmental Management, Office of Science and Technology, through the Mixed Waste Focus Area. The purpose of the project is to develop instrumentation and methods for spectroscopic field-monitoring applications. During FY01 this included continued development and testing of an echelle spectrometer system for the detection of mercury (Hg) by atomic absorption. Due to the relatively poor limits of detection for Hg by optical emission techniques, the CEM has been designed for the detection of elemental Hg by optical absorption. The sampling system allows continuous introduction of stack gas into the CEM for analysis of elemental and total Hg in the gas stream. A heated pyrolysis tube is used in this system to convert oxidized Hg compounds to elemental Hg prior to analysis for total Hg. The pyrolysis tube is bypassed to measure elemental Hg. The CEM is designed to measure the elemental Hg concentration of the gas sample, measure the total Hg concentration, perform a zero check (analysis of room air), and then re-zero the system (to correct for any instrumental drift that occurs over time). This is done in an automated, sequential measurement cycle to provide continuous monitoring of Hg concentrations in the stack gas. The continuous sampling Hg CEM was tested at the EPA-Rotary Kiln in Durham, NC at the beginning of FY02. This report describes the characteristics and performance of the system and the results of the field tests performed at EPA.

The Hg CEM system was developed in response to the need of DOE and other organizations to monitor Hg that may be released during the processing or combustion of hazardous or mixed-waste materials. The promulgation of regulations limiting the release of Hg and requiring continuous monitoring of stack gases from combustion and treatment processes would seriously impact the operations of DOE waste treatment facilities. Therefore, it is important to develop and validate techniques that adequately meet proposed sensitivity and accuracy requirements. The most likely form of validation for such a technique involves comparison of CEM results with a reference test method for a test combustion system. Therefore, the CEM system was tested at EPA by monitoring Hg emissions in a natural gas combustion exhaust (that was spiked with Hg) while simultaneously collecting samples using the

Ontario-Hydro mercury speciation method[1] as the reference method. The CEM results were available continuously during the on-line monitoring that was performed. The results of the reference method sampling were received a number of weeks after the testing at EPA. These results are discussed in this report, with a comparison and evaluation of the reference method and Hg CEM data.

Experimental

Continuous Sampling System A description of the continuous sampling system developed for this project has been published,[2,3] and is only summarized here. A schematic diagram of the system is shown in Figure 1.

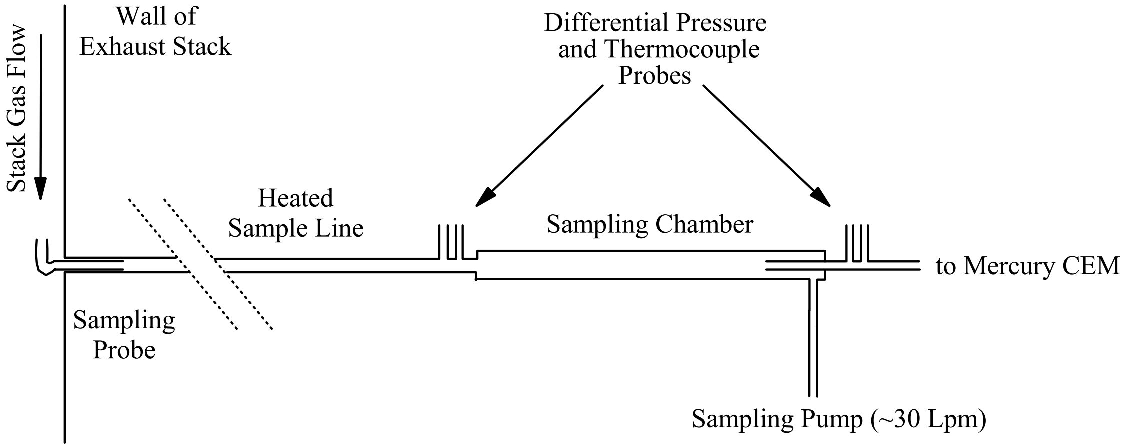


Figure 1. Schematic diagram of the continuous sampling system, connected to an exhaust stack. A 3.66-m heat-traced Teflon sample line was used to connect the Teflon sampling chamber to the sampling probe, inserted into the stack.

The continuous sampling system is a dual-stage sampling system. A high-volume primary sample (approximately 30 standard liters per minute, Lpm) is drawn isokinetically from a process pipe or exhaust stack using a standard EPA isokinetic glass-lined probe with an integral heater (Apex Instruments). The sampling probe, which has a ½"-ID nozzle, is connected to the Teflon sampling chamber by a 3.66-m, heat-traced Teflon sample line (Technical Heaters). A rotary vane pump (Gast Manufacturing model 0523-V4-G180DX) draws gas out of the stack, through the sampling chamber in a laminar-flow arrangement, with over 95% of the sample being removed through an exit port and exhaust line at the end of the chamber. On the inlet side of the sampling chamber, there are two ports (Teflon tees) for connecting a differential pressure transducer (Validyne model P55D) and a Teflon-coated thermocouple (Omega Engineering) to a

Teflon differential pressure flow cell, so that the gas flow rate and temperature of the primary sample can be monitored. The sampling probe, sample line, and sampling chamber were operated at approximately 110°C during the test at EPA.

A secondary sample is drawn isokinetically from the gas flowing through the sampling chamber using a ¼"-OD Teflon sampling tube that is inserted approximately 10 cm into the end of the chamber. The tube has a 0.51-cm ID, with a 30° taper at the sampling end. The outlet side of the sampling tube is connected to a ¼" Teflon Swagelok tee that is followed by another Teflon differential pressure flow cell, to monitor the gas flow rate out of the sampling chamber. A Teflon-coated thermocouple (Omega) is inserted into the inlet of this flow cell to measure the gas temperature. The differential pressure is monitored using an oil-filled manometer (Dwyer Instrument model 101) that has a range of 0-0.5" of water. The primary flow cell, Teflon sampling chamber, and secondary flow cell are heat-traced using electrical heating tape inside an insulated tube (Accessible Products Company). A linear pump (Gast Manufacturing model SPP-6GAS-101) is used to draw a sample flow of approximately 1 standard Lpm out of the sampling chamber and through the 1-m absorption cell, for the determination of Hg in the stack gas.

Mercury CEM The Hg CEM system was assembled and tested at Ames Laboratory and used for stack Hg monitoring during an FY00 field test at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University.[4] The Hg CEM was modified in FY01 to sequentially monitor elemental and total (oxidized plus elemental) Hg and tested at the EPA-Rotary Kiln in Durham, NC. Mercury is detected as elemental Hg by atomic absorption in a 1-m pathlength absorption cell, using a Hg pen lamp as the light source, a 0.38-m focal-length echelle spectrometer, and a photodiode array (PDA) detector. This echelle spectrometer has no cross-dispersing optical element or order-sorting pre-filter, so all orders of the echelle grating are spatially superimposed at the detector. This spectrometer provides simultaneous detection of all of the strong Hg lines from 253-579 nm from the pen lamp (diffracted from different orders of the echelle grating), without spectral overlap of these lines at the detector, as shown in Figure 3.

