

FINAL TECHNICAL REPORT  
January 1, 2010, through March 31, 2011

Project Title: **DETERMINING THE VARIABILITY OF CONTINUOUS  
MERCURY MONITORS (CMMS) AT LOW MERCURY  
CONCENTRATIONS**

ICCI Project Number: 10/6A-1  
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ABSTRACT

A number of states, including Illinois, have decided it necessary to control mercury. In Illinois essentially 90% removal will be required. Obtaining this level of control will require measuring mercury at concentrations  $<1.0 \mu\text{g}/\text{m}^3$ . To date, there is little if any data as to the validity of the continuous mercury monitors (CMMS) to measure at these low levels. With funding from the Illinois Clean Coal Institute, the Electric Power Research Institute, the U.S. Department of Energy, and the Center for Air Toxic Metals® Affiliates Program, the Energy & Environmental Research Center planned and carried out testing to evaluate both Tekran and Thermo Fisher Scientific CMMS in a pilot-scale system. The primary goal was to determine the ability of the two CMMS to measure mercury concentrations  $<1.0 \mu\text{g}/\text{Nm}^3$ . The project included 2 weeks of pilot-scale testing on natural gas, using mercury-spiking systems and injection of  $\text{SO}_2$ ,  $\text{HCl}$ , and  $\text{O}_2$ , and a third week of pilot-scale testing firing coal. At the completion of each week of pilot-scale testing, statistical analysis was performed to determine the accuracy and variability of the CMMS as compared to sorbent trap samples at the different mercury concentrations ranging from 0.25 to  $1.0 \mu\text{g}/\text{m}^3$ . The results showed that both instruments operated with little or no maintenance for 3 months. The Tekran and sorbent trap results were nearly identical under all test conditions. However, when coal was fired, the Thermo Scientific CMM did not perform as well as expected.

## EXECUTIVE SUMMARY

A number of states, including Illinois, have decided it necessary to control mercury. In Illinois essentially 90% removal will be required. Obtaining this level of control will require measuring mercury at concentrations  $<1.0 \mu\text{g}/\text{m}^3$ . There is little data in the literature as to the validity of using continuous mercury monitors (CMMs) to consistently measure mercury at levels  $<1.0 \mu\text{g}/\text{Nm}^3$ , and there has been no testing done to systematically determine the variability that is associated with CMMs when measuring mercury at these levels. The Illinois Clean Coal Institute, the Electric Power Research Institute, the U.S. Department of Energy, and the Energy & Environmental Research Center (EERC) Center for Air Toxic Metals<sup>®</sup> Affiliates Program funded a project at the EERC to evaluate the two CMMs most widely used by the utility industry, those manufactured by Tekran and Thermo Fisher Scientific. The only way this could be done was to provide a situation where all aspects of the process were under controlled conditions. Tests were performed at the pilot-scale level, first firing natural gas and utilizing mercury-spiking systems, then completing a test firing coal but in a manner that generated consistently low mercury emissions.

### Objectives

The primary goal of the project was to determine the actual variability of CMMs at mercury concentrations  $<1.0 \mu\text{g}/\text{Nm}^3$ . To realize this goal, specific objectives of the project were to:

- Determine the uncertainty of the components of the mercury-spiking systems.
- Determine the zero mercury concentration for the instruments.
- Based on “true” spiking values for  $\text{Hg}^0$  and  $\text{HgCl}_2$ , determine the variability of the CMMs.
- Compare the variability results with and without acid gases ( $\text{SO}_2$  and  $\text{HCl}$ ) added to the flue gas generated firing natural gas.
- Determine the performance of the CMMs measuring low levels of mercury ( $<1.0 \mu\text{g}/\text{Nm}^3$ ) when coal was fired.

To accomplish this goal, pilot-scale tests were conducted, and the variability of instruments was determined and compared to a reference method (Environmental Protection Agency [EPA] Method 30B—sorbent traps). The project also required that the variability of the sorbent trap sampling be determined. Therefore, to assess the precision of the sorbent traps, quad train samples were taken. In addition, spiked and blank samples were analyzed.

All of this required a very high level of quality control/quality assurance to ensure that all equipment (the pilot-scale combustor, the mercury-spiking systems, the sorbent trap

sampling equipment, the OhioLumex sorbent trap analyzer, and the CMMs) was operating at the highest level—prior to the test, during the test, and at the conclusion of the project.

## Approach

The overall approach to determining the actual variability of CMMs at mercury concentrations  $<1.0 \mu\text{g}/\text{Nm}^3$  was to compare the CMM results to those obtained based on a reference method (EPA Method 30B). To do this, three primary tasks were completed. The first task was the initial preparation of the equipment, including the particulate test combustor (PTC), the spiking systems, the CMMs, and the OhioLumex. The other two tasks were pilot-scale tests. The initial activity, Task 1, was designed to ensure that all the equipment (spiking systems, combustor, sorbent trap sampling systems, and OhioLumex sorbent trap analyzer) was operating at the highest level. The second task was to complete two weeks of pilot-scale testing firing natural gas and adding mercury using the spiking systems that were developed at the EERC. Various levels of elemental mercury and mercury(II) chloride were added to the combustor. During the second week, the test was repeated, but this time with HCl and SO<sub>2</sub> being added. For each of the test conditions, at least one set of four sorbent trap samples were taken simultaneously.

For the third week of testing (Task 3), an Illinois eastern bituminous coal was fired in the EERC pilot-scale combustor. To reduce the mercury concentration to  $<1 \mu\text{g}/\text{Nm}^3$ , the flue gas was passed through an electrostatic precipitator, then a high-efficiency fabric filter, and finally a wet lime-based scrubber. Again, at least one set of quad sorbent trap samples was taken a day.

At the completion of the testing, the data were statistically analyzed to determine the variability associated with the various parts of the process and to determine the true lower limit of quantification for each of the CMMs.

## Results and Findings

In comparison to multiple sorbent trap samples, both instruments performed very well when natural gas was fired. However, the Tekran instrument did provide a lower detection limit compared to the Thermo Scientific Instrument, and as a result the lower limit of quantification for the Tekran was  $\sim 0.1 \mu\text{g}/\text{Nm}^3$  compared to  $\sim 0.4 \mu\text{g}/\text{Nm}^3$  for the Thermo Scientific CMM. When coal was fired in the pilot-scale combustor, the Thermo Scientific CMM did not perform as well as expected because it was biased high. The Tekran instrument had a very high correlation ( $r^2$  value of 0.990) with the sorbent traps at all test concentrations, including those obtained when coal was fired. There are plans to retest the Thermo Scientific instrument on the same coal, once the problem has been diagnosed by Thermo Scientific. These tests will be independent of the ICCI project; however, the results will be reported to the ICCI project manager.

## OBJECTIVES

The primary goal of the project was to determine the actual variability of continuous mercury monitors (CMMs) at mercury concentrations  $<1.0 \mu\text{g}/\text{Nm}^3$ . To accomplish this goal, pilot-scale tests were conducted, and the variability of instruments was determined and compared to a reference method (Environmental Protection Agency [EPA] Method 30B – sorbent traps). To realize this goal, specific objectives of the project were:

- Determine the uncertainty of the components of the mercury-spiking systems. To be acceptable, the total uncertainty must be  $<10\%$  of the actual value.
- Determine the zero mercury concentration for the instruments. The zero value can be no more than  $10\%$  of the concentration that is expected to be measured. For example, if the mercury concentration is expected to be  $0.25 \mu\text{g}/\text{Nm}^3$ , the zero value must be  $<0.025 \mu\text{g}/\text{Nm}^3$ .
- Based on “true” spiking values for  $\text{Hg}^0$  and  $\text{HgCl}_2$ , determine the variability of the CMMs over a 4-hour time frame for three different mercury concentrations.
- Based on “true” spiking values for  $\text{Hg}^0$  and  $\text{HgCl}_2$ , determine the variability of the CMMs over a 4-hour time frame when both mercury types are added simultaneously.
- Compare the variability of carbon trap measurements using the OhioLumex and Modified EPA Method 1631.
- Compare the variability results with and without acid gases ( $\text{SO}_2$  and  $\text{HCl}$ ) added to the flue gas.
- Determine the performance of the CMMs measuring low levels of mercury ( $<0.5 \mu\text{g}/\text{Nm}^3$ ) when coal is fired.

The project also required that the variability of the sorbent trap sampling be determined. Therefore, to assess the precision of the sorbent traps, quad train samples were taken. In addition, spiked and blank samples were analyzed.

All of this required a very high level of quality control/quality assurance to ensure that all equipment (the pilot-scale combustor, the mercury-spiking systems, the sorbent trap sampling equipment, the OhioLumex sorbent trap analyzer, and the CMMs) was operating at the highest level—prior to the test, during the test, and at the conclusion of the project.

## INTRODUCTION AND BACKGROUND

Under a consent decree, in November 2011, EPA will finalize a National Emission Standard for Hazardous Air Pollutants (NESHAPS) for the utility industry. The floor for mercury emissions will be determined using the maximum achievable control technology (MACT) basis under Section 112 of the 1990 Clean Air Act Amendments. It is expected that mercury emission limits will be considerably lower than those originally required under the court-vacated Clean Air Mercury Rule (CAMR). As a result, it is expected that many coal-fired utilities will be required to continuously measure mercury concentrations at  $<1.0 \mu\text{g}/\text{m}^3$ . In addition, a number of states such as Illinois have promulgated or are

proposing mercury emission limits that are significantly lower than proposed in CAMR or even possibly under the new mercury MACT. Although extensions are being granted, in Illinois essentially 90% removal was required on a systemwide basis by July 1, 2009 (75% plantwide) and plantwide by January 1, 2013. Also, in efforts to obtain permits for new coal-fired power plants, even lower mercury emissions ( $<0.5 \mu\text{g}/\text{Nm}^3$ ) are being agreed to. Obtaining this level of control requires measuring mercury at very low concentrations.

Currently, there is little data in the literature as to the validity of CMMs to consistently measure mercury at levels  $<1.0 \mu\text{g}/\text{Nm}^3$ . There has been no testing done to systematically determine the variability that is associated with the CMMs when measuring mercury at these levels. As a result, the Illinois Clean Coal Institute (ICCI), the Electric Power Research Institute (EPRI), the U.S. Department of Energy (DOE), and the Energy & Environmental Research Center (EERC) Center for Air Toxic Metals<sup>®</sup> (CATM<sup>®</sup>) Affiliates Program funded a project at the EERC to evaluate the two CMMs most widely used by the utility industry: those manufactured by Tekran and Thermo Fisher Scientific.

## EXPERIMENTAL PROCEDURES

The intent of the project was to systematically test both Tekran and Thermo Scientific instruments (the two instruments currently used and most likely to be used in the future) in a pilot-scale system to determine their variability when measuring low mercury concentrations. In the pilot-scale unit, a known quantity of elemental mercury ( $\text{Hg}^0$ ) and oxidized mercury ( $\text{Hg}^{2+}$ ) was added to natural gas, followed by a test firing eastern bituminous coal. The results were then compared to a reference method (EPA Method 30B).

### Project Test Plan

The project was designed to have three primary tasks in addition to reporting requirements. The first task was to develop and test the mercury-spiking systems and to ensure that the pilot-scale combustor was operating at peak performance. This included adding additional piping to allow multiple sorbent trap sampling and to accommodate the two CMMs. Also included in the Task 1 effort was ensuring that the baseline mercury concentration (with no mercury injected) when natural gas was fired was very low ( $<0.05 \mu\text{g}/\text{Nm}^3$ ). This was important because the combustor has been used for numerous mercury projects over the years. The second task included 2 weeks of natural gas tests. The first week was with only mercury being added to the flue gas, and the second week was with  $\text{SO}_2$  and  $\text{HCl}$  being added as well as mercury. Table 1 provides the nominal mercury injection concentrations for each of the natural gas test conditions.

Task 3 was a weeklong test firing an Illinois eastern bituminous coal. The configuration of the pilot-scale system was arranged such that the mercury emissions were consistently  $<1.0 \mu\text{g}/\text{Nm}^3$ . This was done by passing the flue gas first through an electrostatic precipitator (ESP) and then a high-efficiency baghouse followed by a wet flue gas

Table 1. Tentative Natural Gas Test Conditions for Task 2\*

Test Condition	Spiked Mercury	Nominal Concentration, $\mu\text{g}/\text{Nm}^3$
Baseline	Blank	0
1	$\text{Hg}^0$	0.25
2	$\text{Hg}^0$	0.50
3	$\text{Hg}^0$	1.0
4	$\text{HgCl}_2$	0.25
5	$\text{HgCl}_2$	0.5
6	$\text{HgCl}_2$	1.0
7	$\text{Hg}^0$ and $\text{HgCl}_2$	0.25/0.25

\* For the second week of testing (Test Conditions 8–14) nominally 1000 ppmv  $\text{SO}_2$  and 50 ppmv HCl were added to the flue gas.

desulfurization (FGD) unit. To ensure that the CMMs and sorbent trap sampling locations were not exposed to water condensation, external heaters were utilized.

#### Equipment Description

To accomplish the project objectives required the use of the following major equipment items:

- Pilot-scale combustor
- $\text{Hg}^0$  and  $\text{HgCl}_2$  generators for spiking flue gas
- Tekran CMM with  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  calibrators
- Thermo Scientific CMM with  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  calibrators
- OhioLumex sorbent trap analyzer

#### *Pilot-Scale Combustor*

The pilot-scale combustor used for project was the same test combustor successfully used to validate ASTM International (ASTM) D6784–02, “Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).” The pilot furnace, known as the particulate test combustor (PTC), is a 550,000-Btu/hr (580-MJ/hr) pulverized coal (pc)-fired unit designed to generate fly ash and flue gas that are representative of the types produced in a full-scale utility boiler.

PTC instrumentation-permitted system temperatures, pressures, flow rates, flue gas constituent concentrations, and operating data were monitored continuously and recorded by the unit’s data acquisition system. Flue gas samples were taken at the outlet of the combustor and at a location near the CMM and sorbent trap sampling point. After passing through sample conditioners to remove the moisture, the flue gas was analyzed for  $\text{O}_2$ , CO,  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$ . Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

For all tests, the flue gas was passed through a fabric filter. This was true even for Task 2 when natural gas was fired in the PTC. Since the combustor produces about 200 acfm of flue gas at 300°F (149°C), three 13-ft by 5-in. (4-m by 8-cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). The bags used for the tests were all Teflon with a Teflon membrane and were designed to provide very high particulate removal efficiencies. Each bag was cleaned separately with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than cleaning being initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession online. A schematic of the PTC is shown in Figure 1 (this schematic does not show the wet FGD unit).

For Task 3, a pilot-scale ESP was also used. The ESP, shown in Figure 2, is a single-wire, tubular ESP, with a specific collection area of 125 ft<sup>2</sup>/ 1000 acfm at 300°F (149°C). Because the flue gas flow rate for the PTC is about 130 scfm, the gas velocity through the ESP is 5 ft/min (1.5 m/min), typical for a full-scale ESP.

In addition to the fabric filter and ESP for the coal-fired test (Task 3), a small wet FGD was used. The wet FGD was designed to simulate forced oxidation by using air sparging. Lime/water slurry was used to remove the SO<sub>2</sub>.

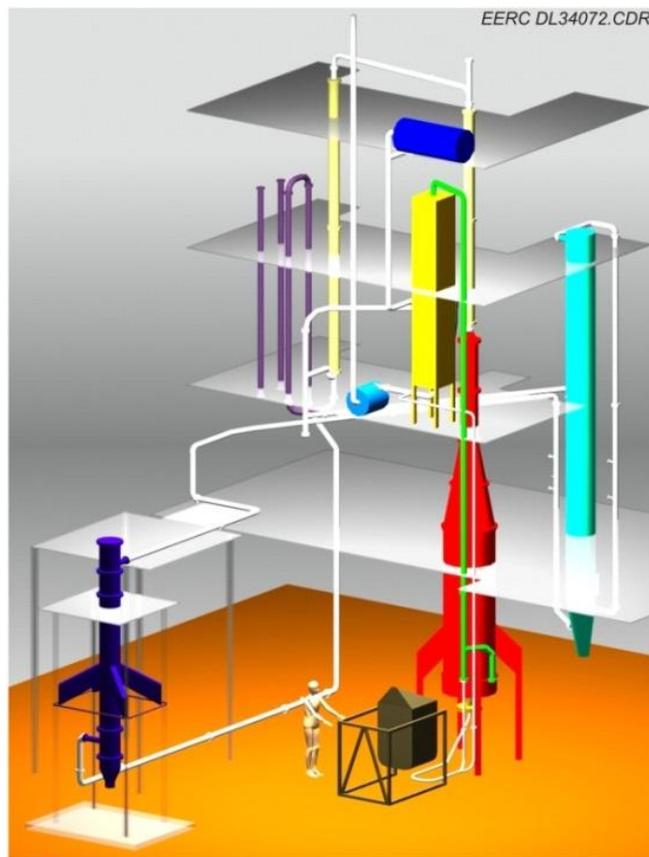


Figure 1. Schematic of the PTC.

