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Power Plant Validation of the Mercury Speciation Sampling Method

TR-112588

Final Report, April 1999

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REPORT SUMMARY

This report presents results for the field validation study of the Ontario Hydro mercury speciation method. The tests were conducted at a Midwestern plant—designated as Site E-29—burning bituminous coal.

Background

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether mercury in stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. Given the current state of mercury control technology, EPA concluded that mercury controls on coal-fired electric power stations would not be required at this time. However, EPA did indicate that it views mercury as a potential threat to human health. EPA indicated that additional research and information were necessary before any definitive statement could be made. This has led EPA to issue an information collection request (ICR). The mercury-sampling method proposed for the ICR is the Ontario Hydro mercury speciation method. This method was extensively tested at the Energy & Environmental Research Center (EERC) in a program funded by EPRI and the U.S. Department of Energy (DOE). These tests showed the method accurately measured speciated mercury in coal-fired flue gases. However, testing took place primarily at the pilot-scale level. Therefore, EPRI and DOE funded Radian International and the EERC to more formally validate the Ontario Hydro method at a Midwestern power plant using a modification of the EPA Method 301 validation procedures. The testing was done as part of a larger program entitled “Characterization and Modeling of the Forms of Mercury from Coal-Fired Power Plants.” This program, which was initiated in October 1997, was to develop models to predict mercury speciation in flue gas from coal-fired systems based on relatively simple inputs such as coal analyses, plant configuration, and coal type.

Objectives

- To more formally validate the Ontario Hydro mercury speciation method in the field using a modified EPA Method 301 procedure.

- To collect data at the power plant for mercury speciation-modeling activities (if Site E-29 is selected, the collected data can be used to satisfy the requirements of the ICR).

Approach

The investigative team conducted the validation of the Ontario Hydro mercury speciation method using a modification of EPA Method 301 test validation procedures. The team took five quadtrain samples (20 total samples) at a location after the electrostatic precipitator but before the wet flue gas desulfurization system. Investigators spiked half the samples with a known mercury analyte prior to sampling. In this way, they could determine the statistical precision and bias of the method. According to the criteria established in EPA Method 301, for the method to be successfully validated, the relative standard deviation must be less than 50% and the bias must be between 0.7 and 1.3.

Results

Although there was some data variability, results clearly show that the Ontario Hydro mercury speciation method is valid according to the criteria established in EPA Method 301.

EPRI Perspective

Knowledge of mercury speciation in utility flue gas is critical for predicting the ecological pathways of emitted mercury, for estimating health and ecological risks, and for developing effective control technologies, if needed. EPRI plans to apply the Ontario Hydro method in field tests to confirm its performance and to collect data on mercury speciation in flue gas from coal-fired utility power plants.

TR-112588

Keywords
Mercury
Speciation
Sampling
Analytical methods
Flue gas
Air toxics

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1

INTRODUCTION AND BACKGROUND

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and the *Utility Air Toxics Report to Congress* (1). The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam–electric generating units. Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations would be required. However, the reports did indicate that EPA views mercury as a potential threat to human health. EPA indicated that additional research and information were necessary before any definitive statement could be made. This has led EPA to issue an information collection request (ICR). The mercury-sampling method proposed for the ICR is the Ontario Hydro mercury speciation method. This method was extensively tested at the Energy & Environmental Research Center (EERC) in a program funded by EPRI and the U.S. Department of Energy (DOE). However, because the testing had primarily been done at the pilot-scale level, it was decided to more formally evaluate the method in the field.

The more formal validation of the Ontario Hydro method was done at a midwestern power plant burning a bituminous coal. For purposes of this report, the plant has been labeled Site E-29. The testing was done as part of a program entitled "Characterization and Modeling of the Forms of Mercury from Coal-Fired Power Plants." This program, which was initiated in October 1997, was to develop models to predict mercury speciation in flue gas from coal-fired systems based on relatively simple inputs such as coal analyses, plant configuration, and coal type. This program is sponsored by EPRI and DOE, and the work is being done by Radian International and the EERC. Site E-29 was chosen for this validation test because the high sulfur and chloride content of the coal being burned at this facility would provide a challenge to the method. In addition, pilot-scale tests done with the coal burned indicated that the concentration of elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) was well above the comfort level of detection for the method ($>0.5\ \mu g/Nm^3$).

2

TEST PROGRAM OBJECTIVES

The two objectives of the test program are as follows:

- To more formally validate the Ontario Hydro mercury speciation method in the field using a modified EPA Method 301 procedure.
- To collect data at the power plant for mercury speciation modeling activities. In addition, it is expected that the collected data can be used to satisfy the requirements of the ICR.

3

TEST DESCRIPTION

Site E-29 is located in the Midwest and has a capacity of 1330 megawatts (MW). Site E-29 is designed to burn up to 3.7 million tons of coal per year. The plant has two electrostatic precipitators (ESPs) to control particulate matter and a limestone wet flue gas desulfurization system (FGD) to control SO_2 emissions. As stated earlier, the coal burned at the plant is a bituminous coal that is brought to the plant by rail where it is stockpiled prior to crushing and pulverization. The pulverized coal is fed to the boilers pneumatically and injected into the furnace through the burners.

3.1 Process Conditions During Testing

Table 3-1 summarizes the average load and gas emissions during the mercury speciation test program. The FGD system for this plant was very efficient, >90%. Although the load data are consistent from day to day, there is variability in the inlet SO_2 data. This becomes more apparent when the hourly SO_2 data are plotted as a function of time, as shown in Figure 3-1. This indicates variability in the coal being fired in the boiler.