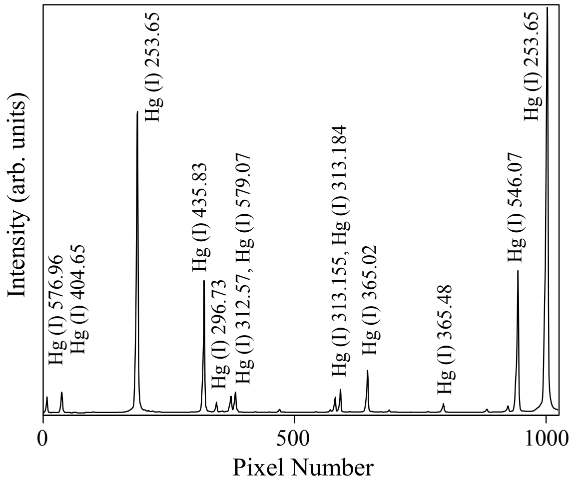
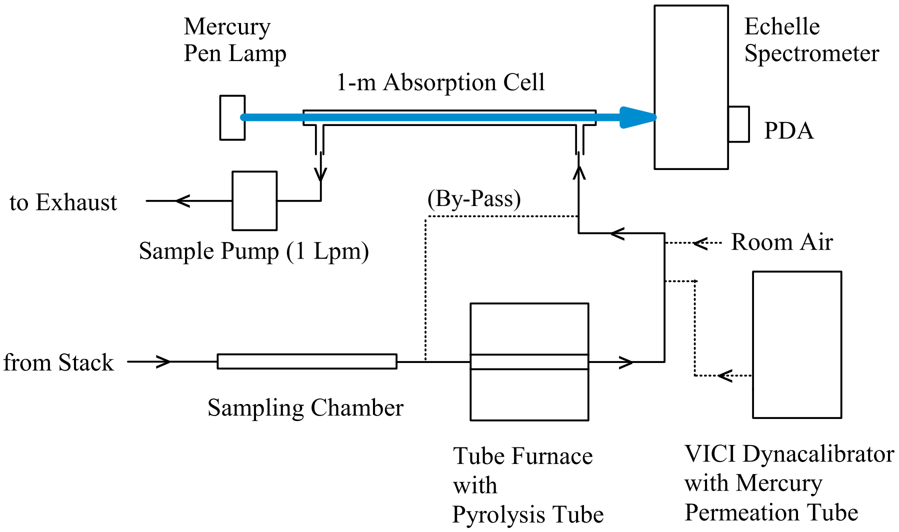


Figure 3. Mercury pen lamp spectrum, obtained using the echelle spectrometer.

The Hg (I) 253.65-nm line is used to measure absorption due to Hg in the 1-m cell. Other Hg lines (non-ground-state electronic transitions not subject to Hg absorption) can be used to correct for fluctuations in the light-source intensity, light scattering by particles, and absorption due to species other than Hg. Since all the Hg lines can be monitored simultaneously, this system in effect provides a dual-beam (or "multiple-beam") optical arrangement with a reference channel, using only a single light source, absorption cell, spectrometer, and detector. A schematic diagram and a photograph of the Hg CEM are shown in Figure 4.

4a.



4b.

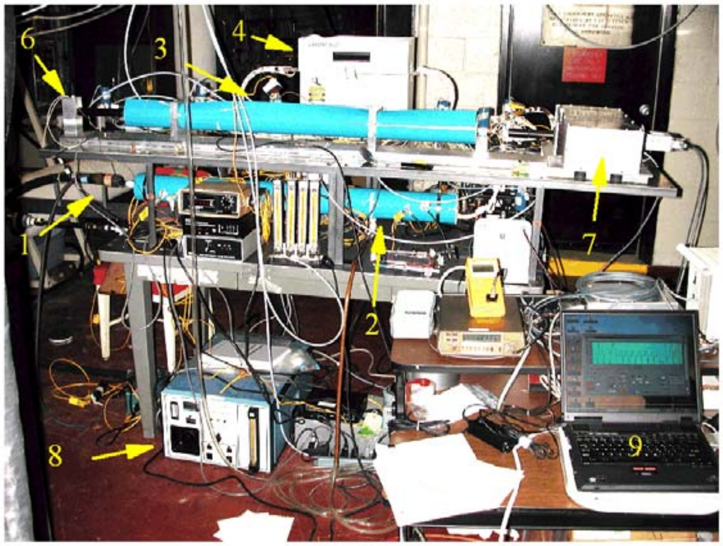


Figure 4. Schematic diagram (a) and photograph (b) of the Hg CEM system. The photograph shows the heat-traced Teflon sample line (1) from the stack sampling probe, connected to the Teflon sampling chamber that is inside a 1.2-m-long insulated tube (2). The 1-m absorption cell is inside a 1.2-m-long insulated tube (3), mounted on the metal frame, along with the Hg pen lamp (6, left side), optics, and 0.38-m echelle spectrometer (7, right side) with PDA detector. A sampling pump draws gas (~30 Lpm flow rate) out of the stack, through the sampling probe and Teflon sampling chamber. A linear pump draws gas (1 Lpm flow rate) out of the sampling chamber, through the pyrolysis tube in the tube furnace (4) and through the 1-m absorption cell. The VICI calibrator (8) and data acquisition and control computer (9) are also shown.

Light from the Hg pen lamp (Oriel model 6035 Hg-Argon lamp operated at 10-mA AC current, using an Oriel model 6060 power supply) is collected using a 25-mm diameter, 150-mm focal-length fused silica lens, with the lamp emission approximately collimated through the 1-m absorption cell. The lamp is housed in an aluminum block, heated to 35°C using a cartridge heater (Omega Engineering model CIR-1031/120) and temperature controller (Valco Instruments model ITC10399). The 253-nm emission from the pen lamp is monitored using a narrow-line interference filter (Oriel model 56400) and photodiode (Hamamatsu model S1226-8BQ) attached to the aluminum block. The absorption cell has quartz windows, and is heated to approximately 125°C using electrical heating tape inside a 1.2-m-long insulated tube (Accessible Products Company). Light from the Hg pen lamp that passes through the cell is focused onto the entrance slit of the echelle spectrometer, using another 25-mm diameter, 150-mm focal-length fused silica lens. This spectrometer is a modified version of the 0.38-m echelle spectrometer described previously.[5] The optics in this spectrometer consist of a 25-mm diameter flat turning mirror, two

50.8-mm diameter, 0.38-m focal-length concave spherical mirrors (Optics for Research) used as the collimating and focusing mirrors, the grating (Richardson Grating Laboratory model 35-13-19-417 echelle, 52.67 grooves per mm, 69° blaze angle), and a 50-mm diameter flat turning mirror. The PDA is a Hamamatsu model C5964-1011 detector.

Sample stack gas is introduced into the Hg CEM using the continuous sampling system described above. For monitoring total Hg, a linear pump is used to draw a sample flow of approximately 1 standard Lpm from the Teflon sampling chamber, through the heated pyrolysis tube and through the 1-m absorption cell. The pyrolysis tube is a 25-mm diameter, 0.56-m-long quartz tube, filled with 0.64-cm-long quartz rings cut from 6-mm OD tubing, which is positioned inside the tube furnace (Lindberg/BlueM model TF55030A). The pyrolysis tube is used to thermally decompose oxidized Hg compounds to elemental Hg, prior to introduction into the absorption cell;[6,7] the tube furnace is operated at a temperature of approximately 1000°C. The ¼"-OD Teflon tubing that connects the sampling chamber to the pyrolysis tube in the tube furnace and to the absorption cell is heat-traced using electrical heating tape and operated at approximately 110°C. Teflon solenoid valves (TEQCOM model M443W2DFS-HT) are integrated into the gas-line connections to allow automated switching between stack gas sampling (for determination of elemental and total Hg) and zero checks using room air (to correct for any instrumental drift). Elemental Hg in the stack gas sample is determined when the solenoid valves are switched to bypass the pyrolysis tube; the total Hg concentration is determined for the stack gas sample after it passes through the heated pyrolysis tube. During continuous Hg monitoring, the CEM system performs a sequential determination of the elemental Hg concentration in the stack gas sample, the total Hg concentration in the stack gas sample, and a room air zero-check measurement. This sequence constitutes one measurement cycle for the Hg CEM.