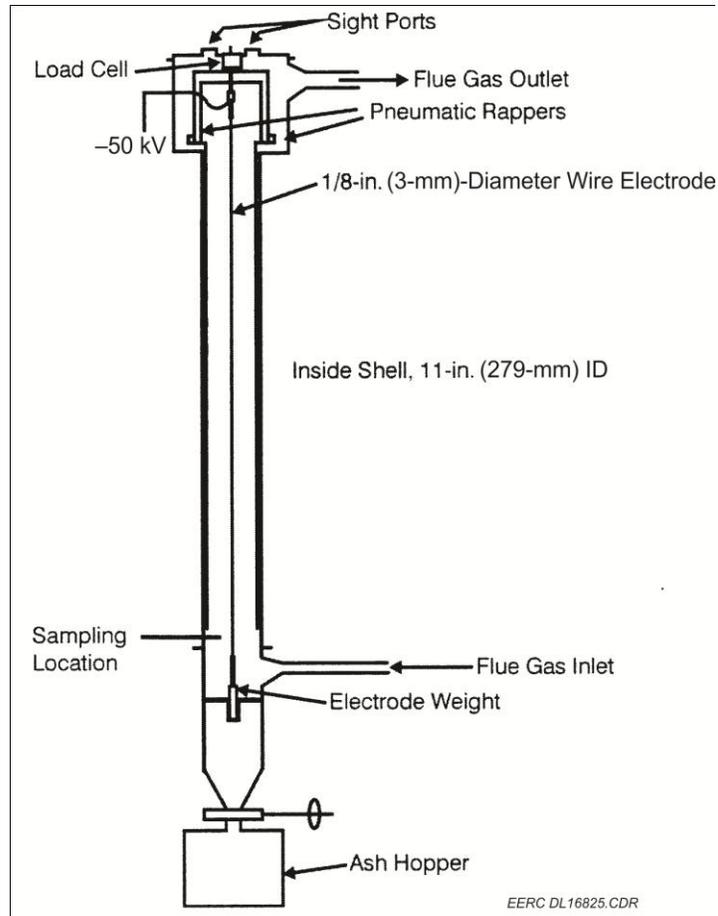


Figure 2. Schematic of the EERC ESP.

Because the test coal had a high-sulfur (~4%) concentration, it was necessary to operate the wet FGD not only to remove mercury but also to ensure that the EERC was in compliance with its North Dakota state permit for SO<sub>2</sub> emissions.

Several modifications were made to the PTC to accommodate the project. A separate sampling leg was put in place to allow for quad train sorbent trap sampling. The inside diameter of most of the existing ductwork is 3.625 in. (92 mm). The new sampling leg ID was increased to 5.25 in. (133 mm) to accommodate the quad sorbent trap sampling. Figure 3 is a schematic and a photograph of the sorbent trap sampling system and layout. In addition, a separate sampling insert was constructed to accommodate the sampling probe systems for the two CMMs. This insert had an ID of 12 in. (305 mm). As shown in the schematic in Figure 4, the insert was designed with separator so that there would be minimal impact of one CMM on the other. Figure 5 is photograph of the CMM location and CMM sampling probes. The instrument housing was located as close to the sampling probes as possible. In this way, the umbilical lines shown in Figure 5 were only 25 ft (7.6 m) long. This was to ensure that the instrument response time was as short as possible.

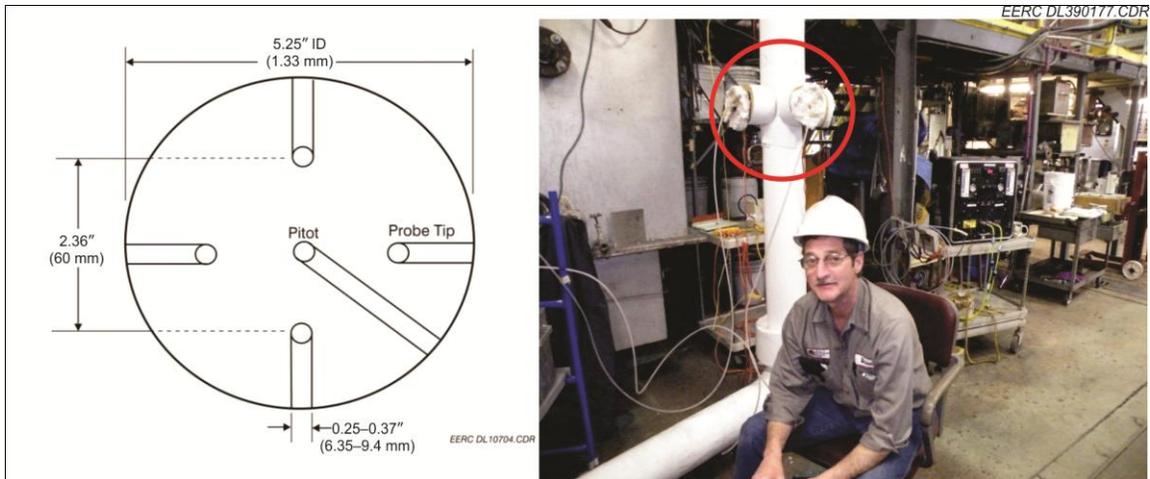


Figure 3. Schematic of carbon trap sampling layout for the PTC.

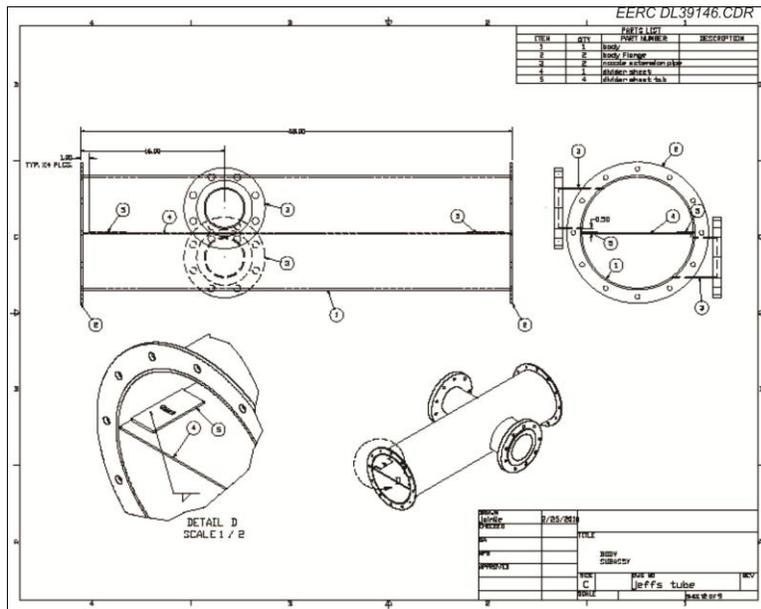


Figure 4. Schematic of the CMM sampling insert for the PTC.

### CMMs

All CMMs have five key components: the extraction probe, the pretreatment/ conversion system, sample transport, the mercury analyzer, and the calibration system. Both the Tekran 3300 and Thermo Scientific Mercury Freedom CMMs use cold-vapor atomic fluorescence spectroscopy to measure the mercury. The pretreatment/conversion systems are designed to prevent interferences and convert all of the mercury to  $Hg^0$ . Both  $Hg^0$  and  $Hg^{2+}$  calibration systems were supplied by the vendors for this test. A complete description of each instrument can be found on the vendor Web sites: [www.tekran.com](http://www.tekran.com) and [www.thermoscientific.com](http://www.thermoscientific.com) and, therefore, will not be repeated in this report.

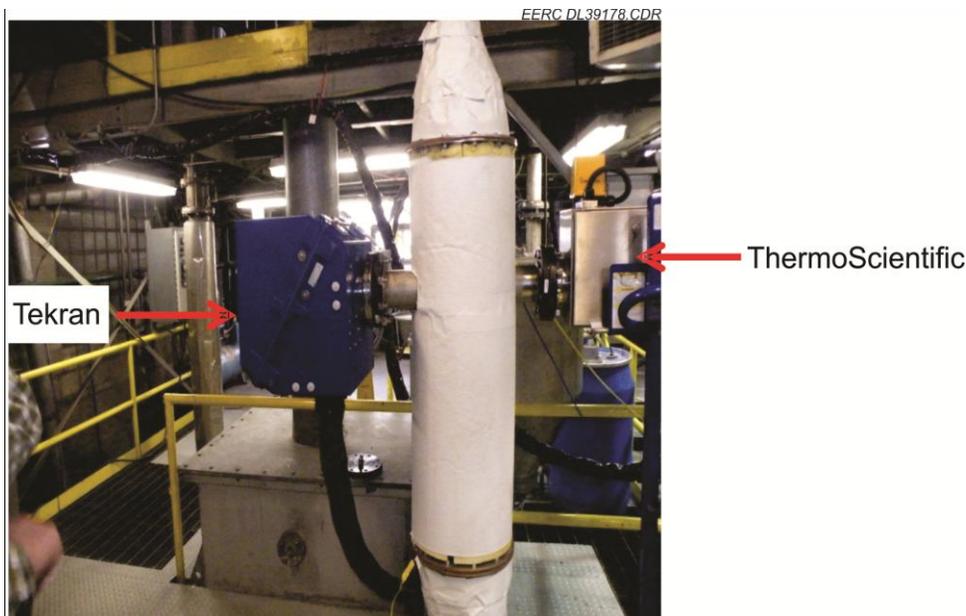


Figure 5. Photograph of the CMM sampling location showing CMM sampling probes.

Although the tests were conducted inside the EERC pilot plant, both CMMs were housed in separate air-conditioned modular sheds to ensure that they were maintained at a constant temperature. As stated previously, to increase CMM response time, the instruments were located as close to the sampling point as possible.

### *Sorbent Trap Sampling*

A modification of EPA Method 30B (sorbent trap) was used as the reference method to compare the CMM results. The sorbent traps used for these tests were purchased from OhioLumex and were designed to provide higher flows and lower background mercury concentrations than the standard sorbent traps. The primary modification to EPA Method 30B was that both quad train and dual train sampling were done during the test program to determine method precision. To help determine accuracy of the method, spiked sorbent traps were also used and analyzed. A schematic of an EPA Method 30B sampling system is shown in Figure 6. For the testing, the sample flow rate was 1.5–2.0 L/min, depending on the concentration of mercury in the flue gas.

With the exception of the samples sent to Frontier Global Sciences (formerly Frontier GeoSciences) for analysis using modified EPA Method 1631, all the sorbent trap samples were analyzed using an OhioLumex RA-915+ mercury analyzer with RP-324 attachment. This instrument uses EPA Method 7473 (thermal desorption) and measures mercury using cold-vapor atomic adsorption with Zeeman shift modulation. The OhioLumex instrument has become the standard method for measuring mercury concentrations based on sorbent traps. Prior to beginning the pilot-scale tests, the EERC instrument was sent to OhioLumex to be cleaned and recalibrated and have all worn parts replaced. This was to ensure that the instrument was operating at its highest level.

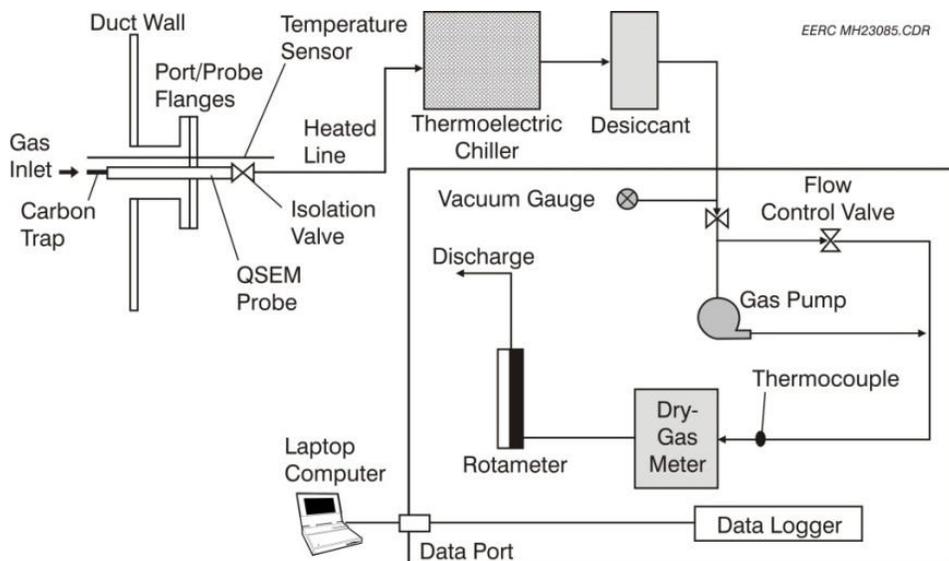


Figure 6. Schematic of EPA Method 30B sorbent trap sampling system.

### *Hg<sup>0</sup>- and HgCl<sub>2</sub>-Spiking Systems*

An important aspect of the overall test program was the ability to consistently inject low levels of mercury at a known concentration into the flue gas generated in the PTC. The spiking systems used for these tests were based on constant output permeation tubes. Constant temperature was maintained using a water bath and calibrated thermocouples. The system was heavily insulated to ensure that there was little temperature loss. During the entire test program (~3 months), the mercury-spiking systems were maintained at constant temperature—again, to ensure a constant output of mercury. A schematic of the elemental mercury spiking system is shown in Figure 7. As can be seen, four different permeation tubes were used to provide the needed concentration. The system was designed so that each tube could be used separately or in combination.

To inject Hg<sup>2+</sup>, exactly the same system was used. However, the output of the Hg<sup>0</sup> permeation tubes was passed through a catalyst bed over which the mercury was oxidized using Cl<sub>2</sub> gas. A schematic is shown in Figure 8. For all tests, the mercury was spiked downstream of the baghouse but prior to the sorbent traps and CMMs.

### *HCl, SO<sub>2</sub>, and O<sub>2</sub> Injection Systems*

As was stated in the test plan, the second week of natural gas tests was a repeat of the first series of tests but included spiking HCl and SO<sub>2</sub> in the flue gas. Both gases were provided by anhydrous cylinders, with the injection location upstream of the baghouse. Based on the test plan, the nominal concentrations of HCl and SO<sub>2</sub> were 50 and 1000 ppmv, respectively. The quantity of each gas needed was calculated and then controlled by a regulator and flowmeter. The concentration of SO<sub>2</sub> was adjusted not only using the flowmeter but also based on the PTC SO<sub>2</sub> analyzers. HCl was added based on the flowmeters and then measured downstream using EPA Method 26A.

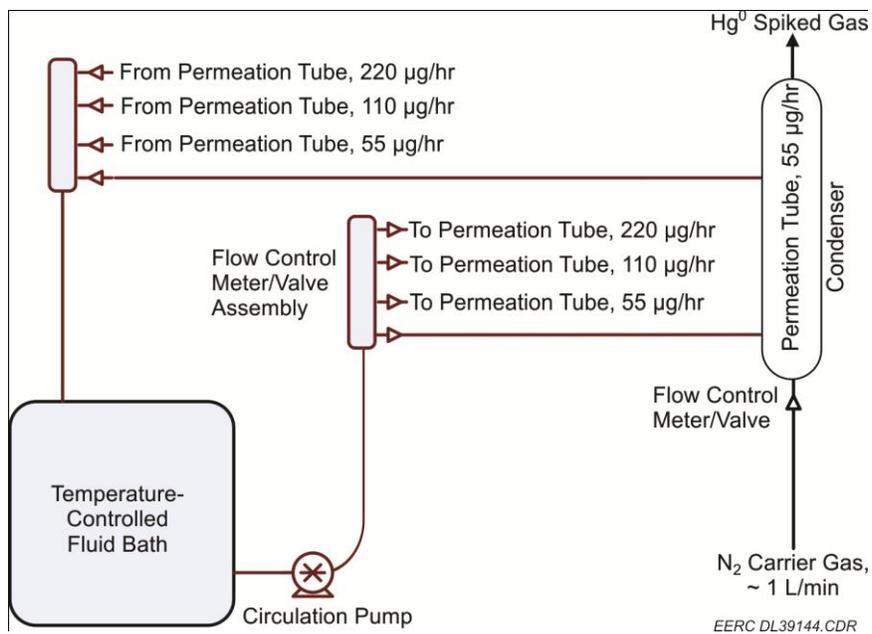


Figure 7. Schematic of  $\text{Hg}^0$ -spiking system.

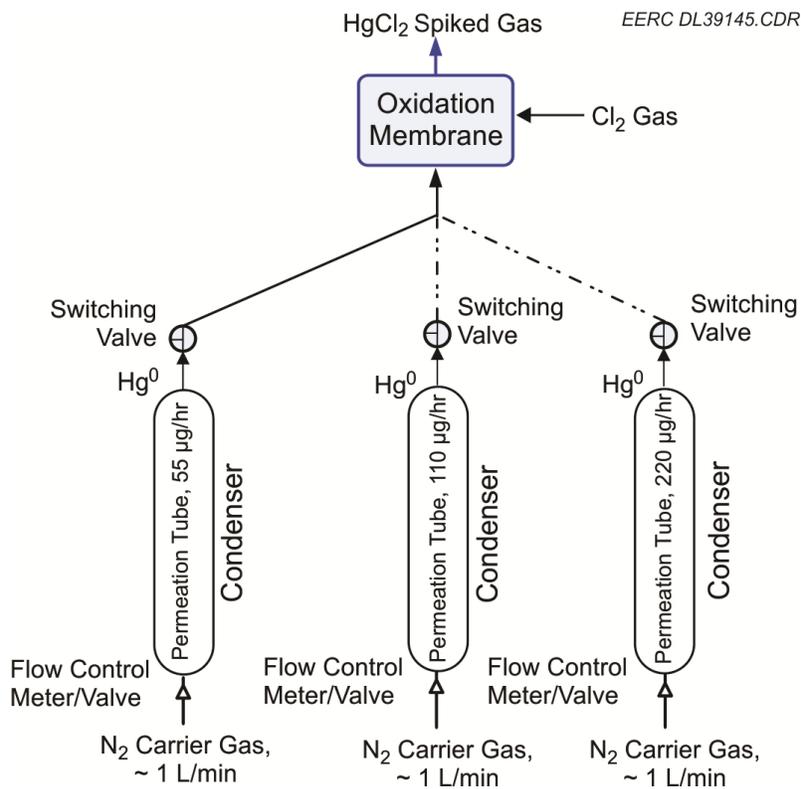


Figure 8. Schematic of  $\text{Hg}^{2+}$ -spiking system.