Table 3-1
Site E-29 Flue Gas Data

Date	Gross Load, MW	NO_x, ppm (v)	CO_2, %	SO_2 at the FGD Inlet, ppm(v)	SO_2 at the FGD Inlet, ppm(v)	SO_2 Removal Across FGD, %
10-15-98	1324	211	11.8	2145	133	93.8
10-16-98	1313	207	11.9	2736	184	93.3
10-17-98	1313	195	11.9	2831	161	94.3
10-18-98	1298	198	11.8	2653	142	94.6

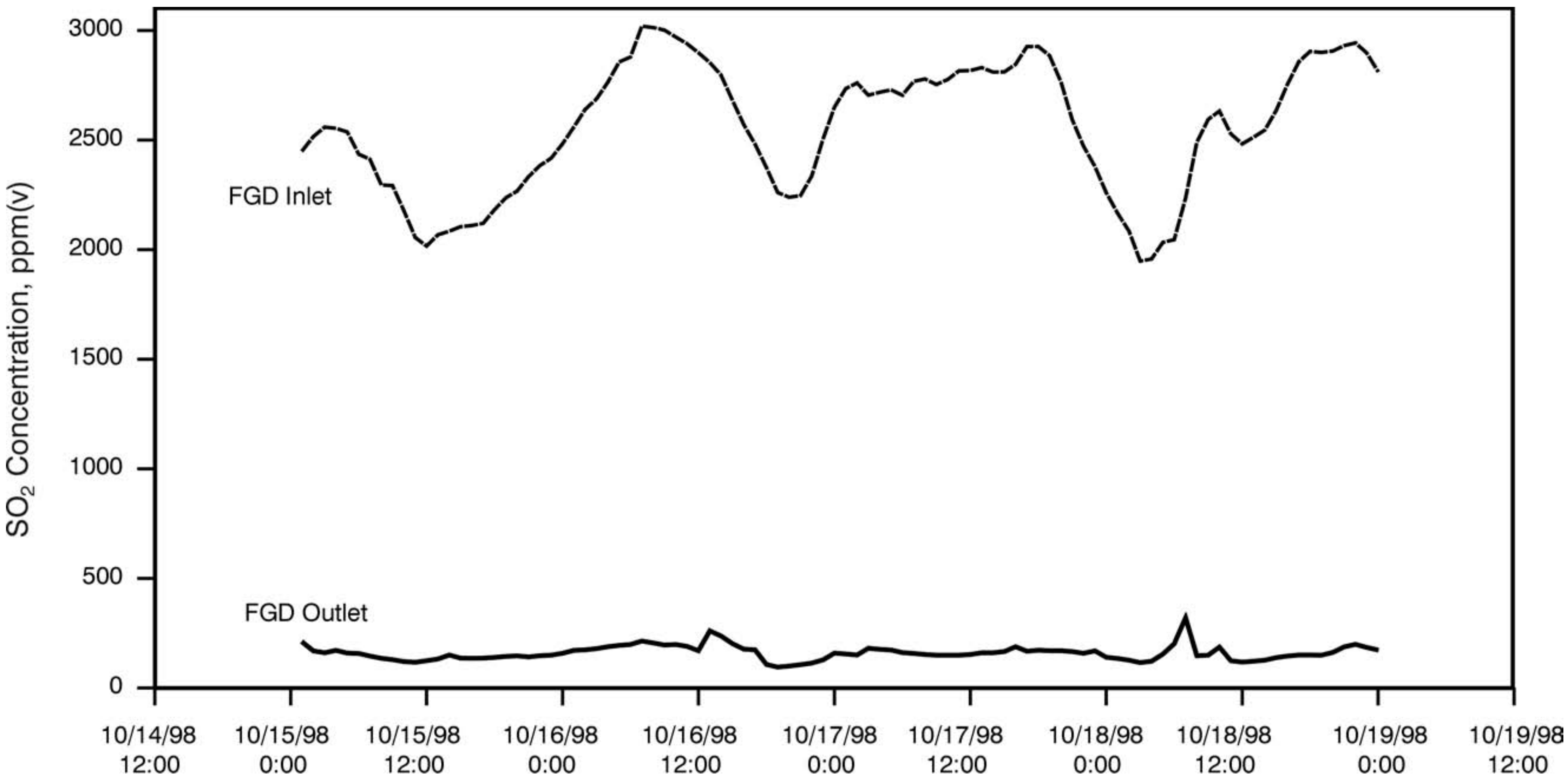

Figure 3-1
SO_2 concentration at the inlet and outlet of the FGD system.

3.2 Sampling Test Plan

The inlet sampling location at the FGD was also the sampling location for the ESP outlet. Because the unit has two ESPs, the flue gas must be split into two streams, but after passing through the ESPs, the flue gas then is recombined into a single duct. The sample port for the ESP outlet/FGD inlet was located after the flue gas streams had recombined but prior to the FGD modules. The sampling activities that were completed at Site E-29 are shown in Table 3-2.

Table 3-2
Test Program Matrix at Site E-29

	Target Species[1]					
Process Stream	**Hg^0**	**Hg^{2+}**	**Total Hg**	**Chlorides (Cl^-)**	**SO_3**	**Other Trace Elements**
Flue Gas Sample Streams						
ESP Outlet/FGD Inlet	X	X	X	X	X	X
Stack	X	X	X			X
Solid Samples						
Coal Feeders			X	X	X[2]	X
ESP Hoppers			X		X	X
Lime			X			

[1] For the flue gas streams, mercury measurements (speciated and total) were made using the Ontario Hydro method; the other trace elements were collected and measured using EPA Method 29. The chlorine in the flue gas was measured using EPA Method 26 (Cl^- as both HCl and Cl_2), and the SO_3 concentration was measured using the selective condensation method.

[2] For coal, the SO_3 is measured as total sulfur content.

All the sampling activities were completed by Radian; however, the analysis of the Ontario Hydro impinger samples was done in the field by the EERC using a portable cold-vapor atomic absorption (CVAA) analyzer. The filter samples were taken back to the EERC and analyzed by the EERC's Analytical Research Laboratory. In addition to doing the analyses, the EERC operated a Semtech Hg 2000 mercury continuous emission monitor (CEM) at the stack.

This report will focus on the Ontario Hydro method and CEM results. Radian and the EERC will provide a complete report for all the sampling activities at Site E-29, including other trace elements and chlorides, prior to completion of the "Characterization and Modeling of the Forms of Mercury from Coal-Fired Power Plants" project.

At the FGD inlet, a modified EPA Method 301 test was completed to validate the Ontario Hydro mercury speciation method. The analyte-spiking protocol procedure detailed in EPA Method 301 was used. For this procedure, it is required that six quadtrain replicates be done with half of the impinger trains being spiked with mercury prior to sampling (two sets of impinger trains in each quadtrain). In this way, the precision and bias of the sampling method being tested can be determined. However, because of time and monetary constraints, it was decided that only five replicate quadtrains, along with all of the pilot-scale work that had been done in the past, would provide enough statistical evidence to determine whether the method was valid. This testing resulted in a total of 20 samples being collected at the FGD inlet.