Mercury absorption is measured by ratioing the intensity of the Hg (I) 253.65-nm line to that of the Hg (I) 546.07-nm line. Absorption by elemental Hg vapor occurs at 253.65 nm, but not at 546.07 nm. Using both of these lines, an improvement in the accuracy and stability of the system is achieved, since short- and long-term fluctuations in the intensity of the mercury lamp can be corrected using the intensity ratio. This detection scheme also corrects for light scatter from particles in the absorption cell, to the extent that this scattering is comparable at 253.65 and 546.07 nm. Prior to the introduction and analysis of stack gas, the Hg CEM was calibrated by measuring the absorption of Hg (8.7 μg/m^3) introduced into the 1-m cell. The Hg calibration gas was generated from a certified permeation tube placed inside the Dynacalibrator (VICI model 340-55B-YD). The permeation rate, 8.7 μg/m^3 Hg ± 10%, is the vendor's certified value for this tube (received in May 2000). However, when this tube was used for calibration of the Hg CEM in September 2001, prior to the EPA tests, the permeation rate had apparently decreased; the absorption at 253.65 nm had decreased significantly compared to the value measured when the tube was received. The uncertainty in the actual Hg permeation rate for this tube led to some ambiguities in determining the relative accuracy performance of the CEM. This will be discussed further in the Results and Discussion section.

Interference at 253.65 nm due to absorption by sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) in the stack gas sample is corrected during data acquisition. The correction involves solving a series of three linear equations, one equation for each species (Hg, SO_2, and NO_2) absorbing at each of three different wavelengths, using a least-squares regression model. It is assumed that the absorbance of each species at a given wavelength is additive (Beer-Lambert law). The wavelengths used are 253.65 nm, where all three species absorb, 313.18 nm, where SO_2 and NO_2 absorb, and 435.83 nm, where only NO_2 has a measurable absorption. The system is calibrated by introducing known concentrations of each species, individually, into the 1-m cell and measuring the absorption at 253.65 nm, 313.18 nm, and 435.83 nm and the intensity of the 546.07-nm reference line. To correct the Hg concentration for SO_2 and NO_2 interference, intensities for all three wavelengths and the reference line are measured simultaneously; the calculated correction factor (from the three-by-three linear equation matrix) is applied to the measured 253.65-nm absorption to yield the SO_2- and NO_2-corrected Hg concentration.

Results and Discussion

Testing of the Ames Laboratory Hg CEM was conducted at the U.S. EPA Environmental Research Center, in Research Triangle Park, NC, at the Rotary Kiln Incinerator Simulator (RKIS) facility. A detailed description of the facility as well as the procedures, equipment, and operating conditions used by the RKIS facility during the October tests can be found in the *Test/QA Plan for Pilot-Scale Verification of Continuous Emission Monitors for Mercury*.[8] A diagram of the RKIS facility, depicting the injection ports (Hg solution and interference gases) and the sampling ports, is shown in Figure 5. The operating conditions (i.e., temperature and stack-gas velocity) of the RKIS facility used during the October tests closely matched those used during a previous Environmental Technology Verification (ETV) test for several Hg CEMs in January 2001; during tests of the Ames Laboratory CEM, the kiln remained in operation (hot) at night, but the air pollution control system was not maintained at its normal operating conditions overnight. Reports from the January 2001 EPA-ETV test for several commercial CEMs can be found on the EPA website.[9] The testing schedule for the Ames Laboratory CEM is summarized in Table I. The RKIS facility was in full operation for three days (October 9-11) during the week of testing; October 8 was a federal holiday, so no stack Hg testing was performed under the facility's operating permit that day. During the week, relative accuracy (RA) tests of the Hg CEM were conducted; three 1-hour RA runs were performed on the first day and two 1-hour RA runs were done on day 2. Single-gas interference tests were performed on day 2 after the RA tests, and gas-mixture interference tests were done at the end of day 3. Sensitivity tests were also performed on day 3. Before each day of testing commenced, the RKIS facility (including the air pollution control system) was allowed to reach an equilibrium state before the introduction of any interferent gases or Hg solutions. Mercury stock solutions were prepared by ARCADIS personnel at a concentration of 20 μg Hg/ml in 0.1 N HNO_3 for the RA tests. Given the short week available for the tests, only a single, intermediate Hg level (approximately 40 μg/m^3) was investigated during the RA tests, rather than the low (8 μg/m^3) and high (80 μg/m^3) Hg levels used during the January 2001 EPA-ETV testing.

Table I. Schedule for Ames Laboratory Hg CEM

Monday 10/08/01	Set up CEM
Tuesday 10/09/01	RA Tests (Runs 1, 2, and 3)
Wednesday 10/10/01	RA Tests (Runs 4 and 5) Single-Gas Interference Tests
Thursday 10/11/01	Sensitivity Tests Gas-Mixture Interference Tests
Friday 10/12/01	Tear Down