At the request of Tekran and with the consent of the program managers, a test was conducted evaluating the impact of increased O<sub>2</sub> concentration on the CMMs. It was decided that a 4-hr test would be conducted on natural gas prior to beginning the test firing the Illinois coal. The average O<sub>2</sub> concentration at the CMM location when natural gas was fired was 4.7%. Additional O<sub>2</sub> was added to increase the O<sub>2</sub> concentration to 10%. To accomplish this, a line was added from the EERC's cryogenic O<sub>2</sub> tank to a point upstream of the PTC baghouse.

## Approach

The overall experimental approach was to compare the Tekran and Thermo Scientific CMMs to sorbent trap results at mercury concentrations <1.0 µg/Nm<sup>3</sup> under a variety of test conditions. As stated previously, the project was laid out in three tasks. The first task was to conduct the preliminary work that was necessary before the actual testing could begin. This included the following:

- Design, construct, and test the Hg<sup>0</sup>- and Hg<sup>2+</sup>-spiking systems.
- Design and construct the modifications for the PTC so that the sorbent trap and CMM sampling could be done as proposed.
- Prove there was little if any offgassing for mercury from the PTC when firing natural gas without any mercury spiking.
- Set up the temperature-controlled housing and install the two CMMs.

The remaining two tasks were to conduct pilot-scale tests first with natural gas and then a test with an Illinois bituminous coal.

## *CMMs*

The two CMMs, provided by Tekran and Thermo Scientific, for the project were standard field units. The only exception was that the calibration systems for each were designed to calibrate at low mercury concentrations. The Tekran was calibrated at 0.5 µg/Nm<sup>3</sup> and the Thermo Scientific at 1.0 µg/Nm<sup>3</sup>. Both calibration units were National Institute of Standards and Technology (NIST) traceable; however, the written protocols are not yet available for calibration systems as low as 0.5 µg/Nm<sup>3</sup>.

Both vendors shipped the instruments to the EERC prior to the test and had a technician on-site to install the instrument and be on-site for the first week of testing. The intent was for the instruments to operate with as little input from EERC personnel as possible. To accomplish this, the instruments were set up so that they could be operated remotely by the vendors. This allowed the vendors to change the calibration cycle or make minor adjustments to the instruments as required. This setup worked very well as the instruments were operated 24 hr/day for essentially 3 months with no obvious malfunctions. During the weeks when tests were not being conducted, the PTC sampling ports were left open so the CMMs sampled ambient air.

Both instruments were programmed to calibrate at approximately midnight each night (including times when tests were not ongoing). Initially, zero gas was introduced, followed by introducing the calibration gas to the probe tip. The instruments were automatically adjusted to compensate for any calibration or zero drift. The entire procedure took approximately 30 minutes. To ensure that the calibrators were working properly, the EERC did a calibrator test using sorbent traps at the outlet of the calibrator. During this time (the process was completed over several days), the instrument was operating, providing long-term calibration data.

One difference between the two CMMs is the time between data points. The Thermo Scientific CMM was designed and programmed to provide a data point every minute. In addition, both total and elemental mercury data are provided simultaneously. The Tekran CMM uses gold traps that must be desorbed, and therefore, the instrument was programmed to provide a data point every 2.5 minutes. The Tekran CMM can provide either total or elemental mercury data but not both simultaneously. For the first test series on natural gas, the instrument was programmed to monitor total and element mercury for the same amount of time (two data points of total followed by two data points of elemental mercury). However, to obtain more total mercury data for the last two pilot-scale tests, this was adjusted so that four data points of total mercury were measured followed by two data points of elemental mercury.

#### *Sorbent Traps*

As stated previously, an insert was placed downstream of the baghouse but upstream of the CMMs to allow quad train sorbent trap sampling. Three types of sorbent traps were purchased from OhioLumex for the project. The first were the standard traps that were used for the bulk of the testing. These were designed to have near-zero background mercury and allowed relatively high flow rates. The second type of traps was the same except the second section was spiked with a known mass of mercury. The final traps used for the project were mercury speciation traps.

For each of the test conditions (1–14 plus the baseline) a minimum of one quad train sample was completed. For several of the tests, additional quad or dual train sorbent trap samples were also taken. Each quad train sample was taken over 2 to 4 hours, depending on the mercury concentration. For the coal test, at least one quad train sample was taken a day.

The sorbent trap testing methodology for the pilot-scale tests is shown in Tables 2–4. The actual mercury concentrations shown are based on the sorbent trap results. The initial intent was that two of the traps would be sent to Frontier Global Sciences for analysis and two of the traps would be analyzed by the EERC using the OhioLumex sorbent trap analyzer. This was done for the first set of natural gas tests, but for later tests it was decided by the project team to analyze all of the samples at the EERC.

Table 2. Sorbent Trap Testing Methodology for the First Natural Gas Test

Test Condition	No. Quad Trains	No. Dual Trains	Sample Time	Hg Type	Nominal Hg Conc. $\mu\text{g}/\text{Nm}^3$	Actual Hg Conc. $\mu\text{g}/\text{Nm}^3$
Baseline	2	1	4	–	0	0.023
1	1	0	3	$\text{Hg}^0$	0.25	0.258
2	1	0	3	$\text{Hg}^0$	0.5	0.586
3	1	0	2	$\text{Hg}^0$	1	0.841
4	1	0	3	$\text{Hg}^{2+}$	0.25	0.231
5	1	1	3/1.5	$\text{Hg}^{2+}$	0.5	0.531
6	1	0	2	$\text{Hg}^{2+}$	1	0.705
7	2	2	2/1.5	$\text{Hg}^{2+}/\text{Hg}^0$	0.25/0.25	0.540

Table 3. Sorbent Trap Testing Methodology for the Second Natural Gas Test

Test Condition	No. Quad Trains	No. Dual Trains	Sample Time	Hg Type	Nominal Hg Conc. $\mu\text{g}/\text{Nm}^3$	Actual Hg Conc. $\mu\text{g}/\text{Nm}^3$
Baseline	3	0	4	–	0	0.026*
8	1	0	3	$\text{Hg}^0$	0.25	0.322
9	1	0	3	$\text{Hg}^0$	0.5	0.690
10	1	0	3	$\text{Hg}^0$	1	1.057
11	1	0	3	$\text{Hg}^{2+}$	0.25	0.249
12	1	0	3	$\text{Hg}^{2+}$	0.5	0.696
13	1	0	3	$\text{Hg}^{2+}$	1	1.024
14	2	0	2	$\text{Hg}^{2+}/\text{Hg}^0$	0.25/0.25	0.718
15	2	0	3	$\text{Hg}^{2+}/\text{Hg}^0$	0.25/0.25	0.629
16	1	0	3	$\text{Hg}^{2+}/\text{Hg}^0$	0.25/0.25	0.610

\* The first baseline quad train results ( $0.087\mu\text{g}/\text{Nm}^3$ ) were not used to calculate actual Hg concentration.

Table 4. Sorbent Trap Testing Methodology for the Test Firing an Illinois Coal

Day	No. Quad Trains	No. Dual Trains	Sample Time, hr	Hg Conc., $\mu\text{g}/\text{Nm}^3$
1 (pretest)	0	1	1.5	0.334
1	1	0	2	0.493
2	3	1	2	0.539
3	1	0	2	0.817

In an effort to determine the mercury conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  for the spiking system, mercury speciation traps were used during Test Conditions 5 and 7. The conversion efficiency of the oxidized mercury-spiking system was found to be 50%–60% (the actual recoveries are presented in the results and discussion section of this report). Therefore, for test conditions that were to be 100%  $\text{Hg}^{2+}$  (Test Conditions 4–6 and 11–13), the actual mercury concentration was a mixture of  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ .

Although not part of the original test plan, an extra day of natural gas pilot-scale tests was conducted prior to testing with coal. The purpose of these tests was to measure the spike recoveries for the sorbent traps and to determine the effect of  $\text{O}_2$  concentration on the

CMMs. For consistency, these tests are referred to as Test Conditions 15 and 16 in Task 2 (Table 3).

## RESULTS AND DISCUSSION

As stated previously, the project was divided into three primary tasks. The first task was to complete all of the preliminary work necessary for a successful project. The remaining two tasks were the pilot-scale tests.

### Task 1: Preliminary Developmental Work

The objective of Task 1 was to design, build, and test the mercury-spiking systems for  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ . A description and schematics of the systems were provided previously (Figures 7 and 8). To determine if the  $\text{Hg}^0$ -spiking system was generating mercury at a level that was in the range of the set point, the output was measured using a CMM that is associated with the EERC bench-scale test rig (PS Analytical Sir Galahad). The results are shown in Figure 9. Even at a set point of  $600 \mu\text{g}/\text{m}^3$  ( $0.6 \mu\text{g}/\text{min}$  at a flow rate of  $1 \text{ L}/\text{min}$ ), the mercury concentrations were reasonable consistent, with a variation of about  $\pm 10\%$ . To improve the spiking consistency, the temperature controllers were replaced, and additional insulation was added. Note: to spike mercury into the PTC at a level of  $0.25 \mu\text{g}/\text{m}^3$ , the mercury flow rate required was about  $1 \mu\text{g}/\text{min}$ .

To determine the percentage of conversion of  $\text{Hg}^0$  to  $\text{HgCl}_2$  for the  $\text{Hg}^{2+}$ -spiking system, speciated mercury sorbent traps were used. The results are shown in Table 5. As can be seen, the average conversion efficiency was in the 50%–60% range. Because of the lower-than-expected conversion rate, the mixed mercury tests were conducted with all of the mercury passing through the conversion system.

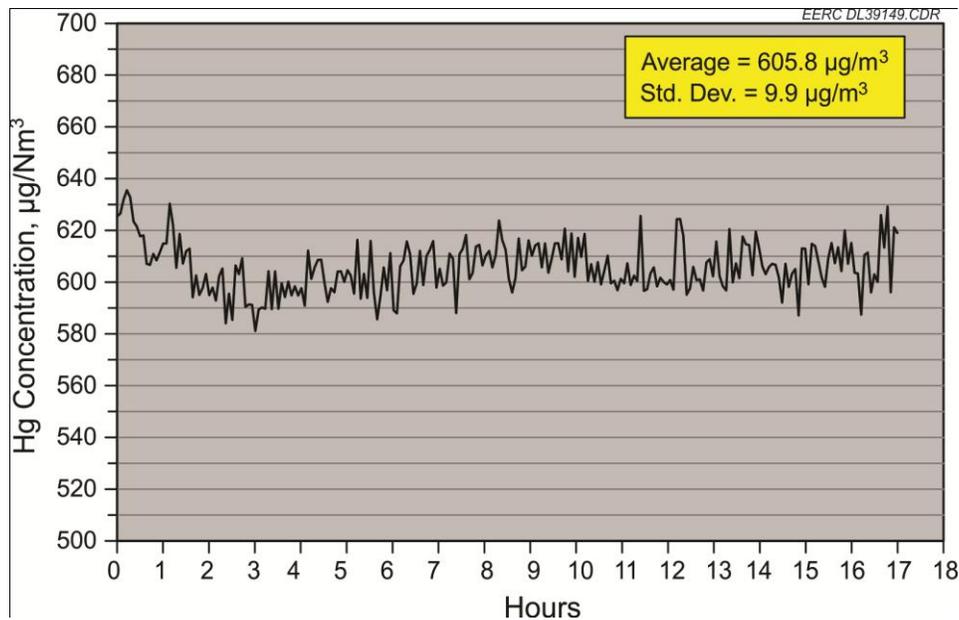


Figure 9. Test of the  $\text{Hg}^0$  mercury-spiking unit.

Table 5. Speciated Mercury Results for HgCl<sub>2</sub>-Spiking System

Test	Mercury Type	Nominal Total Hg Conc., $\mu\text{g}/\text{Nm}^3$	Avg. Hg <sup>0</sup> Conc., $\mu\text{g}/\text{Nm}^3$	Avg. Hg <sup>2+</sup> Conc., $\mu\text{g}/\text{Nm}^3$	Avg. Total Hg Conc., $\mu\text{g}/\text{Nm}^3$	Avg. Hg <sup>0</sup> , %	Avg. Hg <sup>2+</sup> , %	Avg. Conversion, %
1	100% Hg <sup>2+</sup>	0.5	0.268	0.284	0.552	48.5	51.5	51.5
2	50/50 Hg <sup>2+</sup> /Hg <sup>0</sup>	0.5	0.239	0.311	0.550	43.4	56.6	56.6
3	50/50 Hg <sup>2+</sup> /Hg <sup>0</sup>	0.5	0.198	0.337	0.535	37.7	62.3	62.3

A second important objective of Task 1 was to prove that the PTC was not offgassing any substantial mercury when fired with natural gas with no mercury being added to the system. The results for the baseline tests (no mercury added) are shown in Table 6. With the exception of one set of samples taken on May 24, 2010, the results were substantially less than the objective of  $<0.05 \mu\text{g}/\text{Nm}^3$ . The sorbent trap sample taken on May 24, 2010, was just after HCl and SO<sub>2</sub> were added to the flue gas. Therefore, the greater baseline the next day was  $0.033 \mu\text{g}/\text{Nm}^3$ . The measured ambient mercury concentration in the EERC pilot plant was  $13 \text{ ng}/\text{Nm}^3$  ( $0.013 \mu\text{g}/\text{Nm}^3$ ). Mercury concentration may be a result of a small amount of mercury offgassing occurring when these two gases were added. This appeared to dissipate quickly.

Although the testing took place at the end of the project, another objective of Task 1 was to ensure that the CMM calibrators were operating properly. To accomplish this, 14 sorbent trap samples were taken at the outlet of each of the CMMs. Half of the samples were sent to OhioLumex for analysis; the remainder were to be analyzed by NIST (has not yet been done). These results are discussed in the quality control/quality assurance report in Appendix A.

Table 6. Baseline PTC Mercury Concentration

Date	Time Sampled, min	Sample 1 Measured		Sample 2 Measured		Sample 3 Measured		Sample 4 Measured	
		Hg on Trap, ng	Hg Conc., $\mu\text{g}/\text{Nm}^3$	Hg on Trap, ng	Hg Conc., $\mu\text{g}/\text{Nm}^3$	Hg on Trap, ng	Hg Conc., $\mu\text{g}/\text{Nm}^3$	Hg on Trap, ng	Hg Conc., $\mu\text{g}/\text{Nm}^3$
2/15/10	180	12.0	0.033	12.1	0.034	–	–	–	–
4/26/10	240	18.2	0.033	18.2	0.033	18.2	0.034	17.9	0.033
4/27/10	240	13.1	0.024	13.2	0.024	14.3	0.026	15.1	0.027
4/28/10	240	11.5	0.022	11.3	0.021	11.0	0.020	11.3	0.021
4/29/10	240	7.5	0.014	8.1	0.015	–	–	–	–
5/24/10	240	23.3	0.087	35.4	0.088	44.7	0.085	47.7	0.086
5/25/10	240	17.6	0.032	15.7	0.030	15.2	0.030	17.1	0.033
5/26/10	240	12.2	0.022	11.3	0.021	11.1	0.021	11.0	0.020
5/27/10	240	9.9	0.018	10.7	0.020	10.5	0.019	10.0	0.018

## Task 2: Natural Gas Pilot-Scale Tests

### *Operation of the PTC*

Overall, the PTC operated very well during the natural gas tests. The average PTC operational results for the two natural gas test series are shown in Table 7. The graphical results can be provided upon request. Based on the standard deviation, overall operation was steady for each week of testing. Although little particulate matter was generated, it is interesting to note that the pressure drop across the baghouse did go up during the natural gas tests. Starting with new, all-Teflon bags with a Teflon membrane for the first natural gas test, the pressure drop was 0.5 in. (12.7 mm) W.C., and at the end of test, ~90 hr later, the pressure drop was 4.0 in. (102 mm) W.C. For the second natural gas test, the pressure drop was 1.6 in. (40.6 mm) W.C. at the beginning, and at the end of test, ~92 hr later, the pressure drop was 5.2 in. (132 mm) W.C.

### *Comparison of the CMMs to the Sorbent Traps*

The results comparing the CMMs to the sorbent traps for the first natural gas pilot tests are shown in Table 8 and are graphically presented in Appendix B (Figures B-1–B-12). The results for the second natural gas pilot-scale test with SO<sub>2</sub> and HCl added are provided in Table 9 and are provided graphically in Appendix B (Figures B-13–B-24). The complete data set for the sorbent traps and the data set for the CMMs can be provided upon request. Overall, both CMMs matched the sorbent trap data; however, the Tekran performed better (defined as being closer to the sorbent trap results) at the very low mercury concentrations <0.3 µg/Nm<sup>3</sup>. The addition of SO<sub>2</sub> and HCl did not appear to affect the results. The same was true when the O<sub>2</sub> was increased from 4.7% to 10% (Test Condition 16). The only effect was a very slight dilution effect due to the extra gas being added to the system. It is clear that when oxidized mercury was spiked into the PTC, the CMM data were somewhat more variable. As will be discussed later, this variability was primarily a result of the combustor and spiking system rather than the CMMs. Most likely the oxidized mercury, being sticky, would hang up in the combustor piping and/or spiking systems.