At the stack, four sets of duplicate Ontario Hydro method samples were taken. Simultaneously, duplicate EPA Method 29 samples were taken at both the FGD inlet and stack. The EPA Method 29 samples were done to measure trace elements other than mercury. EPA Method 26A (chlorides) and SO_3 samples were taken when the quadtrain samples were being done. The EPA Method 29, EPA Method 26A, and SO_3 samples were taken and analyzed by Radian and are unavailable for this report.

The duplicate Ontario Hydro and EPA Method 29 samples were taken using a full traverse procedure. However, because of the nature of quadtrains, traversing was not possible, and these samples were taken at a single point. The average moisture and oxygen content at each sample point is shown in Table 3-3. The samples taken each day are listed in Table 3-4.

Table 3-3
Average Excess Oxygen and Moisture Content at Mercury Speciation Sampling Points

Sample Location	Excess O_2 (on a dry basis), %	Moisture Content, %
ESP Outlet/FGD Inlet	7.8	8.6
Stack	9.6	14.4

Table 3-4
Samples Taken Each Day

Day	**ESP Outlet/FGD Inlet**[1,2]		**Stack**	
	Ontario Hydro Method	**EPA Method 29**	**Ontario Hydro Method**	**EPA Method 29**
1	1 quadtrain			
2	1 quadtrain	1 duplicate	1 duplicate	1 duplicate
3	1 quadtrain	2 duplicates	2 duplicates	2 duplicates
4	2 quadtrains			

[1] Three EPA Method 26A samples were also completed for chlorides and selective condensation samples for SO_3.

[2] The Semtech Hg 2000 CEM was to be used to measure total mercury and Hg^0 at the FGD inlet.

4

FLUE GAS SAMPLING AND ANALYTICAL METHODS AND QUALITY ASSURANCE/QUALITY CONTROL

This section describes the Ontario Hydro mercury speciation method, the Semtech Hg 2000 mercury CEM, and analytical procedures that were used for this test program to determine the mercury speciation.

4.1 Ontario Hydro Mercury Speciation Method

The Ontario Hydro method was developed by Keith Curtis and other researchers at Ontario Hydro Technologies in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the nitric acid–hydrogen peroxide (HNO_3–H_2O_2) impingers, an attempt was made to more selectively capture the Hg^{2+} by substituting three aqueous 1N potassium chloride (KCl) impinger solutions for one of the HNO_3–H_2O_2 solutions. A schematic of the impinger train is shown in Figure 4-1. The Ontario Hydro method has been extensively tested at the EERC and has been shown to provide accurate mercury speciation data for coal-fired boilers (2, 3). The method is currently being evaluated by American Society for Testing and Materials (ASTM) Subcommittee D22.03.01. A complete description of the Ontario Hydro method in the ASTM format is available at http://www.epa.gov/ttn/emc/prelim.html.

All glassware for the sample trains was precleaned using a 4-hr soak in a 10% HNO_3 solution. No impinger glassware was used more than once in the field test. Samples collected using the Ontario Hydro method were recovered into the following fractions:

Probe ash and particulate filter and ash – Container No. 1

- Probe rinse with 0.1N HNO_3 solution – Container No. 2A
- Back half of the filter holder and connecting U-tubes 0.1N HNO_3 rinses plus the three KCl impinger solutions and their 0.1N HNO_3 rinses – Container No. 2B
- The HNO_3–H_2O_2 solution and its 0.1N HNO_3 rinse and the rinse of the U-tube between the last KCl impinger and H_2O_2 – Container No. 3

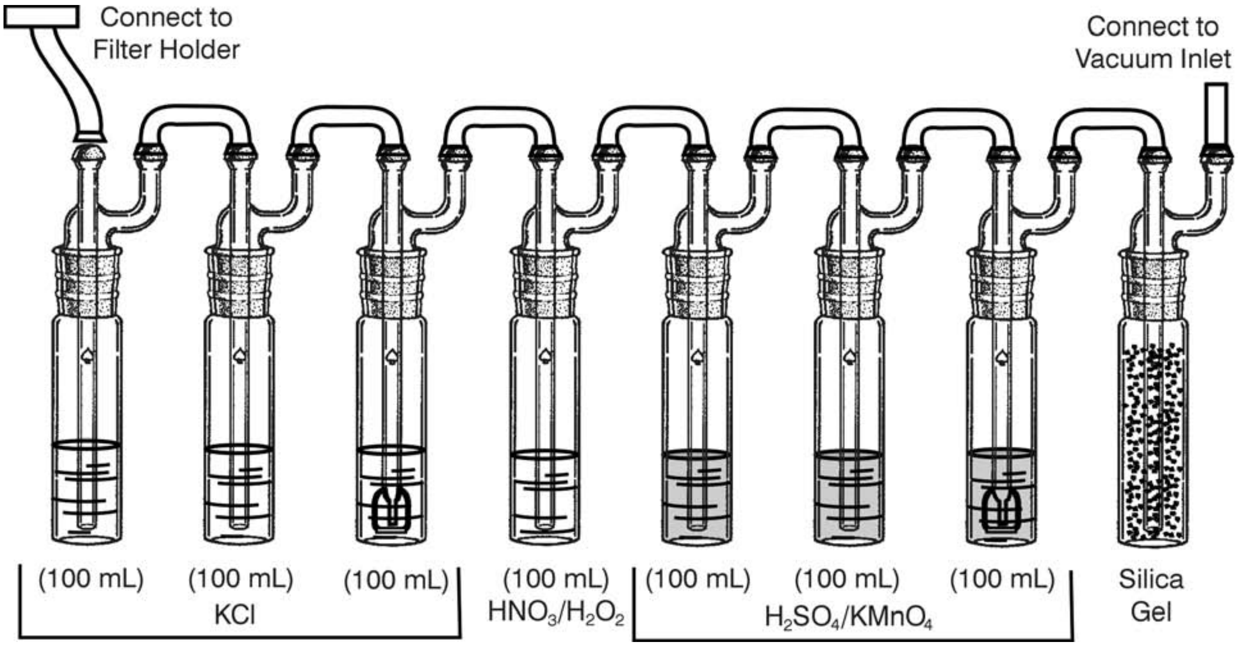

Figure 4-1
Schematic of the Ontario Hydro mercury speciation method sampling train.