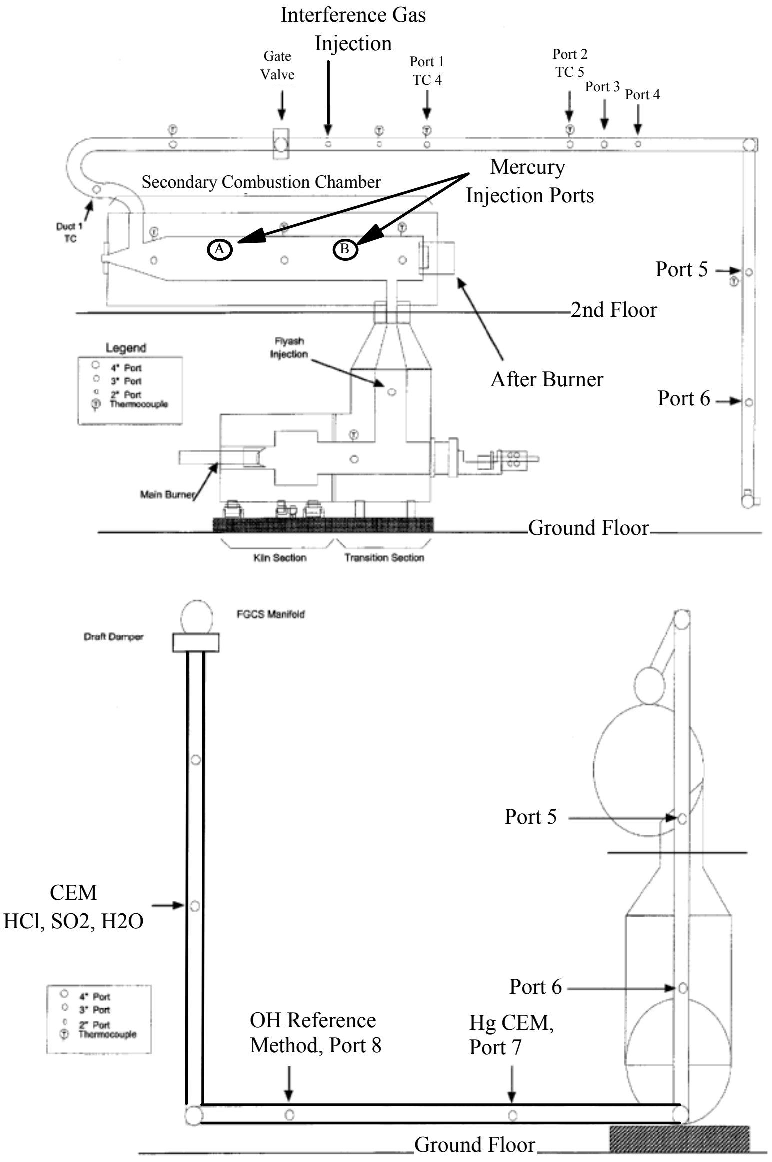


Figure 5. Side View (top) and End View (bottom) of the RKIS Test Facility

Relative Accuracy Tests Relative accuracy (RA) testing was performed by comparing the stack Hg concentrations measured by the Ames Laboratory CEM and the Hg speciation reference method, the Ontario-Hydro (OH) method.[1] During these RA tests, the injection port labeled A in Figure 5 was used for the introduction of Hg. The Hg stock solution (20 μg Hg/ml in 0.1 N HNO_3) was injected into the secondary combustion chamber of the RKIS through a stainless steel tube, at a rate of 12 ml/minute using a peristaltic pump. At this delivery rate and concentration, the Hg concentration in the RKIS flue gas stream was approximately 60 μg/m^3. RA test runs 1, 2, and 3 were performed on the first day, and runs 4 and 5 were performed on the second day. In the middle of RA test run 2, the Hg stock solution ran dry and an old stock solution was used to finish the run. A fresh Hg stock solution was used for RA run 3. Prior to RA run 4 (on the following day), it was discovered that the injection probe had deteriorated and needed to be replaced. A new injection probe was inserted into the same injection port used for the previous RA runs. Soon after the probe was inserted, RA test run 4 commenced. ARCADIS personnel indicated that the new sample probe was positioned radially closer to the centerline of the afterburner, thereby affecting the ratio of elemental to oxidized Hg in the flue gas (i.e., increasing the elemental Hg concentration).

Interferent gases (NO, CO, SO_2, HCl, and Cl_2) were injected into the flue gas stream from cylinders of pure compressed gases during the RA testing. The interferent gas concentrations in the flue gas were determined using the RKIS facility CEMs. No on-line CEM was available for chlorine (Cl_2) gas; the Cl_2 concentration in the stack was inferred from the measured HCl concentration during the introduction of Cl_2. Chlorine gas was first injected directly into the afterburner (where it is completely converted to HCl) and measured as hydrogen chloride using the RKIS CEM. Once the desired concentration was obtained, Cl_2 was injected downstream from the afterburner, in the normal gas injection port. Some conversion of the injected NO gas into NO_2 occurs in the RKIS stack. The on-line RKIS CEM measures total NO_x (NO + NO_2) present in the stack gas, using a chemiluminescence technique. Concentration values for NO_2 measured using the Ames Laboratory CEM (in Table VI below) are based on absorption at 435.83 nm; since NO has no measurable absorption at this wavelength, only the NO_2 concentration is determined. The interferent gas concentrations measured during the RA tests using the RKIS CEMs are shown in Table II. No particulate matter was introduced into the flue gas stream during these tests.

Table II. Interferent Gas Concentrations (ppmV) Measured during RA Tests

	NO_x	CO	SO_2	HCl
Run 1	139.0 (±3.6)	83.2 (±1.1)	62.2 (±9.0)	123.3 (±5.9)
Run 2	111.0 (±20.2)	83.1 (±1.6)	66.6 (±8.4)	103.9 (±22.9)
Run 3	117.2 (±8.0)	83.5 (±0.8)	79.5 (±7.5)	152.1 (±5.0)
Run 4	144.9 (±1.1)	73.3 (±0.6)	48.5 (±8.2)	100.3 (±6.0)
Run 5	145.9 (±0.9)	72.5 (±0.6)	61.5 (±7.1)	94.4 (±5.3)

The Ontario-Hydro (OH) reference method was used during the RA tests for the determination of elemental and total Hg. A description of the OH method can be found in the EPA-ETV test plan.[8] In conjunction with the RA tests, ARCADIS personnel operated the PS Analytical (PSA) Sir Galahad II Hg CEM. A description of the PSA Hg CEM and details of its operation can be found in the EPA-ETV Report on the EPA website.[9] The CEM and OH reference method sampling probes were installed in port positions 7 and 8, respectively, shown in Figure 5. The sampling probes for the Ames Laboratory and PSA Hg CEMs were inserted into the stack through opposing ports at position 7, within a few centimeters of each other. The OH reference sampling consisted of dual-sampling trains positioned at port 8. The reference method sample trains were prepared and collected by ARCADIS and Mississippi State University–DIAL personnel. The OH trains were prepared in a laboratory near the RKIS facility, and sample recovery occurred in the laboratory after each RA test run. The recovered OH samples were sent to Oxford Laboratories, Wilmington, NC, for analysis.

The Ames Laboratory CEM was operated in the "monitor mode" during the RA tests. This mode yields a graphical display of the Hg levels being measured (in μg/m^3) from the RKIS stack, after correction for SO_2 and NO_2, as the CEM cycles through elemental and total Hg monitoring, and zero checks. Figure 6 shows the monitor data from RA test run 5; these measured Hg concentrations have not been corrected for moisture in the flue gas or for the stack background values (and are based on the Ames (I) calibration - see discussion below).

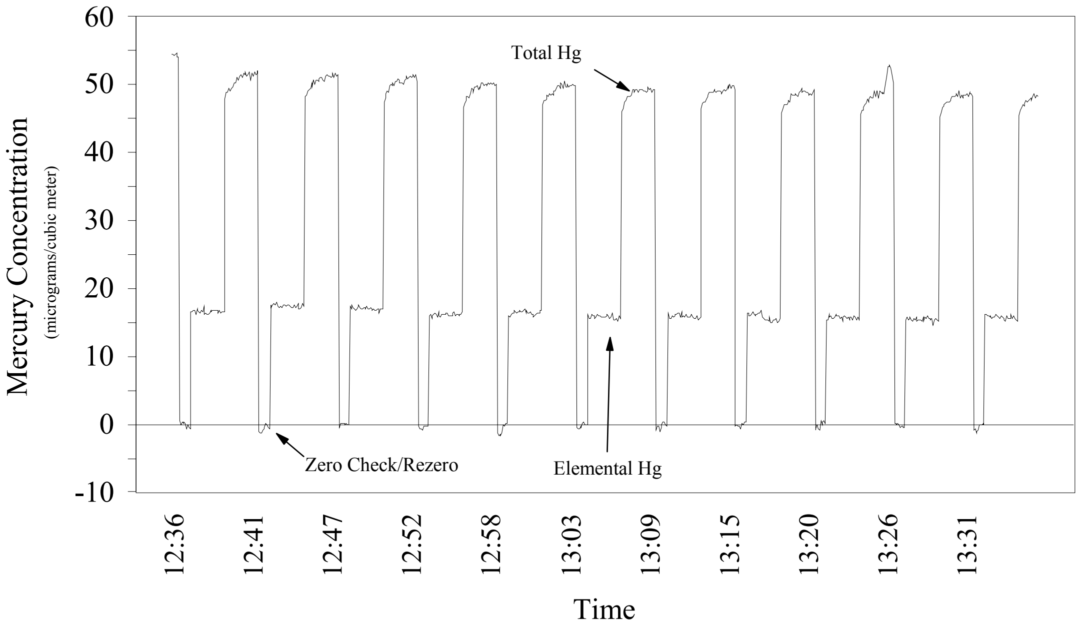


Figure 6. Mercury concentrations measured during RA Run 5 on 10/10/01.