Table 7. PTC Operational Data for Natural Gas Tests

	First Natural Gas Test		Second Natural Gas Test	
	Value	Std. Dev.	Value	Std. Dev.
Baghouse Inlet Temperature, °F	355	10.5	352	10.8
Sample Loop Temperature, °F	306	1.3	302	2.0
Flue Gas Flow at Sample Loop, scfm	130	4.6	132	2.6
O <sub>2</sub> , %	4.9	0.26	4.7	0.23
NO <sub>x</sub> , ppmv	182	12.6	184	29.4
SO <sub>2</sub> , ppmv	26	6.85	1050	94
HCl, ppmv	NA	–	73.8*	–

\* Measured using EPA Method 26A.

Table 8. Results Comparing Sorbent Trap Data to the CMM Data for the First Natural Gas Test

Date	Test	Time, hr	Thermo Scientific, $\mu\text{g}/\text{Nm}^3$				Tekran, $\mu\text{g}/\text{Nm}^3$				Sorbent Traps, $\mu\text{g}/\text{Nm}^3$			
			No. Data Points	Avg.	Std. Dev.	Conf. Int. <sup>a</sup> ( $\lambda$ 95%)	No. Data Points	Avg.	Std. Dev.	Conf. Int. <sup>a</sup> ( $\lambda$ 95%)	No. Data Points	Avg.	Std. Dev.	Conf. Int. <sup>a</sup> ( $\lambda$ 95%)
4/26/10	Baseline	4	236	-0.039	0.017	0.002	48	0.036	0.008	0.002	4	0.033	0.001	0.001
4/27/10	Baseline	4	231	-0.037	0.017	0.002	49	0.030	0.005	0.002	4	0.025	0.001	0.002
4/28/10	Baseline	4	210	0.129	0.021	0.002	65	0.035	0.005	0.001	4	0.021	0.001	0.001
4/29/10	Baseline	4	178	0.144	0.022	0.002	64	0.027	0.002	0.001	4	0.015	0.001	0.008
4/26/10	TC <sup>b</sup> 1	3	176	0.179	0.028	0.002	37	0.237	0.004	0.001	2 <sup>c</sup>	0.258	0.005	0.044
4/26/10	TC 2	3	176	0.476	0.065	0.002	36	0.532	0.006	0.002	2 <sup>c</sup>	0.586	0.012	0.104
4/28/10	TC 3	2	116	0.805	0.131	0.003	32	0.773	0.005	0.002	2 <sup>c</sup>	0.840	0.007	0.060
4/27/10	TC 4	3	176	0.311	0.046	0.003	39	0.190	0.042	0.014	2 <sup>c</sup>	0.231	0.002	0.013
4/27/10	TC 5	3	162	0.465	0.134	0.007	46	0.442	0.025	0.007	2 <sup>c</sup>	0.511	0.001	0.002
4/27/10	TC 5	1.5	86	0.510	0.102	0.008	25	0.456	0.028	0.012	2	0.552	0.008	0.074
4/28/10	TC 6	2	119	0.690	0.072	0.006	32	0.608	0.016	0.006	2 <sup>c</sup>	0.705	0.017	0.153
4/29/10	TC 7	2	115	0.501	0.122	0.018	32	0.455	0.088	0.032	2 <sup>c</sup>	0.538	0.009	0.081
4/29/10	TC 7	1.4	80	0.545	0.090	0.006	22	0.478	0.040	0.018	2	0.549	0.004	0.035
4/29/10	TC 7	2	117	0.511	0.078	0.005	32	0.474	0.037	0.013	2	0.537	0.008	0.073
4/29/10	TC 7	2	119	0.537	0.061	0.006	32	0.490	0.035	0.013	2	0.534	0.006	0.050

<sup>a</sup> Confidence Interval.

<sup>b</sup> Test condition.

<sup>c</sup> Two samples were sent to Frontier Global Sciences for analysis and are not included in the results (discussed in Section 5).

Table 9. Results Comparing Sorbent Trap Data to the CMM Data for the Second Natural Gas Test

Date	Test	Time, hr	Thermo Scientific, $\mu\text{g}/\text{Nm}^3$				Tekran, $\mu\text{g}/\text{Nm}^3$				Sorbent Traps, $\mu\text{g}/\text{Nm}^3$			
			No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )	No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )	No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )
5/24/10	Baseline	4	237	0.132	0.036	0.002	62	0.108	0.017	0.009	4	0.087	0.001	0.002
5/25/10	Baseline	4	237	0.050	0.006	0.002	61	0.185	0.015	0.001	4	0.031	0.001	0.002
5/26/10	Baseline	4	237	0.030	0.004	0.001	62	0.232	0.010	0.001	4	0.021	0.001	0.001
5/27/10	Baseline	4	237	0.032	0.016	0.001	62	0.281	0.010	0.004	4	0.019	0.001	0.002
5/24/10	TC 8	3	177	0.302	0.014	0.002	48	0.275	0.014	0.004	4	0.322	0.036	0.057
5/24/10	TC 9	3	177	0.657	0.027	0.002	48	0.562	0.013	0.008	4	0.690	0.010	0.016
5/26/10	TC 10	3	177	0.986	0.008	0.002	49	1.005	0.013	0.002	4	1.057	0.026	0.041
5/25/10	TC 11	3	177	0.248	0.052	0.011	49	0.413	0.075	0.015	3	0.258	0.005	0.013
5/25/10	TC 12	3	177	0.622	0.043	0.009	48	0.792	0.060	0.013	4	0.696	0.009	0.014
5/26/10	TC 13	3	177	0.943	0.062	0.008	49	0.984	0.057	0.018	4	1.024	0.014	0.022
5/27/10	TC 14	2	117	0.673	0.129	0.016	32	0.791	0.088	0.047	4	0.736	0.008	0.013
5/27/10	TC 14	2	121	0.630	0.079	0.009	29	0.758	0.049	0.030	2	0.697	0.006	0.057
5/27/10	TC 14	2	121	0.623	0.061	0.013	33	0.755	0.071	0.022	2	0.705	0.000	0.002
6/21/10*	TC 15	3	177	0.646	0.012	0.002	32	0.648	0.007	0.003	4	0.623	0.081	0.129
6/21/10*	TC 15	3	177	0.626	0.012	0.002	49	0.632	0.013	0.004	4	0.636	0.003	0.005
6/21/10*	TC 16	3	177	0.612	0.011	0.002	45	0.615	0.007	0.002	4	0.610	0.013	0.021

\* TC 15 and 16 were natural gas tests performed prior to the coal test. TC 15 was spike recovery tests, and TC 16 was a test to evaluate the effect of  $\text{O}_2$  on CMMs.

### Task 3: Illinois Coal-Fired Pilot-Scale Tests

The coal chosen for series of tests was an Illinois eastern bituminous coal from the Knight Hawk seam. This coal was selected because ICCI was a project sponsor and also because tests had been completed previously on the PTC firing this coal. The coal analyses are shown in Table 10. As seen in the table, this is a high-sulfur coal but has very low chlorine content for an eastern bituminous coal, typically >500 ppm. A wet FGD unit was operated for this test both to reduce mercury emissions and to ensure that the EERC was operating within its air permit for SO<sub>2</sub> emissions. Also, in an effort to reduce mercury emissions and overall system pressure drop, both an ESP and the high-efficiency baghouse were operated.

Although not needed, to further reduce the mercury concentration at the CMM and sorbent trap sampling locations, it was planned that activated carbon could be injected into the baghouse and/or lime could be injected at the top of the combustor to reduce SO<sub>3</sub>.

#### *Operation of the PTC*

An important objective for Task 3 was that the mercury being measured by the sorbent traps and CMMs was <1 µg/Nm<sup>3</sup> and was reasonably steady during the test. As seen in Table 11, the objective was met, but there was an increase in the mercury concentration after Day 1. This was a result of a problem with the coal feed that caused a substantial amount of unburned carbon to coat the inside of the ESP and the bags of the fabric filter. That evening, the ESP was cleaned, and the bags were taken out and vacuumed. Although there was some variation in the mercury concentration over the week, it appeared to vary little (based on the CMM results) during the sampling that was occurring each day.

Because of the higher pressure drop across this configuration and limited fan capacity of the PTC, the flow rate through the boiler was reduced from ~130 to ~120 scfm (June 22, 2010). The reduction in flow rate also resulted in an increase in NO<sub>x</sub> emissions. The average PTC operation results for the coal test are shown in Table 11. There was some concern that pressure drop across the baghouse would be a problem necessitating frequent bag cleaning, thereby disrupting the sampling activities. However, the ESP removed enough particulate matter that pressure drop across the baghouse was not a problem. The pressure drop at the beginning of the test (vacuum-cleaned bags) was 1.2 in. (30.5 mm) W.C., and at no time did it go above 2.5 in. (63.5 mm) W.C. As a result, the baghouse bags were cleaned only during the night shift prior to any sampling activities.

Because the wet FGD was only designed to ensure that the operation of the PTC was meeting air-permitting requirements, the unit was not highly efficient for removing SO<sub>2</sub>. Although the inlet SO<sub>2</sub> concentration was not directly measured, based on the coal sulfur content of ~4%, it was expected to be 3500 to 4000 ppm, resulting in an FGD removal efficiency of 65%–70%.

Table 10. Coal Analysis, on an As-Received Basis (except where noted)

	6/22/10	6/23/10	6/24/10	Average
Mercury, mg/kg	0.0879	0.0935	0.101	0.0941
Chlorine, ppmv	123	127	128	126
Heating Value, Btu/lb	10,412	10,262	10,576	10,417
Proximate, wt%				
Moisture	5.41	7.42	6.77	6.53
Ash	13.82	13.17	12.28	13.09
Fixed Carbon	48.70	47.95	48.57	48.41
Volatile Matter	32.08	31.46	32.39	31.98
Ultimate, wt%				
Carbon	64.53	63.51	65.35	64.46
Hydrogen	5.01	5.14	5.16	5.10
Nitrogen	0.96	0.96	1.02	0.98
Oxygen	11.46	13.15	12.08	12.23
Sulfur	4.22	4.07	4.11	4.13

Table 11. PTC Operational Data for Coal Test

	6/21/10		6/22/10		6/23/10		6/24/10	
	Value	Std. Dev.						
Baghouse Inlet Temperature, °F	279	8.1	274	15.1	275	5.6	273	5.0
Sample Loop Temperature, °F	291	10.5	222	15.7	229	13.8	227	7.0
Flue Gas Flow at Sample Loop, scfm	131	1.2	118	5.6	121	4.4	124	2.8
O <sub>2</sub> , %	6.0	0.31	5.9	0.58	6.1	0.46	6.0	5.9
NO <sub>x</sub> at the Sample Loop, ppmv	146	11.2	606	95.5	674	42.4	504	40.0
SO <sub>2</sub> at the Sample Loop, ppmv	899	116	979	79.4	977	78.5	950	80.0

*Comparison of the CMMs to the Sorbent Traps*

The results comparing the CMMs to the sorbent traps for the coal pilot-scale test are shown in Table 12 and presented graphically in Appendix B (Figures B-25–B-27). The complete data set for the sorbent traps and CMMs are available upon request.

Based on comparing the sorbent trap results to those obtained by CMMs when coal was fired, the Thermo Scientific instrument did not perform as well as expected. Earlier in the week when natural gas was being fired (Test Conditions 15 and 16), both instrument results were very consistent with each other and the sorbent traps. But as soon as coal was introduced, the Thermo Scientific CMM was reading higher than either the sorbent traps or the Tekran CMM. Although not directly part of this test program, it was noticed during the natural gas tests that the Thermo Scientific CMM was not speciating correctly. It was reading zero or near-zero oxidized mercury even when it was known that oxidized mercury was being added to the system (based on speciated mercury traps and the Tekran readings). In an unsuccessful effort to improve this, Thermo Scientific technicians changed the operating temperature of the probe unit. This may or may not have been a factor in the less-than-optimal results obtained when coal was fired.

Table 12. Results Comparing Sorbent Trap Data to the CMM Data for the Illinois Coal Test

Date	Test	Thermo Scientific, $\mu\text{g}/\text{Nm}^3$					Tekran, $\mu\text{g}/\text{Nm}^3$				Sorbent Traps, $\mu\text{g}/\text{Nm}^3$			
		Time, hr	No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )	No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )	No. Data Points	Avg.	Std. Dev.	Conf. Int. ( $\lambda 95\%$ )
6/22/10	High LOI	1.5	87	0.791	0.062	0.062	24	0.334	0.044	0.044	2	0.334	0.003	0.024
6/22/10	High LOI	3	177	0.857	0.027	0.027	48	0.433	0.032	0.032	4	0.493	0.047	0.075
6/23/10	Normal LOI	2	119	0.960	0.023	0.023	32	0.587	0.022	0.022	4	0.620	0.009	0.014
6/23/10	Normal LOI	2	121	0.914	0.047	0.047	32	0.517	0.058	0.058	4	0.556	0.013	0.020
6/23/10	Normal LOI	2	117	0.873	0.060	0.060	33	0.477	0.057	0.057	4	0.514	0.005	0.008
6/23/10	Normal LOI	2	121	0.822	0.050	0.050	32	0.376	0.069	0.069	2	0.393	0.003	0.026
6/24/10	Normal LOI	2	121	1.065	0.020	0.020	33	0.805	0.027	0.028	4	0.844	0.038	0.060
6/24/10	Normal LOI	2	121	1.028	0.019	0.019	33	0.784	0.028	0.028	4	0.812	0.042	0.067
6/24/10	Normal LOI	2	121	0.977	0.021	0.021	32	0.734	0.029	0.029	2	0.774	0.023	0.211

## Sampling Results Summary

The complete results for all of the tests are summarized in Figures 10 and 11. In these figures, the 45° line represents a 1:1 agreement between the CMMs and the sorbent traps, and the other lines represent a 20% relative accuracy (RA). Both CMMs operated well on natural gas; however, the Tekran appears to have a lower working limit than the Thermo Scientific CMM. Also, it is clear that there is a concern with the Thermo Scientific CMM when the Illinois coal is fired. The coal results seem to indicate not a random error but a more systemic problem, as the data from the Thermo Scientific CMM appear to form a relatively straight line that is somewhat parallel to the 45° line but clearly outside the 20% RA criteria. Thermo Scientific has taken the instrument back to its facility and is currently attempting to determine the problem. Additional tests are planned to be conducted at the EERC with a revised Thermo Scientific instrument. Although the additional tests are not funded by ICCI, results will be provided to ICCI when they become available.

## Statistical Analysis Results

### *Instrument Precision*

For all of the pilot-scale tests, the accuracy of the CMMs was determined based on comparison to the reference sorbent trap method, EPA Method 30B. In this way, the test was consistent with previous rule-making (CAMR) and most likely with the MACT determination. Figures 10 and 11 showed the overall comparison of CMM data to sorbent trap data for all test conditions. It should be noted that the CMM data points represent averages over the same time frame that the sorbent traps were collected, making these data directly comparable. The 95% confidence interval ( $\lambda_{95\%}$ ) for the CMM and sorbent trap data was calculated and is also shown in Tables 8, 9, and 12. Overall, the reproducibility for the quad sorbent trap sampling ( $\sigma = 3.6\%$ ) contributes to a high level of confidence, with the larger  $\lambda$  values being a direct result of limited data points when dual traps were collected.

Although it was not part of the original scope of work, the data were used to calculate detection limits for the CMMs using the EPA specified method (1). Data from the baseline (natural gas-only) test conditions were used to calculate a method detection limit (MDL) for the Tekran and Thermo Scientific CMMs. The MDL for the Tekran was  $0.01 \mu\text{g}/\text{m}^3$ , and it was  $0.04 \mu\text{g}/\text{m}^3$  for the Thermo Scientific. Using these results and a factor of 10, the lower limit of quantification (LLQ) can be calculated for each instrument, resulting in a LLQ of 0.1 and  $0.4 \mu\text{g}/\text{m}^3$ , respectively.

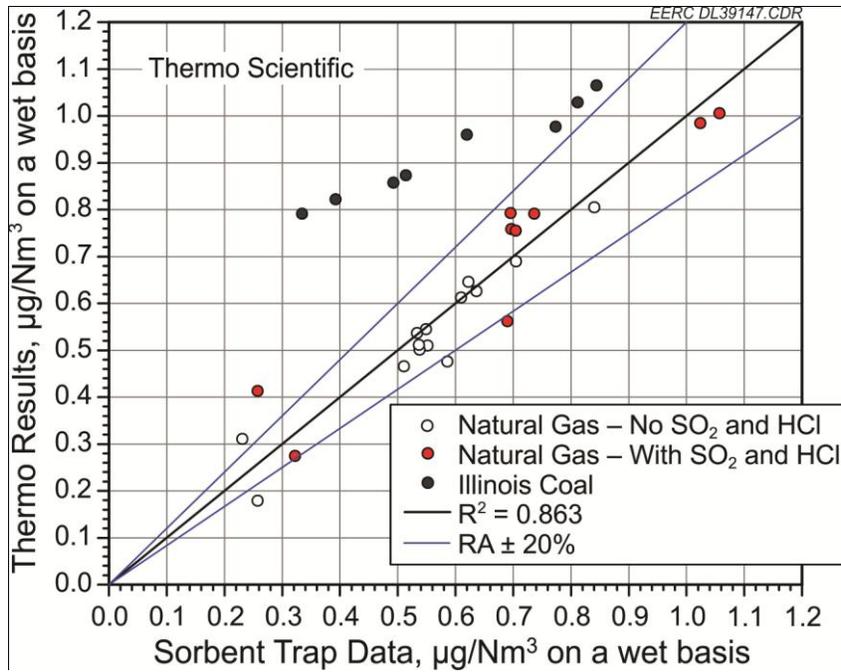


Figure 10. Summary of overall results for the Thermo Scientific CMM.