- H_2SO_4–$KMnO_4$ impinger and rinses (0.1N HNO_3 rinses and 8N HCl rinses) and the rinse of the U-tubes rinses – Container No. 4

The solutions were analyzed on-site using a Leeman CVAA instrument. The particulate fraction, which was taken back to the EERC, was analyzed first using an HCl–HF microwave digestion procedure followed by CVAA analysis for mercury. A schematic of the teardown of the sample train and the different fractions is shown in Figure 4-2.

For each of the three liquid solutions of the Ontario Hydro method, prior to analyses, a different preparation procedure must be used. The preparation steps for each solution are described below.

KCl Solution. The KCl sample fractions are immediately preserved with acidified $KMnO_4$ after sampling. This solution is then digested using a potassium persulfate digest procedure.

HNO_3–H_2O_2 Solution. The solution is first preserved with 10% $^{v}/_{v}$ HCl, then combined with H_2SO_4–$KMnO_4$ solution until a purple color persists. At this point, hydroxylamine sulfate is added until the solution becomes clear.

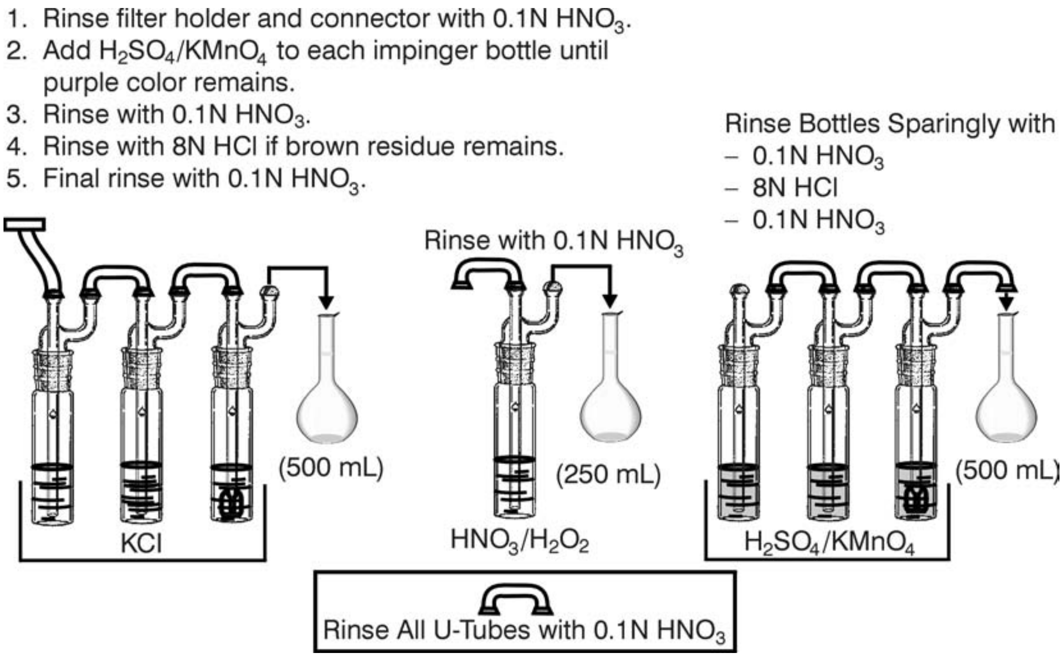

Figure 4-2
Teardown schematic of the Ontario Hydro mercury speciation method sampling train.

H_2SO_4–$KMnO_4$ Solution. Hydroxylamine sulfate is added to the $KMnO_4$–H_2SO_4 sample until the solution turns clear.

For the Ontario Hydro method, the KCl fraction results are reported as Hg^{2+}, and the sum of the mercury measured in the HNO_3–H_2O_2 solution and H_2SO_4–$KMnO_4$ solution is reported as Hg^0. The mercury measured on the filter ash is defined as particulate-bound mercury. The exact form of the mercury on the particulate matter is still unknown.

4.2 Semtech Hg 2000 Analyzer

A Semtech Hg 2000 mercury CEM manufactured by Semtech Metallurgy AB, Lund, Sweden, was used at the stack location. The instrument measures Hg^0 on a real-time basis using a Zeeman-shifted ultraviolet sensor. The Zeeman shift detection technology eliminates interference from SO_2 absorption. Because the instrument is designed to measure only Hg^0, to get total mercury, the other forms of mercury (Hg^{2+}) must be converted to Hg^0. This is done by passing the flue gas first through a carbonate trap to remove the SO_2 and then a stannous chloride solution. The SO_2 must be removed because it interferes with the ability of stannous chloride to convert Hg^{2+} to Hg^0. The operating range of the instrument is 0.3 $\mu g/Nm^3$ to 20 mg/Nm^3. The Semtech Hg 2000 has been certified by TUEV Rheinland for determining compliance with the German legal limit of 50 µg/Nm^3 for total mercury from waste incinerators.

4.3 Oxygen Concentration, Flue Gas Velocity, and Moisture

To determine the O_2 levels at each sample location, an Orsat procedure was used. Flue gas velocity, moisture, and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with the Ontario Hydro method.

4.4 Quality Assurance/Quality Control (QA/QC)

An overall QA/QC program in place at the EERC is designed to maintain overall data integrity. However, additional procedures were instituted specifically for this project.

4.4.1 Instrument Setup and Calibration

The instrument used in the field for mercury determination was a Leeman Labs PS200 CVAA. To measure mercury, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% $^{w}/_{v}$ stannous chloride in 10% $^{v}/_{v}$ HCl as the reductant. Each day, the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% $^{v}/_{v}$ HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This QC standard was prepared from a different stock than the calibration standards. It was required that the values obtained read within 5% of the true value before the instrument was used. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument.

4.4.2 Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The filter samples were placed in premarked petri dishes and taken back to the EERC, where they were analyzed using mixed-acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

4.4.3 Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10% $^{v}/_{v}$ nitric acid for a minimum of 4 hr, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant.