Each RA test run lasted one hour. During this time the Ames Laboratory CEM performed 11 complete, sequential measurement cycles for the zero check, re-zero, elemental Hg concentration, and total Hg concentration, as shown in Figure 6 for RA run 5. Each sequence consisted of collecting 5 data points for the zero check, re-zeroing the instrument and measuring 5 more points for room air, collecting 30 data points (approximately 90 seconds) for elemental Hg monitoring and 30 data points for total Hg monitoring. A 30-second delay time was used when switching between the zero-check, elemental Hg, and total Hg valve positions, to re-establish an equilibrium gas flow condition for room air or stack gas sample introduction. For the number of data points and the delay time used during testing at EPA, each measurement cycle (sequential zero-check, re-zero, elemental Hg, and total Hg measurement) required approximately 5.5 minutes. The delay time and the number of data points collected may be changed to shorten or lengthen the analysis time required for a measurement sequence.

The results for the five RA test runs are summarized in Tables III and IV for total Hg and elemental Hg, along with the OH reference method and PSA results. The two columns of values for the OH reference method are the values obtained for the dual-sampling trains at port position 8, with the two trains designated as 8A and 8B. The reported Hg values for the Ames Laboratory CEM in Tables III and IV are the averages (± one standard deviation) of the 11 measurement cycles during each RA run and have been background- and moisture-corrected. During the weeklong testing, the apparent stack background values measured using the Ames Laboratory CEM for elemental and total Hg (compared to room air) were $2.7 \pm 0.4\ \mu g/m^3$ and $4.4 \pm 0.2\ \mu g/m^3$, respectively. The moisture level in the stack during the RA tests was a constant 8.4%. For each RA run, two different Hg concentrations are reported for the Ames Laboratory CEM because of uncertainties in the permeation rate of the Hg standard used for calibration. The concentrations reported under Ames (I) are based on the vendor's stated emission rate of Hg (8.71 ng Hg/minute ± 10% at 40°C, certified in May 2000) for the permeation tube used in the VICI Dynacalibrator for calibration of the Hg CEM. The concentrations reported under Ames (II) have been calculated using a corrected permeation rate of 6.8 ng Hg/minute. This value was calculated from the ratio of the Hg absorption (9.5 mAU) for this tube measured prior to the test at EPA compared to that measured originally (12.1 mAU), multiplied by the certified rate. This corrected permeation rate is in agreement with a value of 6.6 ng Hg/minute determined "in-house" using a modified Method 29 reference technique, in September 2000.

The reported total Hg concentrations for RA test runs 1-4 measured by the Ames Laboratory CEM are substantially lower than those for the OH reference method and the PSA CEM, as shown in Table III. This is due to the fact that not all of the oxidized Hg in the stack gas sample was being converted to elemental Hg in the pyrolyzer, during these runs. During RA test runs 1-4, the pyrolyzer tube furnace was set to a temperature of 900°C. Before RA test run 5, the temperature of the pyrolyzer was set to 1100°C to more efficiently convert the oxidized Hg to elemental Hg. This increase in the operating temperature of the pyrolyzer for run 5 resulted in an increase in the measured total Hg concentration to a value that is in much better agreement with the OH reference method and PSA values. For RA runs 1, 3, and 5, the measured total Hg concentrations were fairly stable throughout the course of the 1-hour tests. The higher uncertainty (larger standard deviation) in the reported total Hg concentration for RA runs 2 and 4 is due to the occurrence of a large short-term increase in the measured Hg concentration (a "spike" lasting more than 90 seconds) during one measurement cycle for each of these RA runs. A few spikes in the stack Hg concentration were measured during the course of the testing at EPA. In some cases, the spikes were correlated with known stack events such as changing the Hg solution injected into the stack and other momentary changes in stack operating conditions. For some of the spikes observed during testing, the cause of the change in the measured Hg concentration was unknown.

Based on the Hg stock solution concentration (20 µg Hg/ml), the solution delivery rate (12 ml/minute), and the OH-measured volumetric stack gas flow rate (3.72 ± 0.18 dscm/minute for RA runs 1-5), the calculated stack Hg (total) concentration during the RA runs is 64.5 ± 3.1 µg/dscm. This value is significantly higher than the measured OH (and PSA CEM) total Hg concentrations for any of the RA runs, indicating that only about 63% of the injected Hg was detected by the OH reference method, for the operating conditions used during the RA tests. (The average of the OH-determined total Hg concentrations for RA runs 2-5, 40.6 µg/dscm, is only about 0.63 of the calculated stack Hg concentration. For RA run 1, the OH-determined total Hg concentration is only 0.433 of the expected stack value.) This "effective efficiency" of approximately 63% indicates that there may be some uncertainty in the introduction of Hg into the RKIS stack and/or significant losses of Hg in the stack or in sampling Hg from the flue gas stream, for the operating conditions used during the October tests.

Table III. Total Mercury (μg/dscm) Measured during RA Runs

	Ontario-Hydro		Ames (I) [a]	Ames (II) [b]	PSA
	8A	8B			
Run 1	28	27.8	9.0 (±1.8)	7.0 (±1.4)	25.6 (±1.9)
Run 2	41.6	41.4	19.2 (±10.8)	15.0 (±8.4)	37.6 (±16.2)
Run 3	43.1	42.1	13.5 (±1.8)	10.6 (±1.4)	34.9 (±5.3)
Run 4	34.8	36.7	25.6 (±7.8)	20.0 (±6.1)	37.6 (±1.8)
Run 5	40.9	43.9	47.5 (±1.0)	37.1 (±0.8)	37.3 (±1.4)

a. Based on a permeation tube emission rate of 8.71 ng/min Hg.
b. Based on a corrected permeation tube emission rate of 6.8 ng/min Hg.

The results for elemental Hg in the RKIS flue gas stream during RA testing are shown in Table IV. The concentrations measured by the OH reference method, PSA CEM, and Ames Laboratory CEM (using the Ames (II) calibration) are in reasonable agreement for all five of the RA test runs, except for the low value determined during run 4 for the reference method (sampling train 8A). The measured elemental Hg concentrations for RA runs 1, 2, 3, and 5 were fairly stable throughout the course of these runs; for RA run 4, spikes in the elemental Hg concentrations determined during two measurement cycles result in a higher standard deviation in the reported value. The elemental Hg concentrations for RA runs 4 and 5 are significantly higher than the values measured for RA runs 1-3. This is believed to be due to replacement of the Hg injection probe prior to run 4, with the probe positioned radially closer to the centerline of the afterburner (as discussed above), resulting in more oxidized Hg being converted to elemental Hg in the RKIS stack.

Table IV. Elemental Mercury (μg/dscm) Measured during RA Runs

	Ontario-Hydro		Ames (I) [a]	Ames (II) [b]	PSA
	8A	8B			
Run 1	2.9	3.2	4.9 (±1.1)	3.8 (±0.9)	2.0 (±0.4)
Run 2	4.5	4.9	6.2 (±1.9)	4.8 (±1.5)	3.5 (±1.4)
Run 3	2.1	2.1	4.9 (±1.8)	3.8 (±1.4)	1.9 (±0.2)
Run 4	2.5	10.5	16.8 (±4.3)	13.1 (±3.3)	9.0 (±1.9)
Run 5	11.1	11.3	13.8 (±0.8)	10.8 (±0.6)	8.8 (±0.6)

a. Based on a permeation tube emission rate of 8.71 ng/min Hg.
b. Based on a corrected permeation tube emission rate of 6.8 ng/min Hg.