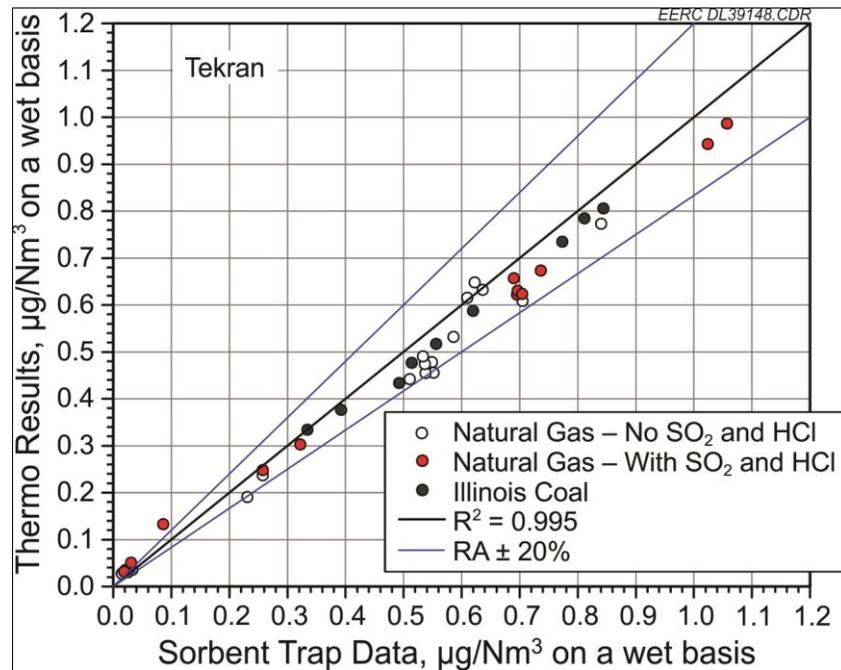


Figure 11. Summary of overall results for the Tekran CMM.

The relative accuracy (RA) was calculated for each instrument using the methods included in PS-12A. As shown in Table 13, the calculated RA for the Tekran was 10.4%, and for the Thermo Scientific, it was 31.4%. Although the concentrations were less than

Table 13. Relative Accuracy of the CMMs, Based on Sorbent Trap Data\*

	Tekran			Thermo Scientific		
	All Data	Coal Only	Nat. Gas Only	All Data	Coal Only	Nat. Gas Only
Avg. Difference (CMM minus sorbent traps), $\mu\text{g}/\text{Nm}^3$	0.041	0.032	0.044	0.130	0.327	0.054
Standard Deviation, $\mu\text{g}/\text{Nm}^3$	0.0285	0.0164	0.0355	0.1377	0.0934	0.0288
Number of CMM Points	40	9	19	34	9	23
t-statistic	2.023	2.306	2.101	2.035	2.306	2.069
Confidence Coefficient	0.00911	0.0126	0.0171	0.0481	0.0717	0.0124
Avg. Sorbent Trap Data, $\mu\text{g}/\text{Nm}^3$	0.487	0.593	0.675	0.569	0.593	0.604
Relative Accuracy, %	10.4	7.6	9.1	31.4	67.3	11.0

\* Only data >MDL was used (0.01  $\mu\text{g}/\text{Nm}^3$  for the Tekran and 0.04  $\mu\text{g}/\text{Nm}^3$  for the Thermo Scientific).

1.0  $\mu\text{g}/\text{m}^3$ , using an acceptance criteria of 20% the Tekran clearly passes but the Thermo Scientific instrument fails. As can be seen in Figure 10, the reason the RA was >20% for the Thermo Scientific instrument was a direct result of the coal test. Excluding the coal data, the RA for the Thermo Scientific instrument was only 9.1%. The RA was essentially the same under all test conditions for the Tekran. As previously stated, the problems with the instrument during the coal test are being investigated, and presumably further testing will result in a considerably lower RA. The RA for the Tekran, based on the nine data points, was only 7.6% during the coal test.

#### *Instrument Variability*

The variability of the data was used to calculate confidence values associated with the average values presented in the previous Tables (8, 9, and 12). From this, it can be seen that the data set is sound and the variability falls within a normal range. In addition to the analysis of data confidence, the data variability analysis can also be used to help determine data “noise” (most likely flue gas mercury variability).

The variability of the CMM data is a combination of the variability of the Hg concentration in the flue gas and the inherent variability of the CMM sampling and analytical method. Ideally, it would be desirable to determine the variability associated with the CMM sampling/analytical method independently of the flue gas variability. Unfortunately, the variability of the flue gas Hg concentration cannot be directly determined independently of the sampling/analytical method that has its own variability.

Although the variability of the sorbent trap data for the different test conditions can give some insight into the variability of the flue gas Hg concentration, it should be noted that the sorbent trap data and CMM variability data are not directly comparable because the two methods differ considerably in sample collection time. Given that the variability of the CMMs cannot be completely separated from the variability of the mercury in the flue gas, some insight as to the extent of the flue gas mercury variability on the CMMs can be determined from the extensive data set collected in this project.

The testing done under this project provided CMM data for a number of different test conditions, and the variability of CMM data for these conditions can be expressed as standard deviation. Table 14 shows the complete data set with the inclusion of relative standard deviation (RSD) for comparative purposes (the average data are reported using only significant figures). Only data collected above the MDL for each instrument are used in the analysis. Furthermore, coal test data for the Thermo Scientific instrument are not included because of the accuracy issues previously discussed. When the RSD is examined for each data set, it is important to remember that the relative noise is greater when the detection limit is approached. This can be seen in the baseline data for the Tekran instrument, where the RSD results are greater than those calculated for test conditions at higher Hg concentrations.

For the natural gas and coal tests, the RSD results for the CMMs were typically <10%, with some outliers. However, a closer examination of the outliers leads to the conclusion that any increase in CMM “noise” is most likely a result of an increase in the variability of the Hg concentration in the flue gas. Test Condition 11, for example, shows an increased RSD for both CMMs, and since the Hg concentration variability in the flue gas is the only common factor in the two data sets, one is led to believe that the source of the noise in the data is from that common factor.

For the natural gas tests, the RSD results are higher for the oxidized mercury tests (Test Conditions 4–6 and 11–13) as compared to tests when only elemental mercury was added (Test Conditions 1–3 and 8–10). This increase in variability can also be clearly seen in the graphical results for these tests. Examination of the previous Figures B-5 through B-12 and B-17 through B-23 also clearly show this increased variability. Although it cannot be determined directly whether the increased variability is from the flue gas Hg concentration or the CMM sampling/analytical method, or both, one is led to believe that the source is the increased variability in Hg flue gas concentration.

Examination of the figures during the coal test (Figures B-25 through B-27) show changing Hg concentration over the test period. Additionally, the data show that a significant number of the outliers in the CMM data are repeated on both instruments. An example of this is the peaks at approximately 12:00, 14:00, and 15:00 on June 23, 2010. This again strongly suggests that the Hg concentration is the source of this variability, not the CMM instruments.

Overall contribution of the variability of the instrument to the overall variability of the CMM data is relatively small (that is, RSD <10%) when the concentrations being measured are less than the LLQ of the instrument. This data set gives confidence that CMMs are a valid measurement method for the levels of Hg for the conditions tested. Again, it is important to note that this only holds true when the concentration is above the calculated LLQ.

Table 14. Summary of the Test Results

Condition	Sorbent Trap		Tekran Std.			Thermo Scientific Std.		
	Average, $\mu\text{g}/\text{m}^3$	RSD, %	Average, $\mu\text{g}/\text{m}^3$	Dev., $\mu\text{g}/\text{m}^3$	RSD, %	Average, $\mu\text{g}/\text{m}^3$	Dev., $\mu\text{g}/\text{m}^3$	RSD, %
Baseline	0.033	1.3	0.04	0.0076	21.2			
Baseline	0.025	5.5	0.03	0.0053	17.6			
Baseline	0.021	4.0	0.04	0.0051	14.8			
Baseline	0.015	6.3	0.03	0.0021	7.8			
TC 1	0.258	1.9	0.24	0.0037	1.6	0.2	0.0142	7.8
TC 2	0.586	2.0	0.53	0.0056	1.1	0.48	0.0166	3.4
TC 3	0.840	0.8	0.77	0.0054	0.7	0.83	0.0144	1.7
TC 4	0.231	0.6	0.19	0.0417	21.9	0.3	0.0213	6.7
TC 5	0.511	0.0	0.44	0.0251	5.7	0.50	0.0433	8.6
TC 5	0.552	1.5	0.46	0.0283	6.2	0.53	0.0363	6.9
TC 6	0.705	2.4	0.61	0.0162	2.7	0.70	0.0308	4.4
TC 7	0.538	1.7	0.45	0.0881	19.4	0.52	0.0919	17.8
TC 7	0.549	0.7	0.48	0.0399	8.4	0.56	0.0249	4.5
TC 7	0.537	1.5	0.47	0.0373	7.9	0.52	0.0275	5.3
TC 7	0.534	1.0	0.49	0.0352	7.2	0.54	0.0355	6.6
Baseline	0.087	1.5	0.13	0.0359	27.2	0.1	0.0169	15.7
Baseline	0.031	4.3	0.05	0.0058	11.5			
Baseline	0.021	4.4	0.03	0.0040	13.5			
Baseline	0.019	5.7	0.03	0.0161	50.8			
TC 8	0.322	11.2	0.30	0.0139	4.6	0.3	0.0136	5.0
TC 9	0.690	1.4	0.66	0.0270	4.1	0.56	0.0133	2.4
TC 10	1.057	2.4	0.99	0.0083	0.8	1.0	0.0131	1.3
TC 11	0.258	2.1	0.25	0.0517	20.8	0.41	0.0747	18.1
TC 12	0.696	1.2	0.62	0.0434	7.0	0.79	0.0598	7.6
TC 13	1.024	1.4	0.94	0.0619	6.6	0.98	0.0574	5.8
TC 14	0.736	1.1	0.67	0.1291	19.2	0.79	0.0881	11.1
TC 14	0.697	0.9	0.63	0.0786	12.5	0.76	0.0492	6.5
TC 14	0.705	0.0	0.62	0.0607	9.7	0.75	0.0712	9.4
TC 15	0.623	13.0	0.65	0.0070	1.1	0.65	0.0123	1.9
TC 15	0.636	0.5	0.63	0.0134	2.1	0.63	0.0123	2.0
TC 16	0.610	2.2	0.62	0.0074	1.2	0.61	0.0106	1.7
KH1*	0.334	0.8	0.33	0.0440	13.2			
KH1	0.493	9.6	0.43	0.0321	7.4			
KH1	0.620	1.4	0.59	0.0223	3.8			
KH1	0.556	2.3	0.52	0.0584	11.3			
KH1	0.514	0.9	0.48	0.0566	11.9			
KH1	0.393	0.7	0.38	0.0685	18.2			
KH1	0.844	4.5	0.81	0.0275	3.4			
KH1	0.812	5.2	0.78	0.0279	3.6			
KH1	0.774	3.0	0.73	0.0286	3.9			

\* KH = Knighthawk.

## THE QUALITY CONTROL/QUALITY ASSURANCE (QA/QC)

Because of the nature of this project, a very important aspect was the QA/QC that was implemented. The QA/QC report is present in Appendix A. This includes the QA/QC associated with precision and accuracy of the sorbent traps, CMMs, and calibrators.

## CONCLUSIONS AND RECOMMENDATIONS

- Overall, the testing went well. Very few problems were encountered. The CMMs were operated continuously over the 3 months, including the time when the PTC was not being operated (it sampled ambient air), with very little input from EERC personnel.
- The EERC mercury-spiking systems worked well and were consistent. However, the oxidized mercury-spiking system converted only 50%–60% of the elemental mercury to HgCl<sub>2</sub>. As a result, the test conditions that were intended as oxidized mercury only were a mix of elemental and oxidized mercury.
- The baseline mercury levels when natural gas was fired were very low. With the exception of one test following the addition of HCl and SO<sub>2</sub> to the flue gas (0.087 µg/Nm<sup>3</sup>), the baseline was <0.035 µg/Nm<sup>3</sup>. This is near the ambient mercury levels of 0.013 µg/Nm<sup>3</sup> in the pilot plant.
- Both the Tekran and the Thermo Scientific CMMs worked well on natural gas with and without the addition of the acid gases. Compared to the sorbent trap data, the RA for the Tekran for the natural gas test was 9.1%, and it was 11.0% for the Thermo Scientific.
- It was clear that the Tekran has a lower MDL than the Thermo Scientific system. Based on the methods outlined in the EPA document OFR99-193, the Tekran MDL was 0.01 µg/Nm<sup>3</sup> compared to 0.04 µg/Nm<sup>3</sup> for the Thermo Scientific instrument. This difference may partly be a result of the Tekran being calibrated at 0.5 µg/Nm<sup>3</sup> compared to 1.0 µg/Nm<sup>3</sup> for the Thermo Scientific CMM. As would be expected, the RA of the CMMs greatly increases as the MDL is approached.
- The quad train sorbent trap results for all of the tests provided a high level of precision. The RSD for all the quad samples was only 3.6%. This includes the precision associated with different sampling boxes, the sorbent traps, and the analysis of the sorbent traps.
- There was little, if any, effect on CMM performance when HCl and SO<sub>2</sub> were added to the flue gas.
- There was no apparent impact of adding additional O<sub>2</sub> to the flue gas for either instrument. The only effect was due to the dilution of the mercury as a result of additional flue gas.
- The calibrators used for both instruments were consistent. Compared to sorbent trap samples taken at the outlet of the calibrators, the Tekran RSD was 1.2% and the Thermo Scientific was 1.4%. Compared to the set point, the recovery was 96.4% for the Tekran and 108.0% for the Thermo Scientific. In calibrator tests (over 3 days), the average CMM readings were within 1% of the sorbent results.

- A concern associated with firing the high-sulfur Illinois coal in the PTC was whether it would be possible to achieve mercury concentrations at the sampling location of  $<1 \mu\text{g}/\text{Nm}^3$ . It was planned that activated carbon and/or lime (to remove  $\text{SO}_3$ ) could be injected if needed. However, when the flue gas was passed through an ESP, followed by a high-efficiency baghouse, and finally a wet FGD, the objective was met without these additives. The mercury concentrations measured over the 3 days of testing with coal ranged from 0.334 to  $0.844 \mu\text{g}/\text{Nm}^3$ . Although there was some variability in the mercury emissions over the 3 days, the mercury concentration was consistent over the time each quad train sorbent trap sample was taken.
- When coal was fired, the Tekran appeared to match the sorbent results, but the Thermo Scientific system did not perform as well as expected. Compared to the sorbent trap results, the RSD for the Tekran when coal was fired was 7.6%, very similar to the RSD for the natural gas tests. However, the RSD for the Thermo Scientific was 67.3%. The difference is not a random error but appears to be more systemic in nature, as the CMM results were consistently higher than those measured using the sorbent traps.
- All QA/QC criteria were met for the sorbent trap sampling method, including calibration checks ( $\pm 5\%$ ), drift checks ( $\pm 10\%$ ), blanks ( $<1 \text{ ng}$ ), spikes (average difference  $<10\%$ ), quad and dual traps ( $<10\% \text{ RD}$ ), and the use of dual labs with dual methods (average difference  $<10\%$ ).

#### REFERENCES

1. The Method Detection Limit Procedure of the U.S. Environmental Protection Agency. [water.usgs.gov/owq/OFR\\_99-193/detection.html](http://water.usgs.gov/owq/OFR_99-193/detection.html) (accessed October 2010).

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**APPENDIX A**

**QUALITY ASSURANCE/QUALITY CONTROL  
(QA/QC) REPORT**

## QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

One of the most important factors affecting QA/QC for any sampling procedure is the experience of the personnel carrying out the method. With respect to sorbent trap methods, the Energy & Environmental Research Center (EERC) has taken part since the beginning of the development of sorbent trap methods for mercury (1, 2). Since the publication of Environmental Protection Agency (EPA) Method 30B, the EERC has been involved with continuous mercury monitor (CMM) validation using EPA Method 30B for several clients (3–5). As part of these programs, the EERC laboratories and sampling equipment have passed the laboratory requirements for EPA Method 30B analysis numerous times. In addition, the EERC has developed and maintained a good working relationship with OhioLumex, the company that is at the forefront of the sorbent trap methods, as evidenced by that company's involvement with this project.

EERC personnel also have extensive experience in setting up and operating CMMs. As a result, the EERC was able to provide support to the vendor technicians during instrument installations. Although the operation of the instruments went very well, EERC personnel had the experience to realize if an instrument was not operating properly.