4.4.4 Analytical Reagents

All acids that were used for the analysis of mercury were trace metal-grade. Other chemicals that were used in the preparation of analytical reagents were analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within ±0.5% and were traceable to NIST standard reference materials.

4.4.5 Blanks

As part of the QA/QC procedures, four field blanks were completed. A field blank is defined as a complete impinger train including all glassware and solutions taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels. However, in all cases, the field blanks taken during the sampling activities at Site E-29 were shown to be insignificant, as shown in Table 4-1.

Table 4-1
Results of Mercury Speciation Field Blanks

Day	KCl Solution, µg/L	H_2O_2 Solution, µg/L	$KMnO_4$ Solution, µg/L
1	<0.03	<0.03	<0.03
2	<0.03	<0.03	<0.03
3	<0.03	<0.03	<0.03
4	<0.03	<0.03	<0.03

All acids, chemical reagents, and deionized water used for mercury determination were analyzed for background levels of mercury. Each time a new batch of reagents was prepared, an aliquot was immediately taken and analyzed for mercury. Again, no mercury contamination was found.

4.4.6 Spiked Samples

In order to ensure that adequate levels of accuracy were maintained, spiked samples were also submitted for analysis. These samples were made up independently of the chemist doing the analyses. The spikes were required to be within 15% of the true value. If the value is not within the specified limits, then the instrument is recalibrated and the samples reanalyzed. The spiking solutions were from a stock separate from the calibration standard stock. The analytical results for the spiked samples are shown in Table 4-2. As can be seen, with only a few exceptions, the analyses of these spikes are easily within the tolerance specified.

Table 4-2
Results of Mercury Speciation Field Spikes

	KCl Solution			**H_2O_2 Solution**			**$KMnO_4$ Solution**		
Date	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**
10-15-98	14.70	15	98.0	3.595	4	89.9	4.51	5	90.2
10-15-98	9.94	10	99.4				4.86	5	97.2
10-15-98	10.03	10	100.3	3.87	4	90.8	5.32	5	106.4
10-16-98	15.12	15	100.8	3.60	4	90.0	4.40	5	88.0
10-16-98	10.22	10	102.2	3.72	4	93.0	4.71	5	94.2
10-16-98	10.51	10	105.1	3.78	4	94.5	5.13	5	102.6
10-17-98	13.85	15	92.3	3.94	4	98.5	4.03	5	80.6
10-17-98	9.79	10	97.9	4.38	5	87.6	4.65	5	93.0
10-17-98	9.77	10	97.7	3.64	4	91.0	4.94	5	96.8
10-17-98	10.15	10	101.5	5.75	5	115.0			
10-18-98	13.35	15	89.0	4.48	5	86.2	4.38	5	87.6
10-18-98	9.53	10	95.3	5.12	5	102.4	4.84	5	96.8
10-18-98	9.57	10	95.7	5.30	5	106.0	4.35	5	87.0
10-18-98				5.86	5	117.2			
	Average		**98.1**	**Average**		**97.5**	**Average**		**93.5**
	Std. Dev.		**4.3**	**Std. Dev.**		**10.0**	**Std. Dev.**		**7.3**

5

MERCURY SPECIATION RESULTS

This section presents the flue gas mercury speciation results for the more formal validation tests and the mercury removal across the FGD system. All data are based on 20±C and dry conditions.

5.1 Ontario Hydro Mercury Speciation Validation Results

The more formal validation of the Ontario Hydro mercury speciation method used a modification of EPA Method 301. As described earlier in Section 3.0, only five sets of quadtrains rather than six were used for the validation test. Analyte spiking was used in two impingers sets of each quadtrain (one-half of the total samples). The entire data set is shown in Table 5-1, and the statistical results are shown in Tables 5-2 and 5-3.

Leaks developing across the quadtrain probe, filter, or impinger train can be a major problem in doing quadtrain sampling. This proved to be a problem in the testing at Site E-29. As shown in Table 5-1, several of the sample trains did not pass the leak check at the end of the sampling period. As a result, the leaks resulted in the mercury concentration being less than would be expected. These samples were not used to determine the relative standard deviation and bias results as shown in Tables 5-2 and 5-3. Originally, only four quadtrains were planned, but a fifth was done to compensate for the lost sample trains due to leaks in the system.

Also based on the speciation results, there does appear to be some variability from day to day. As was shown earlier in Figure 3-1, there is variability in sulfur content of the coal. It is not unreasonable to assume there could be variability in the mercury content as well. However, the statistical results show that the Ontario Hydro method passes the criteria established in EPA Method 301. The relative standard deviation (RSD) is clearly less than 50% in all cases. Also, the calculations show that there is no statistical bias (the pooled standard deviation is less than the t-statistic). Based on the mercury speciation results, the mercury generated by this coal was approximately 70% Hg^{2+} and 30% Hg^{0}. This ratio tended to remain constant regardless of the day-to-day variability in the data.

Table 5-1
Mercury Speciation Quadtrain Sampling Results Using the Ontario Hydro Method[1]

		Without Analyte Spiking					With Analyte Spiking (spike subtracted)				
Date	Quad-train	Leak Check	Hg on Filter, μg/Nm^3	Hg^{2+}, μg/Nm^3	Hg^0, μg/Nm^3	Total Hg, μg/Nm^3	Leak Check	Hg on Filter, μg/Nm^3	Hg^{2+}, μg/Nm^3	Hg^0, μg/Nm^3	Total Hg, μg/Nm^3
10-15-98	1	Yes	0.01	10.34	4.77	15.12	Yes	0.01	8.94	5.26	14.20
10-15-98	1	No	0.01	5.32	4.88	10.22	Yes	0.01	9.35	4.60	13.96
10-16-98	2	Yes	0.01	4.59	2.43	7.03	No	0.01	2.01	3.96	5.98
10-16-98	2	Yes	0.01	5.93	4.06	10.00	Yes	0.01	3.46	3.97	7.43
10-17-98	3	Yes	0.01	9.27	2.51	11.79	No	0.01	1.42	3.76	5.18
10-17-98	3	Yes	0.01	8.44	2.31	10.76	Yes	0.01	5.65	2.20	7.85
10-18-98	4	Yes	0.01	8.52	2.92	11.45	Yes	0.01	8.38	3.40	11.78
10-18-98	4	Yes	0.00	7.81	2.32	10.13	Yes	0.00	8.48	2.90	11.38
10-18-98	5	Yes	0.01	10.93	4.20	15.14	Yes	0.01	10.84	2.34	13.18
10-18-98	5	Yes	0.00	10.81	4.26	15.07	Yes	0.00	8.90	4.18	13.09

[1] Results are presented on a dry basis and normal conditions (20∝C, and 1 atmosphere of pressure).