The elemental Hg concentrations measured during the RA runs using the Ames Laboratory CEM (using the Ames (II) calibration), PSA CEM, and OH reference method are plotted in Figure 7. For the OH reference method, the plotted value is the average result for the two sampling trains, except for RA run 4, where only the higher value (10.5 µg/dscm) is plotted. For the Ames Laboratory and PSA CEMs, the error bars show the uncertainty (one standard deviation) in the measured values during the 1-hour RA runs. The PSA CEM was operated on a 5-minute data acquisition interval during the tests, so six data points for elemental Hg and six data points for total Hg were acquired during an RA run; for the Ames Laboratory CEM, 11 sequential measurement cycles were performed during an RA run. Good agreement between the elemental Hg concentrations measured using the Ames Laboratory CEM, PSA CEM, and OH reference method during the five RA tests was observed, as shown in Figure 7.

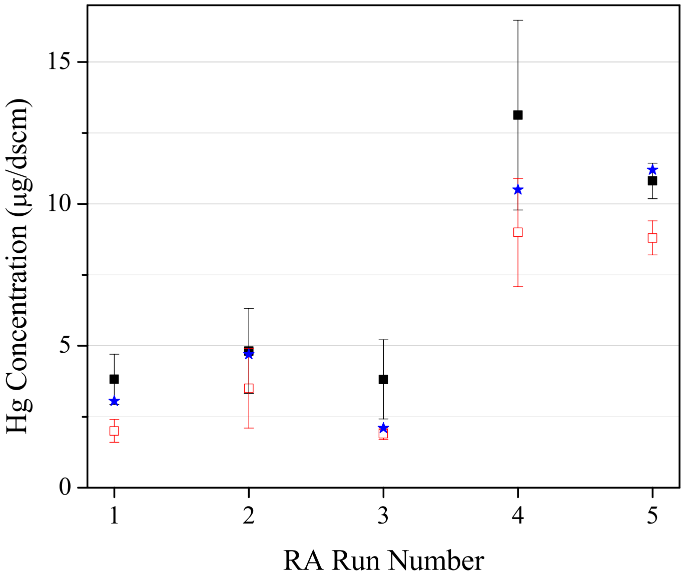


Figure 7. Elemental Hg concentrations measured using the Ames Laboratory CEM (■), PSA CEM (□), and OH reference method (★) during the five 1-hour RA test runs.

Interferent Gas Challenges The effects of potential gas interferents on the response of the Ames Laboratory Hg CEM were investigated by introducing a series of gases (CO, NO, SO_2, HCl, and Cl_2) into the RKIS flue gas stream during testing of the CEM. The gases were introduced singly on day 2 and as mixtures on day 3, at the target levels reported in Table V. During the single-gas interference testing on day 2, the same stock Hg solution was injected through the same port used for the RA tests. The stock solution was injected into the RKIS stack until a baseline Hg concentration from the flue gas stream was established. Once a baseline was established, the series of potential interferent gases was introduced into the flue gas stream. Each gas was introduced for about 20 minutes, and the elemental and total Hg concentrations were measured; after this time period, the first gas was turned off and the next one introduced. The measured elemental and total Hg concentrations and the SO_2 and NO_2 values determined using the Ames Laboratory CEM are reported in Table VI. The Hg concentrations are background- and moisture-corrected values and are calculated using the Ames (II) calibration. The tabulated values are the averages of three to four sequential measurement cycles during the introduction of a given gas. For SO_2 and NO_2, the tabulated "bypass" and "pyrolyzer" concentrations are the values measured during determination of elemental Hg (solenoid valves switched so that the stack sample gas bypasses the pyrolyzer) and total Hg (valves switched so that the sample gas passes through the pyrolyzer).

Table V. Target Interferent Gas Concentrations and Measured Values (ppmV) used during Test

	CO	NO_x	SO_2	HCl	Cl_2	SO_2/Cl_2	SO_2/NO_x
Target	500	500	2000	250	5-10	2000 / 5-10	2000 / 500
Actual	557-553	521-479	2043-1923	280-248	~10	1972-1850 / ~10	2024-1841 / 515-492

For the single-gas interference tests, a fairly constant elemental Hg concentration was measured using the Ames Laboratory CEM, indicating that CO, NO_x, SO_2, HCl, and Cl_2 have no significant effect (at the concentrations used during testing) on the measurement of elemental Hg, as shown in Table VI. The bold values in the table indicate the SO_2 and NO_2 concentrations measured when SO_2 and NO interferent gases were introduced into the stack flue stream. The measured total Hg concentrations during the single-gas interference tests were not perceptibly affected except during the introduction of SO_2 and HCl. During the introduction of HCl at ~250 ppmV, a slightly lower total Hg concentration was measured (37.7 μg/dscm compared to ~40.5 μg/dscm), indicating an incomplete conversion of oxidized Hg in the sample gas to elemental Hg (in the 1100°C pyrolyzer tube) prior to analysis. A similar effect was observed during Hg monitoring after RA run 3, when the HCl gas was turned off. For this run, the pyrolyzer tube was operated at 900°C and a lower concentration of HCl (~150 ppmV, Table II) was used. After the HCl was turned off, an increase in the measured total Hg concentration was observed - indicating that the presence of HCl in the sample gas stream caused a modest decrease in the measured total Hg concentration. After RA run 5 when the HCl gas was turned off, no increase in the measured total Hg concentration was observed. However, for this run, a lower HCl concentration, ~95 ppmV, was introduced into the stack and a higher pyrolyzer temperature, 1100°C, was used. During the introduction of SO_2 at ~2000 ppmV during the single-gas interference tests, a slightly higher total Hg concentration was measured (43.6 µg/dscm compared to ~40.5 µg/dscm). This effect could be a chemical enhancement, but could also be an SO_2-correction artifact. The SO_2 calibration used during the EPA test extended only to 250 ppmV, so it is possible that the ~2000 ppmV SO_2 concentration resulted in an incomplete correction due to an extrapolation error. The fact that the NO_2 concentrations measured using the Ames Laboratory CEM are negative during the introduction of ~2000 ppmV SO_2 also indicates a potential SO_2-correction artifact at this elevated SO_2 concentration. However, it is also possible that a real difference in the sampled stack Hg (total) concentration was measured during the introduction of ~2000 ppmV SO_2 into the RKIS stack. This premise is supported by the fact that higher total Hg concentrations were also measured using the PSA CEM during the introduction of ~2000 ppmV SO_2, as discussed below.

Table VI. Ames Laboratory CEM Hg, SO_2, and NO_2 Concentrations Measured during Gas Interference Tests

	Hg (µg/dscm)		SO_2 (ppmV)		NO_2 (ppmV)	
	Elemental	Total	Bypass	Pyrolyzer	Bypass	Pyrolyzer
CO	14.1 (±0.5)	40.7 (±0.4)	17.0 (±2.3)	15.4 (±2.4)	12.8 (±0.8)	3.2 (±0.2)
NO	14.7 (±0.5)	40.0 (±0.2)	18.2 (±1.3)	16.6 (±0.9)	**21.6 (±0.3)**	**12.4 (±0.5)**
SO_2	15.9 (±1.9)	43.6 (±0.8)	**1658 (±41)**	**1621 (±41)**	-7.8 (±1.3)	-15.7 (±1.5)
HCl	15.7 (±0.7)	37.7 (±0.3)	36.0 (±0.8)	35.7 (±0.1)	16.9 (±0.2)	7.8 (±0.2)
Cl2	15.4 (±2.0)	40.7 (±0.8)	35.4 (±5.9)	30.0 (±2.9)	17.0 (±0.4)	6.9 (±0.3)
Stack	22.5 (±1.0)	36.6 (±1.2)	40.9 (±2.4)	40.2 (±4.0)	22.8 (±0.5)	13.0 (±0.6)
SO_2/Cl_2	20.0 (±0.5)	42.8 (±1.0)	**1446 (±372)**	**1588 (±28)**	5.5 (±5.3)	-5.1 (±0.6)
SO_2/NO	26.0 (±1.2)	42.5 (±1.1)	**1594 (±60)**	**1553 (±31)**	**12.4 (±1.1)**	**5.7 (±0.7)**
Stack	24.2 (±1.1)	38.4 (±0.9)	46.9 (±3.7)	47.2 (±4.2)	25.7 (±0.6)	16.8 (±0.3)