### Sorbent Trap QA/QC

QA/QC for the sorbent trap sampling method required evaluation of both analytical and sampling methodologies. The analytical QA/QC included QC calibration checks, calibration drift checks, the use of dual laboratories for comparative analysis, and the analysis of blank and spiked traps. As part of the analytical method protocol, the instrument must be calibrated in the range of expected samples. Because the mass of mercury on the sorbent traps ranged from 5 to 500 ng depending on the test condition, different calibrations were required, and appropriate carrier flow rates had to be accurately measured. Therefore, at the low end of the range, samples were analyzed utilizing a calibration that included a 5-ng standard, and at the high end (including the spiked samples), calibration required a 500-ng standard. In each case, after the instrument had been warmed up and calibrated, a calibration check standard was run to verify the calibration of the instrument utilizing a standard from a separate lot. The results of the calibration check standards are shown in Table A-1. The specification for the QC calibration standards required that the measured value be within 5% of the known mass. Periodically during analysis, at a minimum once every ten samples, a calibration drift check was performed with a known standard. The results of the calibration drift check analyses are shown in Tables A-2–A-4. The specification for the calibration drift check required that the measured value be within 10% of the known amount or the instrument had to be recalibrated. As shown by the data for QC calibration and calibration drift check analyses, these QA/QC requirements were met.

Table A-1. Calibration Check Standard Results

Date	Value, ng	Reading, ng	Recovery, %	Date	Value, ng	Reading, ng	Recovery, %
04/21/10	10	9.7	97	05/26/10	100	101	101
04/21/10	10	9.6	96	05/26/10	15	14	93
04/23/10	10	10	100	05/26/10	200	203	102
04/23/10	10	9.6	96	05/27/10	240	243	101
04/23/10	10	10	100	05/27/10	7	6.9	99
04/23/10	150	158	105	05/28/10	20	21	105
04/26/10	10	10	100	05/28/10	400	417	104
04/26/10	50	50	100	06/10/10	90	92	102
04/27/10	10	10	100	06/10/10	250	253	101
04/27/10	180	183	102	06/16/10	75	74	99
04/27/10	10	10	100	06/16/10	40	41	103
04/27/10	80	78	98	06/16/10	6	5.7	95
04/28/10	40	42	105	06/16/10	10	10	100
04/28/10	20	20	100	06/21/10	20	19	95
04/29/10	50	50	100	06/21/10	300	287	96
04/29/10	30	30	100	06/22/10	50	49	98
04/30/10	25	26	104	06/22/10	400	386	97
04/30/10	10	10	100	06/23/10	350	363	104
04/30/10	90	87	97	06/23/10	75	79	105
05/24/10	180	180	100	06/24/10	15	15	100
05/25/10	100	100	100	06/24/10	400	404	101
05/25/10	200	194	97	06/25/10	100	104	104
05/26/10	160	166	104	06/25/10	400	393	98
05/26/10	50	48	96	06/25/10	50	49	98

In addition to the internal QA/QC for the sorbent trap analysis, during the first week of testing, 8 of the 11 quad sorbent traps were split into equivalent pairs and along with a pair of blank traps were sent to Frontier Global Sciences for mercury analysis. The blank traps were reported by Frontier Global Sciences at 1.63 and 0.51 ng, indicating a very small amount of mercury in the blank carbon traps. Although this is insignificant compared to the low of 94 ng in the samples from the test conditions, it is significant compared to the 7.5 and 6.5 ng from the traps used for the baseline natural gas tests. Assuming the Frontier Global Sciences blank (unused traps) results are valid, there is an approximately 8% high bias for the baseline tests because of mercury in the traps when purchased. Table A-5 presents the results of the interlab comparison. The data show good agreement between the two methods. In all samples, the relative difference was <10% as defined by the equation below.

$$RD = 100\% \times \frac{|(C_a - C_b)|}{(C_a + C_b)}$$

Where  $C_a$  and  $C_b$  are the Hg concentrations of the two compared samples.

Table A-2. Calibration Drift Check Results for the First Natural Gas Test

Date	Value, ng	Reading, ng	Recovery, %	Date	Value, ng	Reading, ng	Recovery, %
04/21/10	10	10	100	04/27/10	200	198	99
04/21/10	5	4.8	96	04/28/10	10	10	100
04/23/10	5	5.3	106	04/28/10	100	100	100
04/23/10	8	7.2	90	04/28/10	35	37	106
04/23/10	150	138	92	04/28/10	15	16	107
04/23/10	60	63	105	04/28/10	220	228	104
04/23/10	15	15	100	04/28/10	10	10	100
04/23/10	100	102	102	04/28/10	200	203	102
04/23/10	50	53	106	04/29/10	150	155	103
04/26/10	110	112	102	04/29/10	45	47	104
04/26/10	15	15	100	04/30/10	50	52	104
04/26/10	100	94	94	04/30/10	100	104	104
04/26/10	70	68	97	04/30/10	20	22	110
04/26/10	10	10	100	04/30/10	150	153	102
04/26/10	80	80	100	04/30/10	50	52	104
04/26/10	15	14	93	04/30/10	150	155	103
04/26/10	220	214	97	04/30/10	10	10	100
04/27/10	90	95	106	04/30/10	170	174	102
04/27/10	90	89	99	04/30/10	11	11	100
04/27/10	100	100	100	04/30/10	150	164	109

Table A-3. Calibration Drift Check Results for the Second Natural Gas Test

Date	Value, ng	Reading, ng	Recovery, %	Date	Value, ng	Reading, ng	Recovery, %
05/24/10	10	10	100	05/27/10	100	98	98
05/24/10	200	211	106	05/27/10	10	10	100
05/24/10	15	14	93	05/27/10	240	242	101
05/24/10	10	11	110	05/27/10	100	104	104
05/24/10	150	151	101	05/27/10	200	206	103
05/25/10	300	310	103	05/27/10	200	202	101
05/25/10	100	108	108	05/27/10	190	206	108
05/26/10	10	9.8	98	05/27/10	10	10	100
05/26/10	280	284	101	05/27/10	200	207	104
05/26/10	400	438	110	05/27/10	200	211	106
05/26/10	14	13	93	05/27/10	7	7	100
05/26/10	400	432	108	05/28/10	20	21	105
05/27/10	10	10	100	05/28/10	400	396	99

However, it does appear that there was more variation in the results between the two samples when measured using EPA Method 1631 compared to the OhioLumex. As confirmed in conversation between EERC personnel and EPA personnel, this is not uncommon. After discussion with team members, it was decided to forgo any additional splitting of the quad traps beyond the first test to maintain the quad trap integrity for statistical analysis.

Table A-4. Calibration Drift Check Results for the Coal Test

Date	Value, ng	Reading, ng	Recovery, %	Date	Value, ng	Reading, ng	Recovery, %
06/10/10	50	50	100	06/23/10	10	10	100
06/10/10	150	147	98	06/23/10	100	108	108
06/10/10	100	104	104	06/23/10	500	499	100
06/10/10	100	107	107	06/23/10	150	157	105
06/10/10	200	210	105	06/23/10	400	401	100
06/10/10	150	155	103	06/23/10	50	52	104
06/16/10	200	187	94	06/24/10	10	10	100
06/16/10	20	20	100	06/24/10	500	493	99
06/16/10	10	10	100	06/24/10	100	104	104
06/16/10	175	180	103	06/24/10	450	470	104
06/16/10	5	5.2	104	06/24/10	250	252	101
06/16/10	10	10	100	06/24/10	140	139	99
06/16/10	100	101	101	06/24/10	425	429	101
06/16/10	200	209	105	06/24/10	350	345	99
06/21/10	200	181	91	06/24/10	450	440	98
06/21/10	500	514	103	06/24/10	100	103	103
06/22/10	200	201	101	06/25/10	10	10	100
06/22/10	450	425	94	06/25/10	500	497	99
06/22/10	50	52	104	06/25/10	250	243	97
06/22/10	350	365	104				

Table A-5. Sorbent Trap Mercury Analysis Comparison

Test	EERC OhioLumex, $\mu\text{g}/\text{Nm}^3$			Frontier Geosciences EPA Method 1631, $\mu\text{g}/\text{Nm}^3$			Relative Diff., %
	A	B	Avg.	C	D	Avg.	
1	0.254	0.261	0.258	0.281	0.320	0.301	7.79
2	0.578	0.594	0.586	0.585	0.572	0.579	0.60
3	0.836	0.845	0.841	0.814	0.847	0.831	0.59
4	0.232	0.230	0.231	0.264	0.287	0.276	8.88
5	0.511	0.511	0.511	0.525	0.568	0.547	3.40
6	0.717	0.693	0.705	0.799	0.769	0.784	5.31
7	0.532	0.545	0.539	0.557	0.501	0.529	0.89
Blank (baseline)	0.014	0.015	0.015	0.015	0.012	0.013	7.14

Additional QA/QC for the analytical method was carried out with the analysis of three blank traps and six spiked traps provided by OhioLumex, three were spiked in the first section of the trap at 100 ng and three at 200 ng. The results of the laboratory analysis of these traps are shown in Table A-6. The results show that the readings were all within  $\pm 10\%$  of the expected value of the spiked sections and the blanks were very low.

Table A-6. Analytical Results of Blank and Spiked Traps

Trap ID	Spike, ng	Measured Section 1, ng	Measured Section 2, ng	Spike Recovery, %
70401	Blank	0.0	0.1	–
70383	Blank	–0.1	0.1	–
70414	Blank	0.0	0.0	–
71802	100	109	0.0	109
73300	100	108	0.1	108
73260	100	109	0.1	109
68425	200	206	0.1	103
73438	200	210	0.0	105
73259	200	215	0.0	107

QA/QC for the sorbent trap sampling includes regular calibration of the sampling boxes, documentation of the sampling data, the use of spreadsheets for calculation of the mercury concentrations, and verification of the calculated mercury concentrations. The calibration of the EPA Method 30B control boxes (sampling boxes) includes the calibration of the thermocouples and calibration of the dry gas meter. Prior to use for the test, the thermocouples were calibrated with a certified thermocouple calibrator to  $\pm 1.5^{\circ}\text{R}$  ( $1.5/528^{\circ}\text{R} = 0.3\%$ ). The dry gas meter for each sample box was calibrated with a certified wet test meter (certified to  $\pm 0.2\%$ ) with multiple runs at a range of usable flow rates. The individual runs were required to be within  $\pm 2\%$  to meet the specification, and an average value was then used to compute the meter constant ( $C_m$ ). Therefore, the potential error in the final computed control box volume is  $\pm 2.3\%$ .

The sampling QA/QC also included spiked traps as part of the quad trap sampling procedure during the third week of testing. A total of 18 spiked traps were used, and the recoveries were calculated as outlined in EPA Method 30B. Table A-7 presents the results of the spiked traps. Although there was some variation in the spike recoveries (in all cases, the spike recoveries were  $\pm 10\%$  of the known value), the average of all the spiked trap recoveries was 100%.

As part of the sampling plan, the QA/QC methodology included quad sorbent trap sampling for each of the test conditions. The data show very good agreement for the quad traps. In all, 16 quad traps were completed for the test conditions, with an average interquad relative standard deviation (RSD) of 3.6%. As part of the baseline natural gas testing, seven sets of quad sorbent trap samples were completed, with an average interquad RSD of 3.8%. These replicate data were used to calculate the confidence interval ( $\lambda 95\%$ ) of the average values, which was shown in the results previously presented. The very good agreement of the data resulted in tight confidence intervals where quad sorbent trap data were obtained. Alternatively, where quad sorbent trap data were not available (duplicate traps), the confidence intervals were significantly greater, simply because of the limited number of data points. For the same reason, the CMM data had very tight confidence intervals because the results were very consistent with a large number of data points.

Table A-7. Results of the Sampling Spike Recovery Tests

Test	Fuel	Sample 1				Sample 2			
		Hg Spiked Sample $\mu\text{g}/\text{m}^3$	Hg Spike Meas. $\mu\text{g}/\text{m}^3$	Hg Spike Actual, $\mu\text{g}/\text{m}^3$	Spike Recovery %	Hg Spiked Sample $\mu\text{g}/\text{m}^3$	Hg Spike Meas. $\mu\text{g}/\text{m}^3$	Hg Spike Actual $\mu\text{g}/\text{m}^3$	Spike Recovery %
1	Nat. Gas	1.142	0.554	0.558	99.3	1.092	0.506	0.558	90.6
2	Bit. Coal	1.580	0.693	0.677	102.3	1.548	0.674	0.677	99.5
3	Bit. Coal	1.472	0.607	0.614	99.0	1.493	0.628	0.614	102.3
4	Bit. Coal	1.442	0.571	0.564	101.2	1.443	0.566	0.564	100.3
6	Bit. Coal	1.870	0.990	0.916	108.0	1.776	0.901	0.916	98.3
7	Bit. Coal	1.815	0.927	0.914	101.4	1.700	0.828	0.914	90.6

As an additional QA/QC check, it was critical to the test that the baseline condition measurements resulted in a near-zero mercury concentration. As was discussed previously, before each day of testing, sorbent trap samples were taken when natural gas was fired with no mercury being added to the flue gas. As was shown in Table A-6, the results show consistently low ( $\sim 0.03 \mu\text{g}/\text{Nm}^3$ ) mercury concentration under these conditions.

*CMM QA/QC*

The primary QA/QC check for the CMMs was the calibration procedures. Each of the CMMs was programmed to complete a full calibration check each day. This included both zero gas and calibration gas added to the probe tip. Prior to the instrument being sent to the EERC for installation, the CMMs had undergone a complete certification test program, as outlined in Performance Specification (PS)-12A. This included zero and calibration drift tests and an integrity test (these results are available from the vendor).

The calibrators for each of the CMMs included a NIST-traceable mercury source. But because the ability of the calibration systems to provide the appropriate calibration gas to the CMM is critical to the QA/QC of the CMM, a series of calibration tests was completed at the EERC for each instrument. This included a longer-term calibration drift test and sorbent trap sampling directly from the calibrators.

*Longer-Term Calibration Drift Test*

The results of the single-point calibration drift tests (set point at  $0.51 \mu\text{g}/\text{Nm}^3$ ) on the Tekran are shown in Figure A-1 and summarized in Table A-8. In addition to a longer-term single-point calibration, Tekran also conducted a multipoint calibration, and these results are shown in Figure A-2 and summarized in Table A-9. As can be seen in these results, the calibration system for the Tekran remained very constant over time.

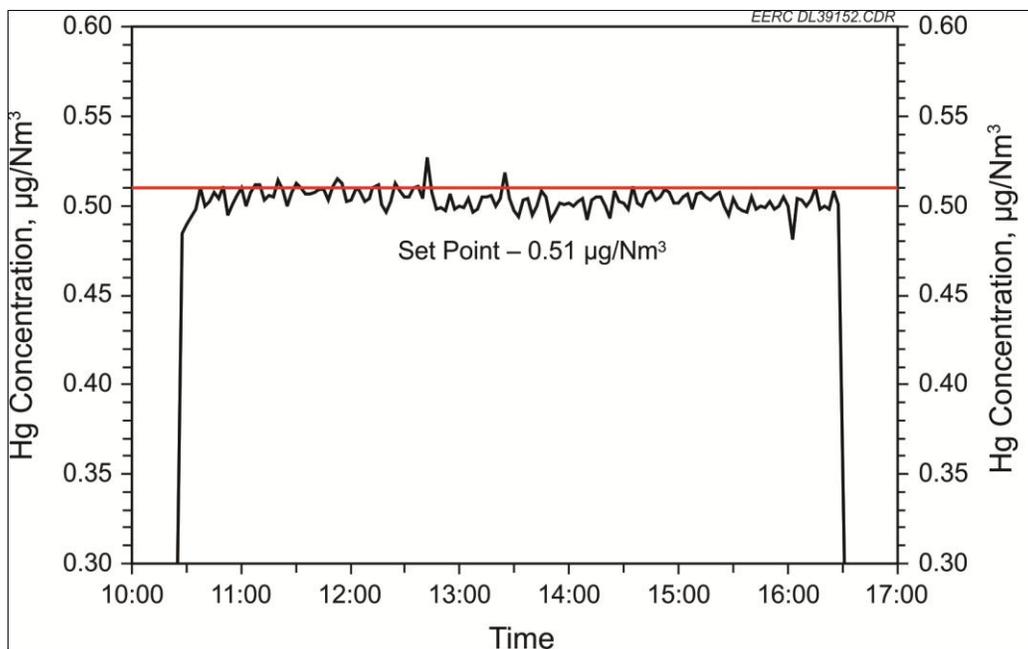


Figure A-1. Results of a longer-term calibration test on the Tekran CMM.

Table A-8. Longer-Term Hg<sup>0</sup> Injection into Probe Tip of the Tekran

Date	6-9-2010
Set Point, µg/Nm <sup>3</sup>	0.51
Duration, hr	6
Number of Points	145
Minimum, µg/Nm <sup>3</sup>	0.481
Maximum, µg/Nm <sup>3</sup>	0.527
Mean, µg/Nm <sup>3</sup>	0.503
Std. Dev., µg/Nm <sup>3</sup>	0.006
RSD, %	1.20
Mean Recovery, %	98.7

The longer-term calibration results for the Thermo Scientific CMM will be completed as part of the planned additional testing with the Thermo Scientific CMM. These results will be reported to ICCI when the testing is complete.