Table 5-2
Statistical Results for Precision for the Quadtrain Data from the Ontario Hydro Method

	With Analyte Spiking (spike subtracted)			Without Analyte Spiking		
	Hg^{2+}, μg/Nm^3	Hg^0, μg/Nm^3	Total Hg, μg/Nm^3	Hg^{2+}, μg/Nm^3	Hg^0, μg/Nm^3	Total Hg, μg/Nm^3
Std. Dev.	0.8	0.8	0.1	0.6	0.6	1.2
% RSD	8.8	21.8	1.4	7.4	19.7	10.5
Mean	9.1	3.7	12.9	8.2	3.1	11.4

Table 5-3
Statistical Results for Bias for the Quadtrain Data from the Ontario Hydro Method

	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3
Bias	0.86	0.65	1.51
Pooled Std. Dev.	1.01	1.03	1.22
t-value	0.850	0.635	1.237
t-statistic	2.571	2.571	2.571

One issue that has been extensively discussed with respect to mercury speciation methods is the temperature at which the particulate filter should be maintained. For these tests, the filters were out of stack (EPA Method 5), but the filters and probes were maintained at the temperature of the flue gas (~320°F). As shown in Table 5-1, the amount of mercury measured on the filter was insignificant. However, because the samples were taken at the outlet of the ESPs, the dust loading was also low.

5.2 Statistical Error/Variability Associated with the Ontario Hydro Method

Data variability results from two sources. The first is actual variability in the compound or element being measured, and the second is error associated with the measurement. The use of paired or quadtrains is designed to help eliminate process variability and determine sample error. Based on very extensive pilot-scale testing using the Ontario Hydro method, the error that can be expected is approximately 10% of the measured value if the measured value is >1.0 µg/Nm^3. These pilot-scale tests were essentially conducted under ideal conditions. It is expected that sampling in the field will result in increased error: people are more cramped; sampling ports are often not ideal; samples must be sent off-site; more chances exist for contamination error, etc. From the field data collected to date using the Ontario Hydro Method, the error associated with paired trains (eliminating process variability) has been between 10% and 20%. For example, in two field tests done by the EERC at plants firing North Dakota lignites, the maximum variability for six measurements at the FGD outlet was 12% and 11%.

It has been found that the greatest source of error in the Ontario Hydro procedure is not in the sampling but in the preparation of the impinger solutions following sampling. The preparation steps include 1) tearing down the impinger train, 2) transferring the solutions to flasks or bottles, and 3) digesting of the solutions so that they can be analyzed using CVAA. In the field tests completed in North Dakota, and at Site E-29, the sample preparation and analysis was done in the field. If qualified people are doing the work, overall measurement error will be reduced, since the sample preparation is done immediately and samples are not shipped off-site.

In the tests completed at Site E-29, the quadtrain sampling resulted in a maximum variability (%RSD) of 22%. Although the sample preparation and analyses were done on-site, this is on the high end of the expected variability. However, the process variability was also high, as shown by the SO_2 data in Figure 3-1 and the mercury CEM data discussed later in this report (Section 5.4). The use of bundled quadtrains also can create the potential for data variability because they are clumsy to use and are prone to leaks. Indeed, several of the tests did not pass the leak check that must be completed prior to sampling and after sampling is completed. Nevertheless, as stated earlier, the Ontario Hydro method clearly passes the statistical criteria established in EPA Method 301.

5.3 Mercury Removal Across the FGD System

The Ontario Hydro mercury speciation results at the inlet and the outlet of the FGD are shown in Table 5-4 and, graphically, in Figure 5-1. It shows in Table 5-2 that the FGD system removed about 88% of the Hg^{2+}, but little if any Hg^0. This is in agreement with all of the mercury data that have been collected in the last several years across wet FGD systems. The overall mercury removal across the FGD system was about 51%. Although it appears that there was an increase in Hg^0 across the FGD, this may not be the case for several reasons. First, all of the data are presented on an as-measured O_2 basis. There were not enough O_2 measurements taken at either the stack or the FGD inlet sample point to ensure an accurate O_2 concentration; therefore, O_2 was not taken into account. Secondly, the inlet to the FGD and stack samples were not taken simultaneously, and there was variability in the data. This is shown in Figure 5-1 by the relatively large error bars on the FGD inlet data. It is also possible that the measured inlet Hg^0 concentration was low. This can occur if there is oxidation of Hg^0 across the sample filter. Although the particulate loading on the sample filter was low, it was not zero. Previous research has shown that particulate matter can convert Hg^0 to Hg^{2+} (2, 4).

Table 5-4
Mercury Speciation Results Across the FGD System

Date	Outlet of FGD			Inlet of FGD*			Hg^{2+} Removed, %	Total Hg Removed, %
	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3		
10-16-98	1.23	4.25	5.47					
10-16-98	0.77	3.86	4.63					
Avg.	**1.00**	**4.05**	**5.05**	**4.66**	**3.49**	**8.15**	**78.5**	**38.0**
Std.	**0.32**	**0.27**	**0.59**	**1.24**	**0.92**	**1.61**		
10-17-98	1.15	4.35	5.50					
10-17-98	0.49	4.19	4.67					
Avg.	**0.82**	**4.27**	**5.09**	**7.79**	**2.34**	**10.13**	**89.5**	**49.7**
Std.	**0.47**	**0.11**	**0.58**	**1.90**	**0.15**	**2.04**		
10-18-98	0.82	3.88	4.70					
10-18-98	0.57	4.52	5.09					
Avg.	**0.70**	**4.20**	**4.90**	**9.33**	**3.32**	**12.65**	**92.5**	**61.3**
Std.	**0.17**	**0.45**	**0.28**	**1.30**	**0.82**	**1.80**		

*The inlet-of-the-FGD data shown are the average and standard deviation values for the valid data from Table 5-1.