The Hg injection probe was moved into position B (Figure 5) just prior to performing the gas-mixture interference tests on day 3, in order to change the ratio of elemental to oxidized Hg in the RKIS flue gas stream. Since position B is closer to the afterburner, the elemental Hg concentration was expected to be higher. The elemental Hg concentrations measured using the Ames Laboratory CEM were indeed higher during the gas-mixture interference tests compared to the values measured during the single-gas tests, as shown in Table VI. During the introduction of the SO_2/Cl_2 and SO_2/NO gas mixtures, the measured total Hg concentrations increased slightly compared to the values measured prior to and following the introduction of these gases. As discussed above, this increase may be an SO_2-correction algorithm artifact or a real difference in the sampled stack Hg (total) concentration, leading to a slight elevation (approximately 10% difference, relative) in the measured total Hg concentration. The elemental Hg concentration measured during the introduction of the SO_2/Cl_2 mixture is slightly lower (20.0 μg/dscm) and that for the SO_2/NO mixture is slightly higher (26.0 μg/dscm) than the values measured for the stack gas prior to and following the introduction of these gas mixtures. The causes for these changes are not known; however, the differences are relatively small, approximately 10% different (relative) from the values measured with no gases added to the stack.

The elemental and total Hg concentrations measured during the single-gas and gas-mixture interference tests are plotted in Figure 8, for the Ames Laboratory and PSA CEMs. For the Ames Laboratory CEM, data for three to four sequential measurement cycles were averaged; for the PSA CEM, the plotted values are the averages of two or three data points for elemental and total Hg acquired during the gas-interference testing. The error bars show the uncertainty (one standard deviation) in the measured values. For total Hg, there is reasonably good correspondence between the values obtained using the Ames Laboratory and PSA CEMs, in the sense that the measured concentrations track with respect to each other; that is, changes (increases or decreases) in the total Hg concentration measured using the PSA CEM are also evident in the results obtained using the Ames Laboratory CEM. This is true except for the results for Cl_2 during the single-gas interference testing. The introduction of Cl_2 has an adverse effect on the response of the PSA CEM,[9] as indicated by the significantly lower total (and elemental) Hg concentration plotted in Figure 8. The results obtained for the PSA system during the gas-mixture interference testing of SO_2/Cl_2, however, do not indicate a similar Cl_2 suppression effect. During the introduction of ~2000 ppmV SO_2 in the single-gas and gas-mixture interference tests, higher total Hg concentrations were measured using both the Ames Laboratory and PSA CEMs, as shown in Figure 8. This result is suggestive of a real difference in the sampled Hg (total) concentration during the introduction of high SO_2 concentrations into the RKIS stack. For elemental Hg on day 2 during the single-gas interference testing, the correspondence between the values measured using the Ames Laboratory and PSA CEMs is also reasonably good (except for the Cl_2 results). During the gas-mixture interference testing on day 3, the correlation between the elemental Hg concentrations measured using the Ames Laboratory and PSA CEMs is not as good. Higher elemental Hg concentrations were measured during the gas-mixture interference testing compared to the single-gas tests, as shown in Figure 8 and discussed above, due to the use of injection port B (closer to the RKIS afterburner) for Hg introduction on day 3.

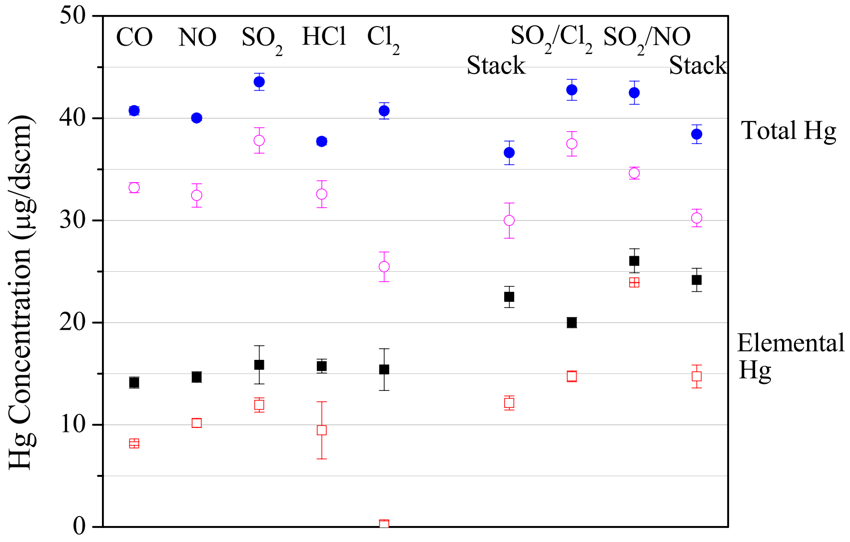


Figure 8. Elemental and total Hg concentrations measured using the Ames Laboratory CEM (■ and ●) and PSA CEM (□ and ○) during gas-interference testing. The single-gas interference data (left side of the plot) were obtained on day 2 of the testing at EPA; the gas-mixture interference data (right side) were obtained on day 3.

The data in Figure 8 show the trends in the elemental and total Hg concentrations measured using the Ames Laboratory and PSA CEMs during the single-gas and gas-mixture interference testing. All the elemental and total Hg concentrations reported for the Ames Laboratory CEM are higher than those for the PSA CEM. It should be noted that some of the difference in the Ames Laboratory and PSA results may be attributed to some operational difficulties for the CEM systems during the gas interference tests. On day 3 for the PSA CEM, the sample gas flow was lower than normal (<0.5 Lpm) due to a slightly clogged sample line, so the reported PSA results on day 3 may be low by 10-20%. During the single-gas interference testing for the Ames Laboratory CEM on day 2, measured elemental and total Hg concentrations were 10-20% higher compared to the results for RA run 5, for an unknown reason. Therefore, there is some uncertainty in the absolute concentration values determined using the two CEMs during some portions of the gas interference tests. However, the trends shown in Figure 8 indicate that the relative response of the two CEMs for elemental and total Hg during the single-gas and gas-mixture interference testing is comparable for most of these tests.

Stability and Reproducibility Tests Reproducibility testing was conducted during the test at EPA by periodically measuring the Hg concentration from the output of the VICI Dynacalibrator. Measurements were taken before and after RA test runs 2 and 4 on days 1 and 2, prior to the sensitivity measurements on day 3, after the gas-mixture interference tests on day 3, and prior to tear-down on day 4. The average measured Hg concentration was 6.3 ± 0.3 $\mu g/m^3$ (Ames (II) calibration) over the course of the weeklong testing, indicating that the Ames Laboratory CEM had a fairly stable response over the course of the test.