#### *Comparison of Calibrators and Sorbent Traps*

To prove the accuracy of the CMM calibrators (as defined by the sorbent trap reference method), each of the calibrators' outputs were sampled using sorbent traps. Fourteen sorbent trap samples were collected from each of the calibrators. Seven of the traps for each system were sent to OhioLumex for analysis, and the other seven traps were sent to the EPA to be submitted to NIST for analysis. The results of the calibrator samples analyzed by OhioLumex are shown in Table A-10. The results were very consistent. The mean recovery met the objective of  $\pm 10\%$  (based on the set point).

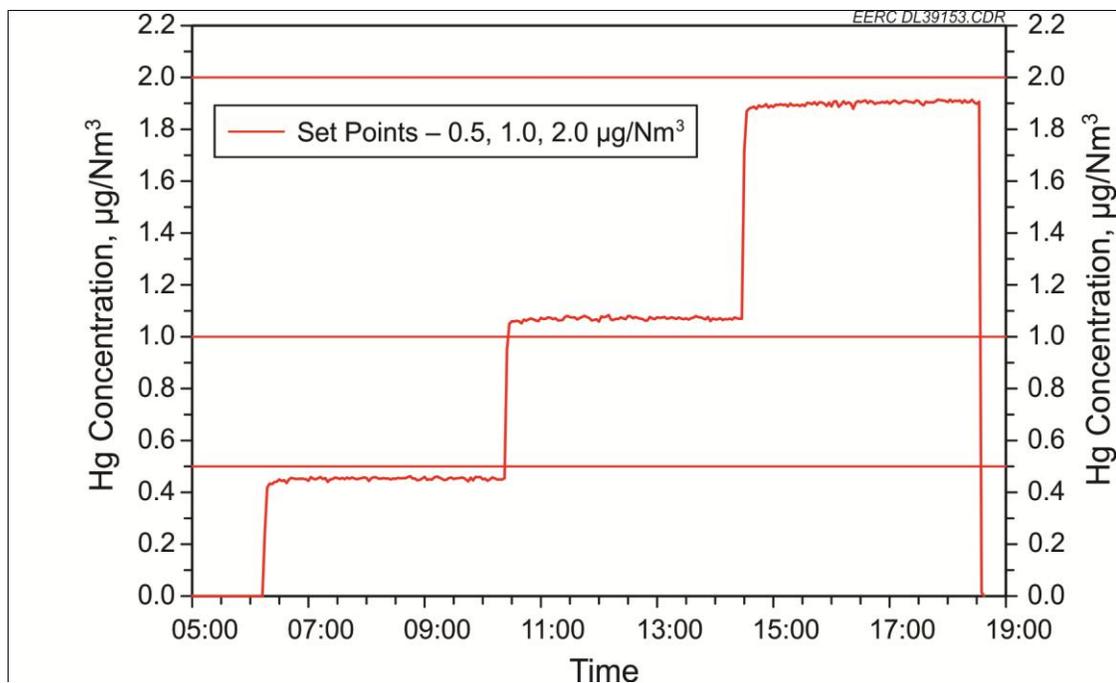


Figure A-2. Results of a multipoint calibration test on the Tekran CMM.

Table A-9. Four-Point Hg<sup>0</sup> Injection into Probe Tip of the Tekran, June 16, 2010

Criteria	Zero	Low	Medium	High
Number of Points	96	95	95	94
Duration, hr	4.00	3.95	3.95	3.92
Set Point, µg/Nm <sup>3</sup>	0.00	0.500	0.100	2.000
Minimum, µg/Nm <sup>3</sup>	0.000	0.436	1.052	1.878
Maximum, µg/Nm <sup>3</sup>	0.000	0.463	1.084	1.915
Mean, µg/Nm <sup>3</sup>	0.000	0.453	1.070	1.901
Std. Dev., µg/Nm <sup>3</sup>	0.000	0.005	0.006	0.008
Mean Recovery, %	–	90.6	107.0	95.1
RSD, %	–	1.04	0.53	0.43

During the calibration tests using the sorbent trap, the CMMs were continuously operated. The results for the Tekran are shown in Figure A-3 and summarized in Table A-11. The results over 74 hr are very similar to those shown in Figure A-1 (6 hr). There are a few minor transient spikes (some of them a result of putting in and taking out sorbent traps), but these have very little impact on the average or standard deviation. Unfortunately, the data for the Thermo Scientific system is not available. However, when the additional testing is done with this instrument at the EERC, a longer-term calibration test will be performed and the data report to ICCI.

Table A-10. Sorbent Trap Results for CMM Calibrators

Sample	Tekran			Thermo Scientific		
	Sorbent Trap, $\mu\text{g}/\text{Nm}^3$	CMM, $\mu\text{g}/\text{Nm}^3$	RD, %	Sorbent Trap, $\mu\text{g}/\text{Nm}^3$	CMM, $\mu\text{g}/\text{Nm}^3$	RD, %
1	0.483	0.473	1.06	1.109		
2	0.472	0.470	0.25	1.077		
3	0.484	0.469	1.58	1.086		
4	0.478	0.472	0.59	1.057		
5	0.481	0.470	1.14	1.078		
6	0.490	0.466	2.48	1.080		
7	0.482	0.468	1.51	1.077		
Average, $\mu\text{g}/\text{Nm}^3$	0.482	0.472	–	1.081		
Set Point, $\mu\text{g}/\text{Nm}^3$	0.500	0.500	–	1.000		
Mean Recovery, %	96.4	94.4	–	108.0		
RSD, %	1.2	1.0	–	1.4		
$\lambda(95\%)$ , $\mu\text{g}/\text{Nm}^3$	0.005	–	–	0.014		

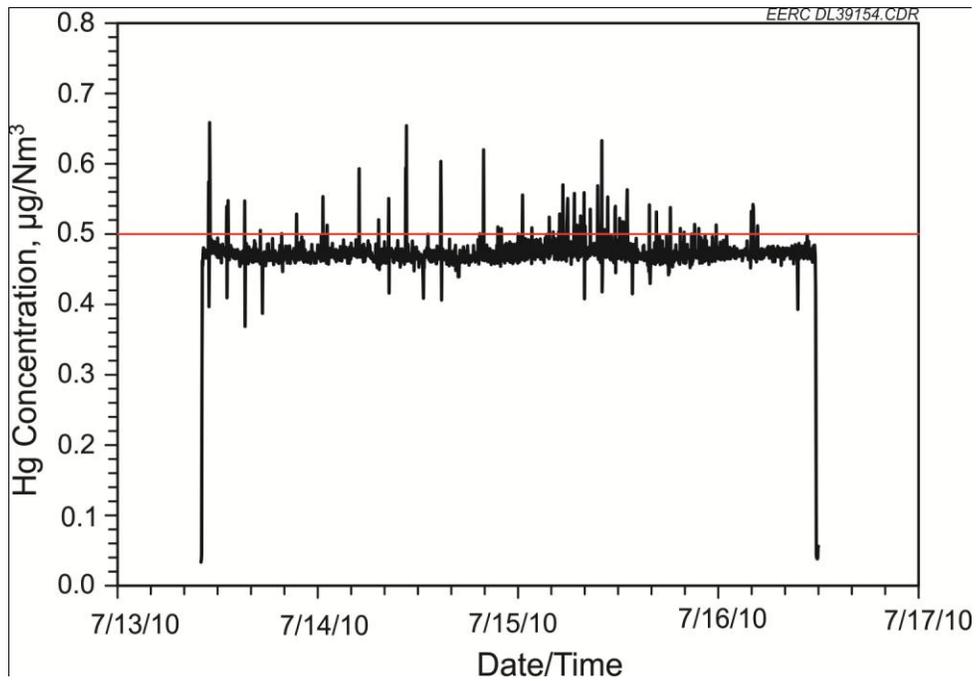


Figure A-3. Long-term calibration results during sorbent trap testing of the Tekran CMM.

Table A-11. Longer-term Hg<sup>0</sup> Injection into Probe Tip of the Tekran

Date	July 13–July 16, 2010
Set Point, µg/Nm <sup>3</sup>	0.50
Duration, hr	74
Number of Points	1759
Minimum, µg/Nm <sup>3</sup>	0.369
Maximum, µg/Nm <sup>3</sup>	0.658
Mean, µg/Nm <sup>3</sup>	0.473
Std. Dev., µg/Nm <sup>3</sup>	0.018
RSD, %	3.60
Mean Recovery, %	94.6

## REFERENCES

1. Pavlish, J.H.; Thompson, J.S.; Martin, C.L.; Musich, M.A.; Hamre, L.L. *Field Testing of Activated Carbon Injection Options for Mercury Control at TXU's Big Brown Station*; Final Report (March 2, 2005 – March 31, 2008) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-05NT42305 and Luminant Power; EERC Publication 2008-EERC-01-05. Energy & Environmental Research Center: Grand Forks, ND, Feb 2008.
2. CATM Staff. *2008 Annual Report for the Center for Air Toxic Metals<sup>®</sup>*; Energy & Environmental Research Center: Grand Forks, ND, May 2008, [www.undeerc.org/catm/pdf/area2/2008SamplingandAnalyticalMethods.pdf](http://www.undeerc.org/catm/pdf/area2/2008SamplingandAnalyticalMethods.pdf) (accessed 2011).
3. Laudal, D.L.; Dene, C.; Roland, E. *Evaluation of Alternatives to the Ontario Hydro Method as a Reference Method for CAMR*; Final Report for U.S. Department of Energy, Cooperative Agreement No. DE-FC27-98FT40321; Energy & Environmental Research Center, Grand Forks, ND, Feb 2007.
4. *Comparison of Mercury Sampling Methods for Certifying Mercury Monitors Using CAMR Protocols*; Electric Power Research Institute, Palo Alto, CA; U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, PA; and Center for Air Toxic Metals at the Energy & Environmental Research Center, Grand Forks, ND, Oct 2007.
5. Laudal, D.L.; Hanson, M. *Relative Accuracy Results for the Continuous Mercury Monitor at Minnesota Power's Boswell Energy Station – Unit 4*; Energy & Environmental Research Center, Grand Forks, ND, June 2009.

## **APPENDIX B**

# **GRAPHICAL RESULTS FROM PILOT-SCALE TESTS**

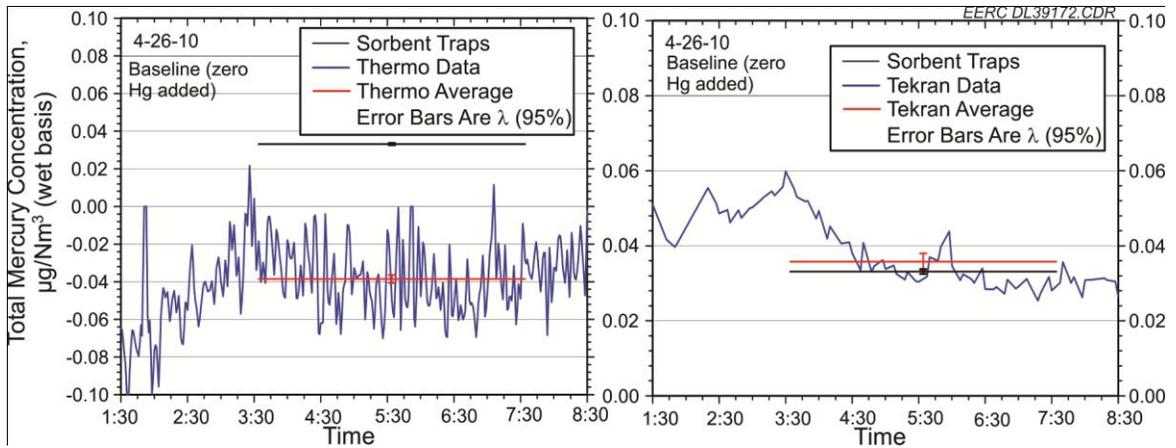


Figure B-1. Comparison of mercury measurement methods under baseline conditions for the first natural gas test (4-26-10).

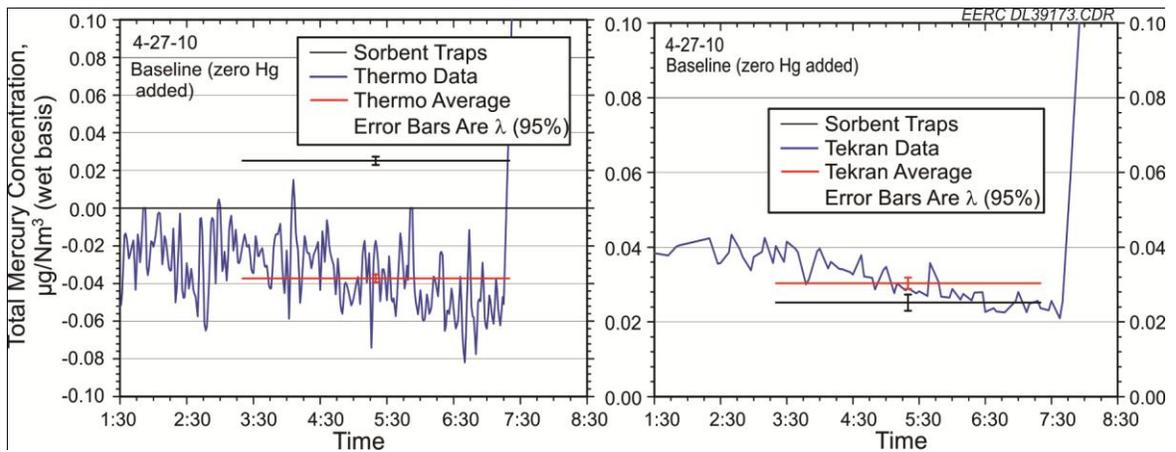


Figure B-2. Comparison of mercury measurement methods under baseline conditions for the first natural gas test (4-27-10).

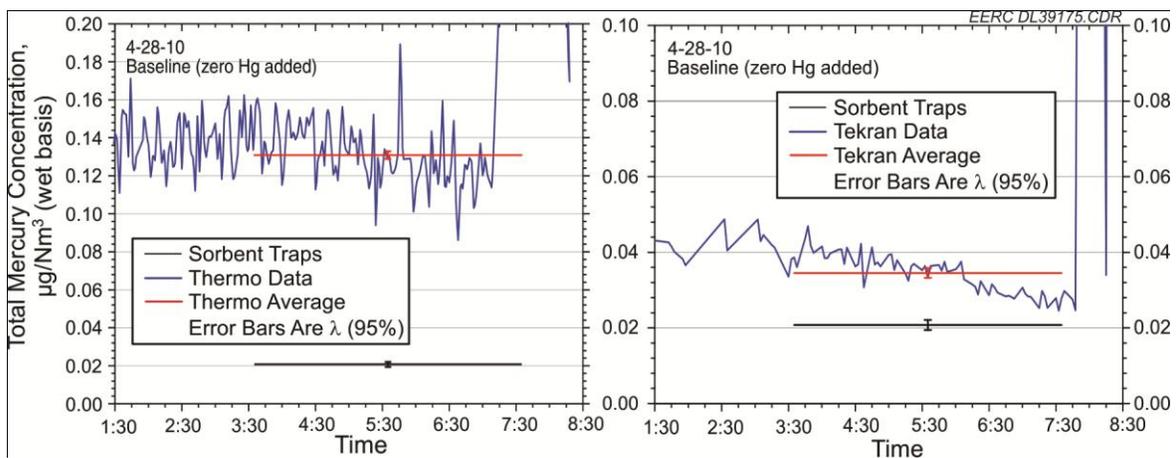


Figure B-3. Comparison of mercury measurement methods under baseline conditions for the first natural gas test (4-28-10).

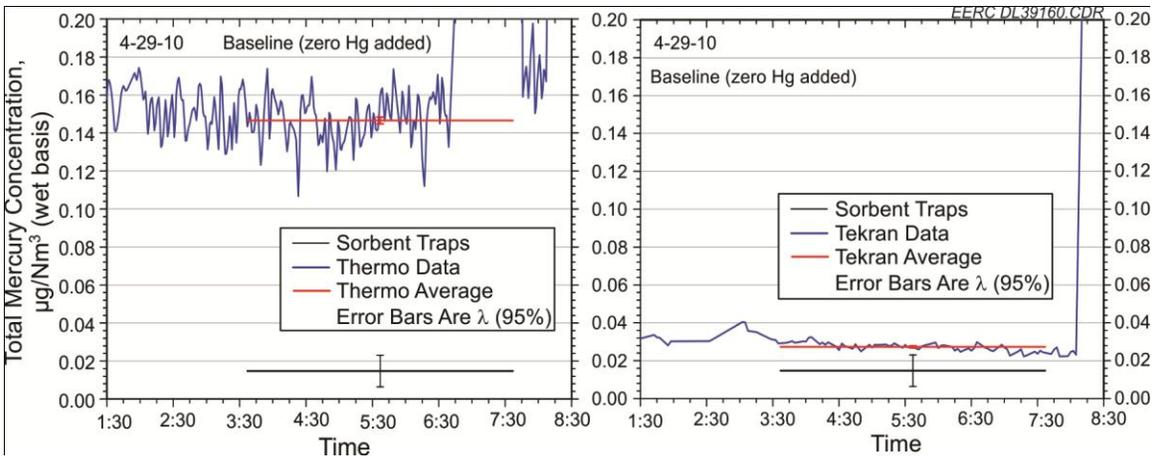


Figure B-4. Comparison of mercury measurement methods under baseline conditions for the first natural gas test (4-29-10).