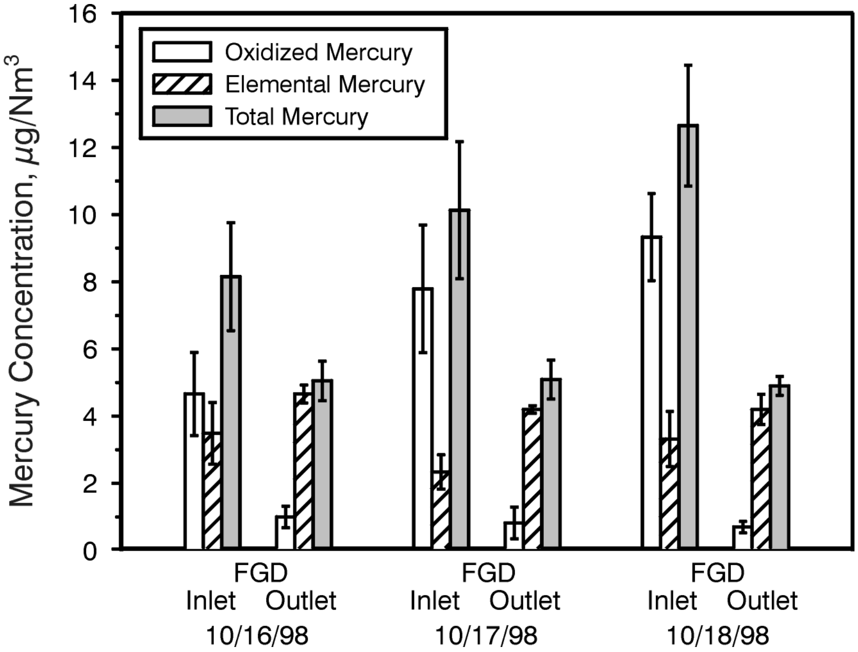

Figure 5-1
The change in vapor-phase speciated mercury across the FGD system.

5.4 Semtech Hg 2000 CEM Results

The Semtech CEM was used at the inlet of the FGD system. Although the instrument was developed to only measure Hg^0, the instrument was able to measure total mercury by including a conversion system designed at the EERC. To provide mercury speciation data, the conversion system was periodically bypassed to measure Hg^0 and, by difference, the concentration of Hg^{2+} in the flue gas could be determined. A comparison between the Semtech CEM data and the Ontario Hydro method data is shown graphically in Figures 5-2 through 5-5. As can be seen from the four graphs, the CEM results for both total Hg and Hg^0 compare quite well with the results obtained using the Ontario Hydro method. On Day 4, the carbonate trap of the conversion system was intentionally bypassed to determine the effect it would have on the conversion of Hg^{2+} to Hg^0. As had been speculated, the resulting high levels of SO_2 in the sample gas stream interfered with the ability of stannous chloride solution to convert Hg^{2+} to Hg^0. As seen in Figure 8, eventually no conversion occurred, and the measured total Hg was the same as the measured concentration of the Hg^0. It should be noted that the Semtech and Ontario Hydro method results are presented on the same basis (dry but not corrected for O_2)

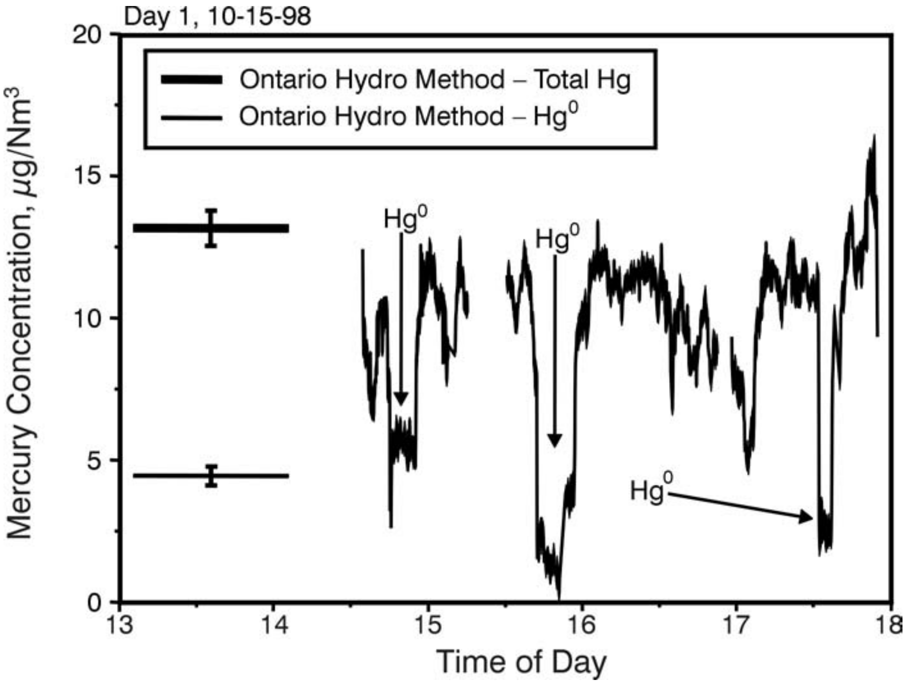

Figure 5-2
Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 1.