Sensitivity Tests Sensitivity tests of the Ames Laboratory Hg CEM were conducted on day 3 of the testing at EPA. The RKIS facility was operated for an extended period of time, introducing a blank solution containing no Hg into the secondary combustion chamber. After operating conditions had stabilized, a solution containing a low concentration of Hg (1 μg Hg/ml in 0.1 N HNO_3) was introduced into the secondary combustion chamber; the target stack Hg concentration for this solution concentration and the solution delivery rate used was approximately 1 $\mu g/m^3$. Mercury CEM data was acquired for this stack Hg level, after which time the peristaltic pump solution delivery rate was increased to increase the stack Hg concentration. During the sensitivity tests, data was acquired for target stack Hg concentrations of approximately 1, 2, 4, and 8 $\mu g/m^3$. The elemental and total Hg concentrations measured using the Ames Laboratory CEM are given in Table VII; these values are background- and moisture-corrected and calculated using the Ames (II) calibration. For the first and second target concentrations (approximately 1 and 2 $\mu g/m^3$), elemental and total Hg were detected at levels slightly higher than the stack background values measured during introduction of the blank solution. However, the change in the measured Hg concentrations was approximately equal to the uncertainty (one standard deviation) in the replicate measurements performed (5 or 6 sequential measurement cycles), as shown in Table VII. No significant differences in the detected elemental and total Hg concentrations were measured for the first and second stack Hg concentrations. For the third and fourth target concentrations (approximately 4 and 8 μg/m^3 Hg), higher values were measured, at values that are statistically different from each other and from the values measured for the first two stack Hg concentrations. Some data were acquired at the end of the sensitivity tests using the PSA CEM for the last target concentration; the elemental and total Hg concentrations measured were 1.6 μg/dscm (two PSA data values) and 4.5 μg/dscm (three PSA measurements), respectively. These values are in good agreement with the Ames Laboratory CEM values for elemental and total Hg for the last target concentration, as shown in Table VII. The calculated stack Hg levels during the sensitivity testing, based on the Hg solution concentration, solution delivery rates, and an average stack gas flow of 3.72 dscm/minute (the average value measured during RA runs 1-5) were 1.1, 2.4, 4.0, and 8.1 μg/dscm Hg (total). These target values were likely subject to the same loss mechanism observed during the RA tests, at higher Hg concentrations in the RKIS stack, so it is not surprising that lower-than-expected Hg concentrations were measured during the sensitivity tests. Based on the uncertainty in the Hg concentrations measured during the sensitivity testing at EPA, the detection limit (three times the standard deviation) of the Ames Laboratory CEM was approximately 1 μg/dscm Hg, under these testing conditions.

Table VII. Elemental and Total Mercury Concentrations Measured during Sensitivity Tests

Target Concentration (μg/m^3)	Elemental Hg (μg/dscm)	Total Hg (μg/dscm)
1	0.2 (±0.2)	0.4 (±0.4)
2	0.2 (±0.2)	0.5 (±0.4)
4	0.6 (±0.3)	1.4 (±0.4)
8	1.7 (±0.3)	4.1 (±0.4)

Conclusions

The Ames Laboratory Hg CEM provides sequential, continuous emission monitoring of elemental and total Hg in stack gas samples. During the testing at EPA, the CEM operated on a 5.5-minute sampling and analysis cycle, measuring elemental and total Hg in the stack gas, measuring a room air zero check, and then re-zeroing the instrument to correct for drift. During this measurement cycle, 10 data points were acquired for room air analysis (approximately 30 seconds), 30 data points were acquired for stack gas elemental Hg monitoring (approximately 90 seconds), and 30 data points were acquired for total Hg monitoring. Changes in the stack Hg concentration during the testing were measured nearly instantaneously, using the Ames Laboratory CEM, as evidenced by observed spikes when changes in the stack operating conditions occurred or when the Hg solution injected into the stack was changed.

Although insufficient numbers of reference method runs were performed to calculate the relative accuracy (RA) for the Ames Laboratory Hg CEM, the accuracy was investigated by comparing the CEM results with the values obtained using the Ontario-Hydro (OH) reference method during five 1-hour RA tests. Due to uncertainties in the Hg emission rate for the permeation tube used to calibrate the Ames Laboratory CEM, there is some uncertainty in the absolute values of the Hg concentrations determined. As shown in Tables III and IV, values that differ by about 20% relative are obtained, depending on whether the vendor's certified emission rate (8.71 ng/min Hg) or a lower value (6.8 ng/min Hg), based on the difference in measured absorption values for the permeation tube, is used. Using the corrected Ames (II) calibration, the elemental Hg concentrations measured during the five RA runs are in very good agreement with the OH reference values and those measured using the PSA CEM. For total Hg, only the value measured for RA run 5 (when the pyrolyzer was operated at 1100°C) is in agreement with the OH and PSA results; for RA runs 1-4 (using a pyrolyzer temperature of 900°C), lower total Hg concentrations were measured using the Ames Laboratory CEM. At the lower pyrolyzer temperature, incomplete conversion of oxidized Hg in the sample gas to elemental Hg (prior to analysis) occurred, leading to low total Hg concentrations for these runs.

Gas interference tests conducted at EPA indicated that high levels of CO, NO, and Cl_2 introduced into the RKIS stack have no significant effect on the measured response of the Ames Laboratory CEM for elemental or total Hg. High levels of HCl (~250 ppmV) in the stack gas resulted in slightly lower measured total Hg concentrations, likely due to an incomplete conversion of oxidized Hg to elemental Hg (in the pyrolyzer) prior to analysis. However, the performance of the Ames Laboratory CEM under these conditions was comparable to that of the PSA CEM, and better during the introduction of high Cl_2 concentrations into the stack. High levels of SO_2 (~2000 ppmV) in the stack gas resulted in higher measured total Hg concentrations. This effect may be an SO_2 algorithm-correction artifact (SO_2 was introduced at a concentration 8 times higher than the highest value used during calibration of the Ames Laboratory CEM), but higher total Hg concentrations were also measured using the PSA CEM during the introduction of ~2000 ppmV SO_2. Minor effects on the measured elemental Hg concentrations were observed during the SO_2/Cl_2 and SO_2/NO gas-mixture interference tests; the measured concentrations differed by about 10% (relative) from the stack Hg concentrations measured in the absence of these gas mixtures. Although the elemental and total Hg concentrations measured using the Ames Laboratory CEM were slightly higher than those measured using the PSA CEM, there was reasonable correspondence in the relative results for the two CEM systems during the single-gas and gas-mixture interference testing.

Sensitivity testing of the Ames Laboratory Hg CEM was conducted by introducing Hg into the RKIS stack at four low levels, approximately 1.1, 2.4, 4.0, and 8.1 μg/dscm Hg. The detection limit for the Hg CEM during the testing at EPA was approximately 1 μg/dscm Hg, so these four levels are at or slightly above the detection limit of the Ames Laboratory CEM for these stack conditions. The Hg total concentrations measured (0.4, 0.5, 1.4, and 4.1 μg/dscm Hg) are lower than the target stack concentrations. For the highest Hg concentration used during the sensitivity testing, values measured using the PSA CEM are in good agreement with the Ames Laboratory CEM results; values for the other three stack Hg levels were (unfortunately) not measured using the PSA system. As discussed above, the target stack Hg concentrations during the RA testing were significantly higher than the values determined using the OH reference method, the PSA CEM, or the Ames Laboratory CEM (using the Ames (II) calibration); the Hg concentrations determined using the OH reference method were only about 63% of the calculated stack Hg concentrations. Therefore, the lower-than-expected Hg concentrations measured during the sensitivity tests may be another indication of some uncertainty in the introduction of Hg into the RKIS stack and/or losses of Hg in the stack or in sampling Hg from the flue gas stream.

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