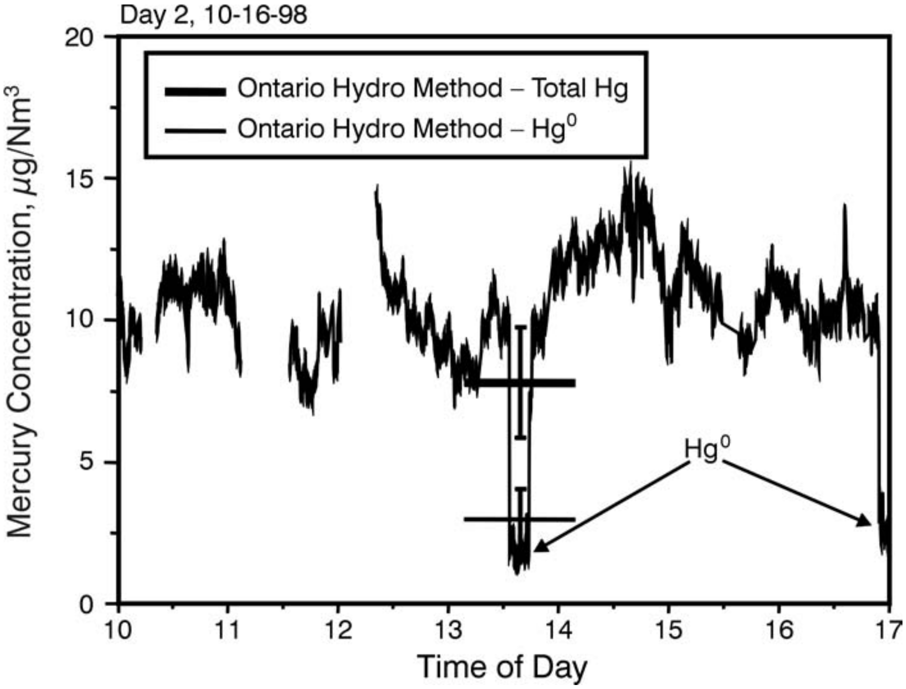

Figure 5-3
Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 2.

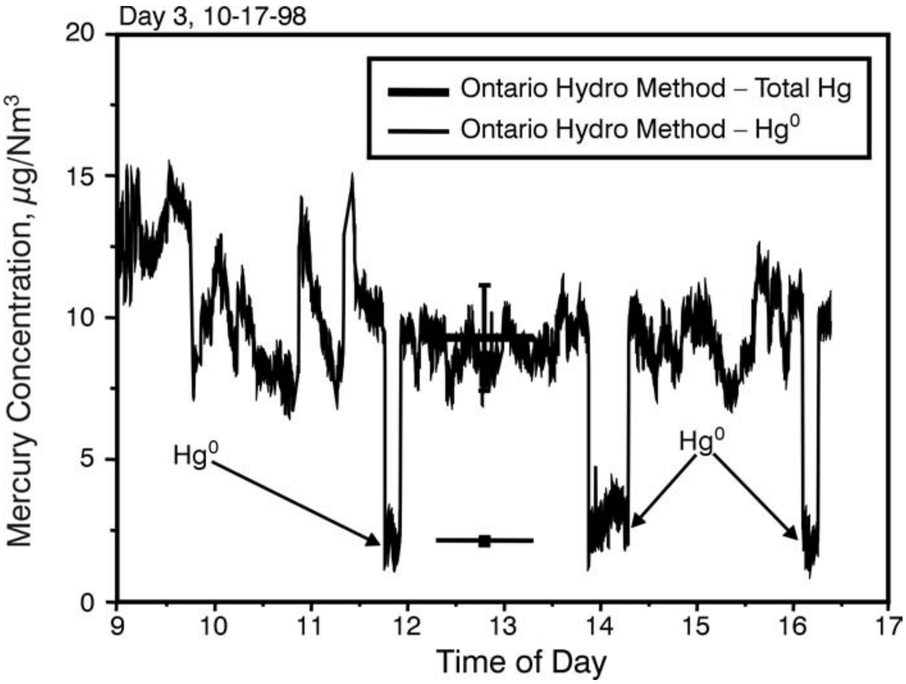

Figure 5-4
Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 3.

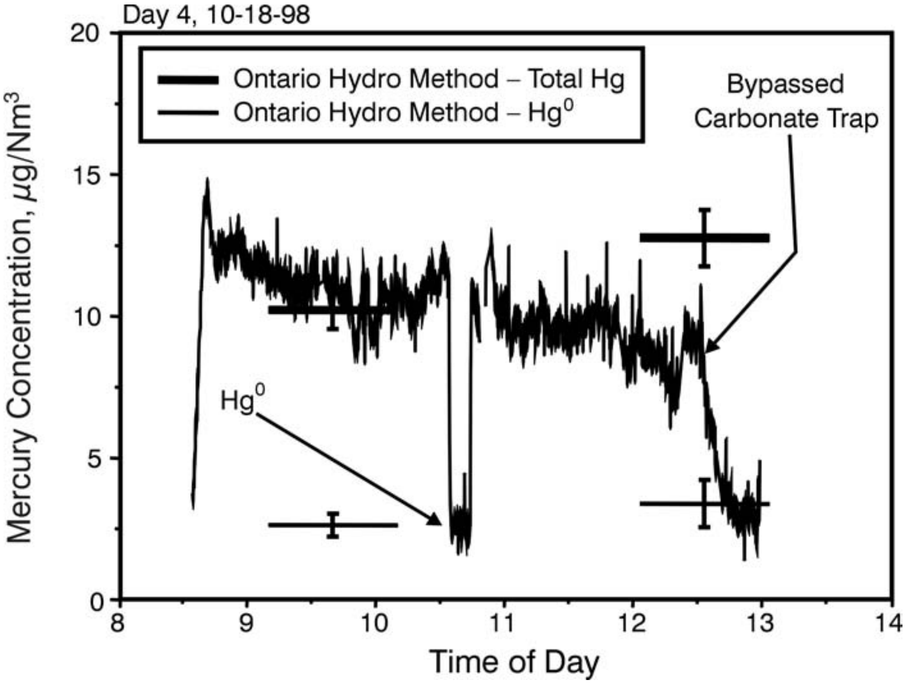

Figure 5-5
Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 4.

6

CONCLUSIONS

On the basis of the results from the Ontario Hydro mercury speciation sampling project at Site E-29, the following conclusions can be drawn:

- The Ontario Hydro method results were well within the statistical criteria established by EPA Method 301. The method is valid for measuring mercury speciation in the field.
- The mercury emitted at the stack was about 10% Hg^{2+} and 90% Hg^{0}.
- No mercury was captured on the filters of the sampling train at either the FGD inlet or the stack.
- The FGD system removed about 88% of the Hg^{2+}. The overall mercury removal of the FGD system was 51%.
- The Semtech Hg 2000 gave total mercury results comparable to those obtained using the Ontario Hydro mercury speciation sampling method for both total Hg and Hg^{0}.

7

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