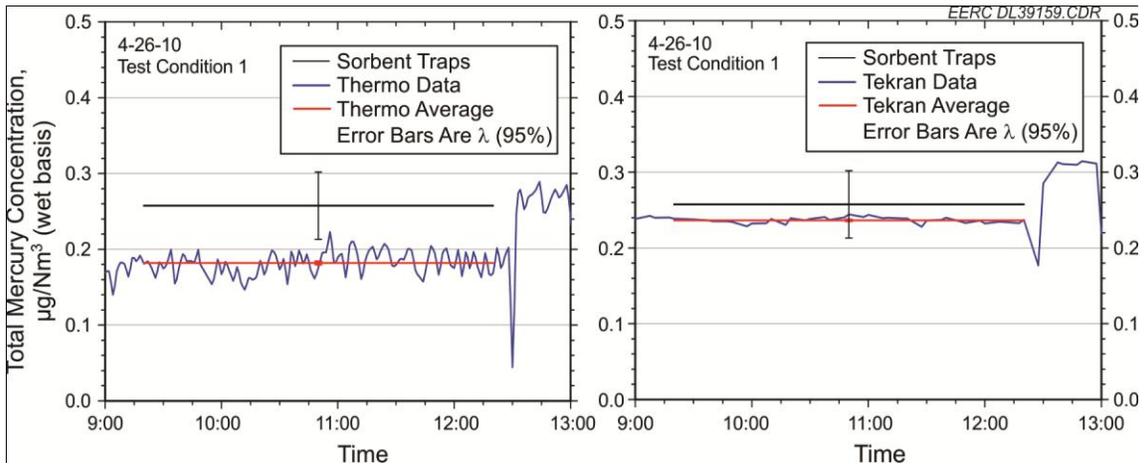


Figure B-5. Comparison of mercury measurement methods for Test Condition 1 for the first natural gas test.

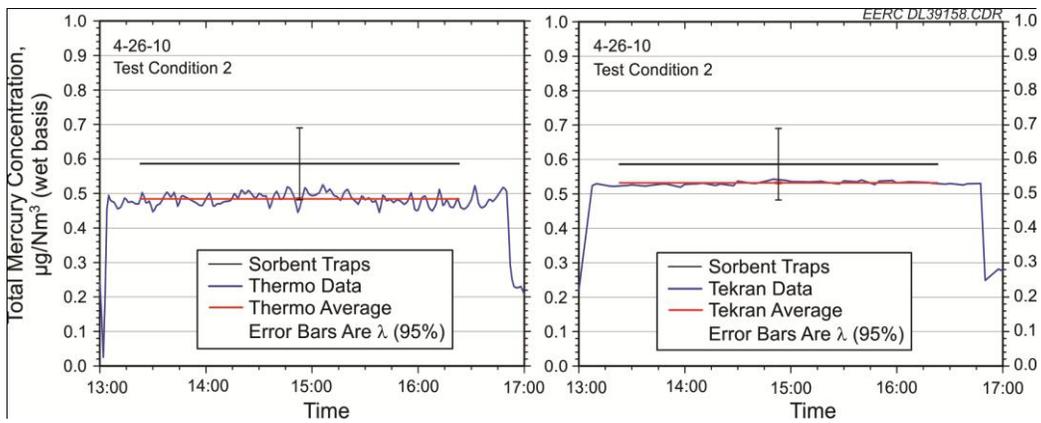


Figure B-6. Comparison of mercury measurement methods for Test Condition 2 for the first natural gas test.

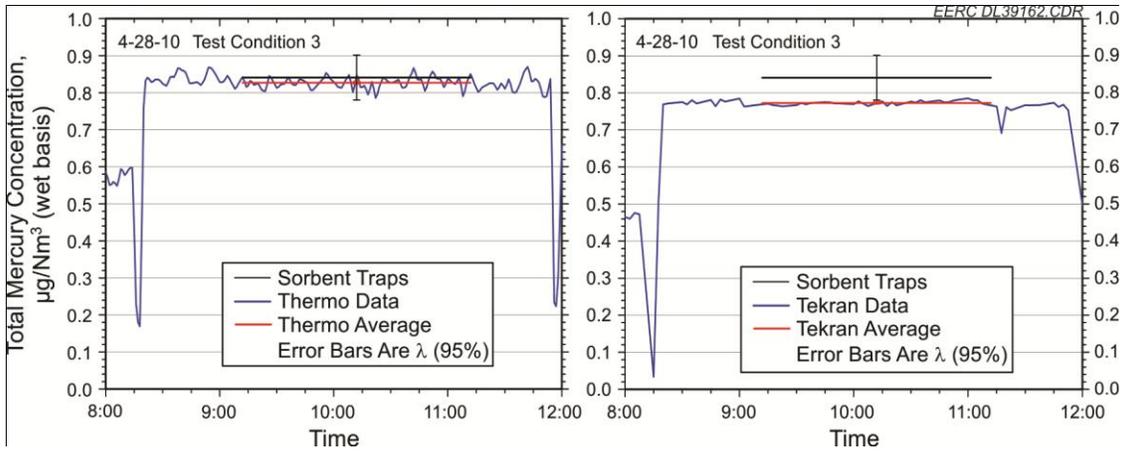


Figure B-7. Comparison of mercury measurement methods for Test Condition 3 for the first natural gas test.

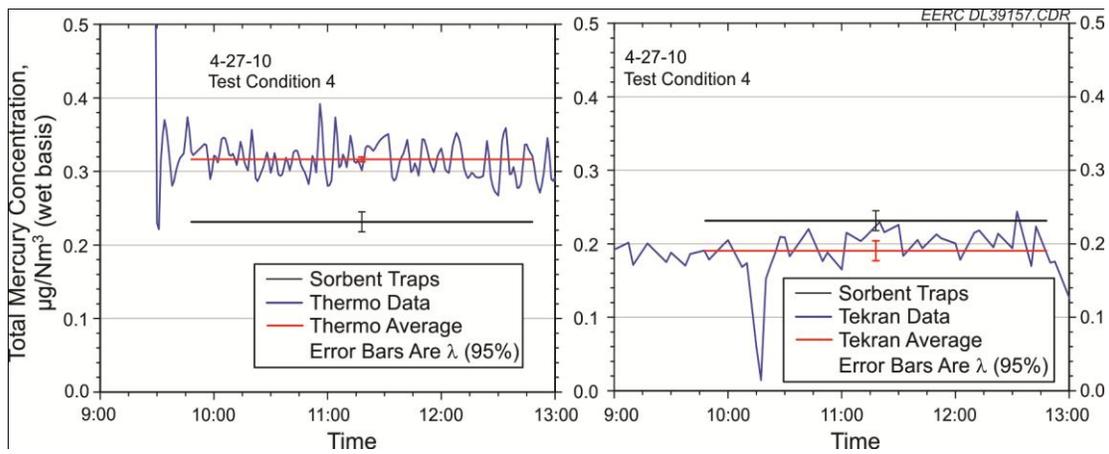


Figure B-8. Comparison of mercury measurement methods for Test Condition 4 for the first natural gas test.

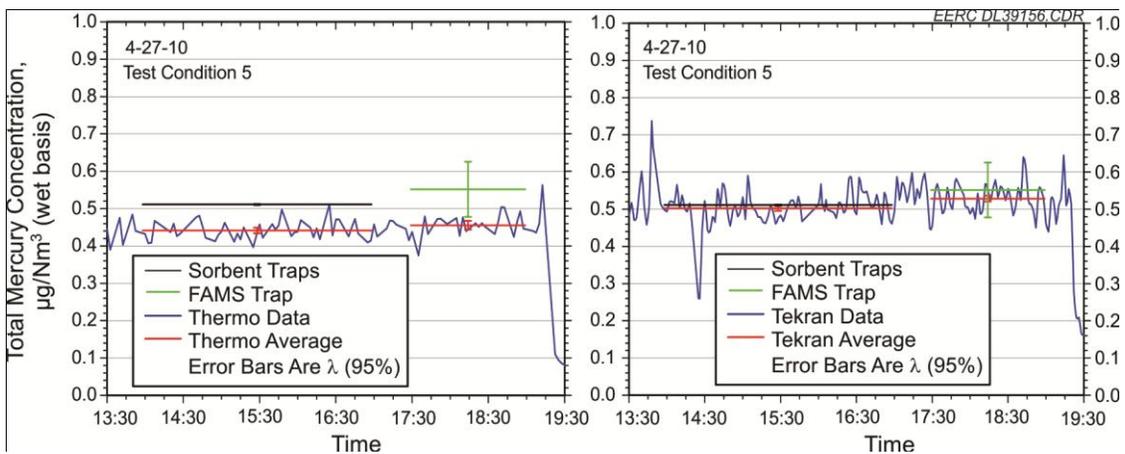


Figure B-9. Comparison of mercury measurement methods for Test Condition 5 for the first natural gas test.

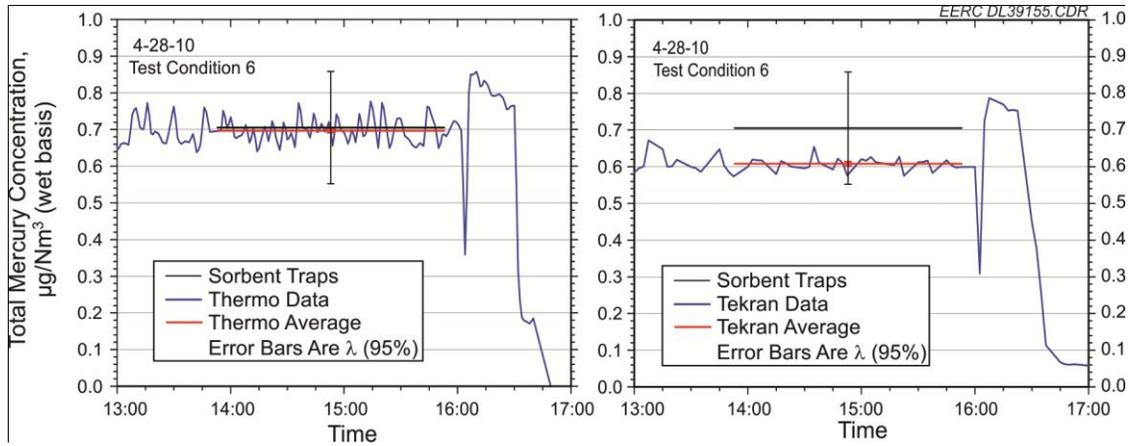


Figure B-101. Comparison of mercury measurement methods for Test Condition 6 for the first natural gas test.

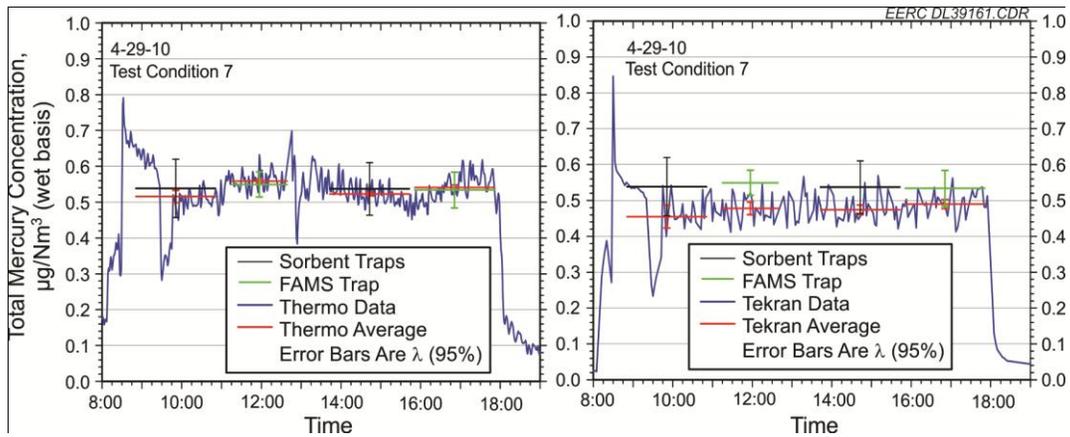


Figure B-11. Comparison of mercury measurement methods for Test Condition 7 for the first natural gas test.

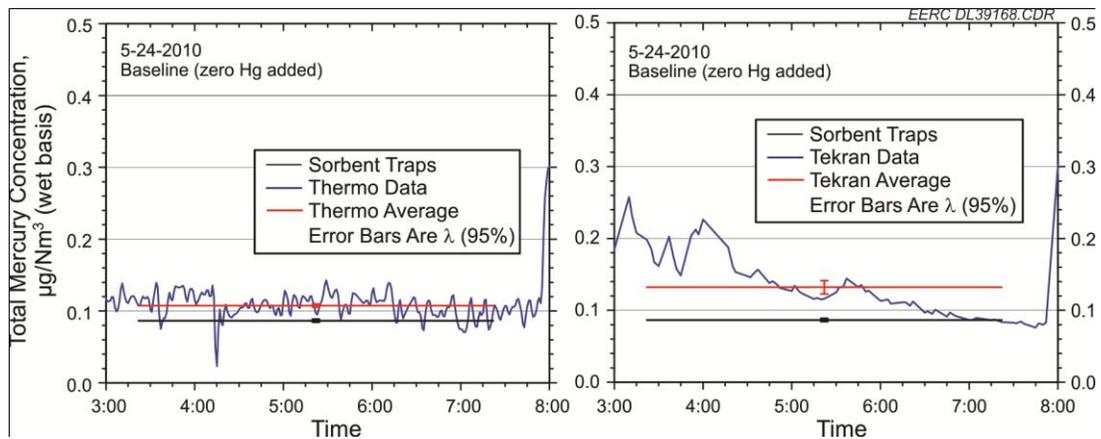


Figure B-12. Comparison of mercury measurement methods under baseline conditions for the second natural gas test (5-24-10).

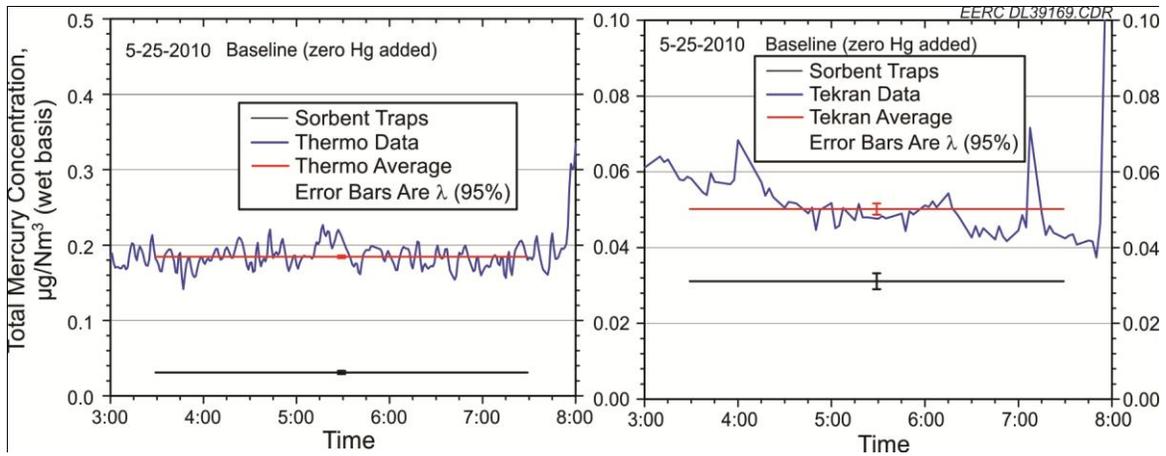


Figure B-13. Comparison of mercury measurement methods under baseline conditions for the second natural gas test (5-25-10).

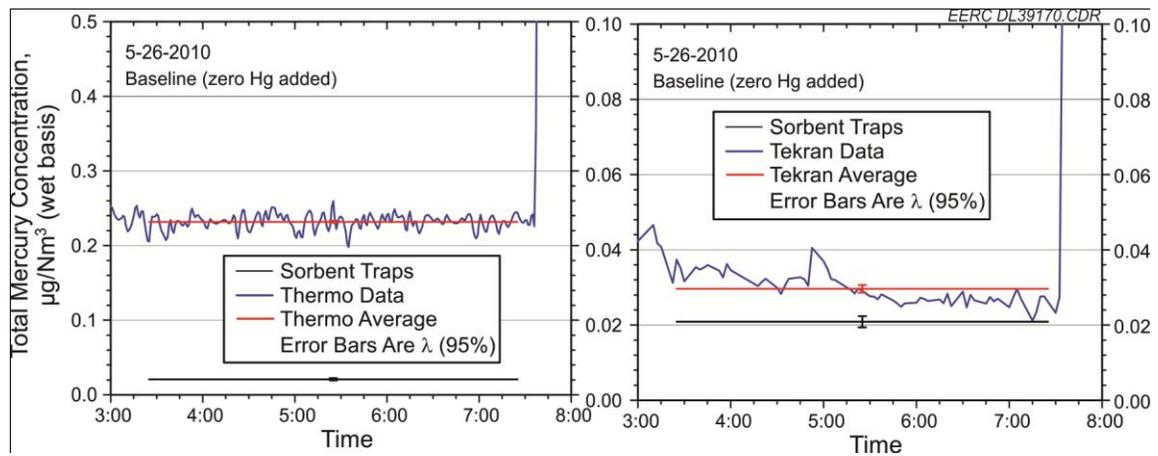


Figure B-14. Comparison of mercury measurement methods under baseline conditions for the second natural gas test (5-26-10).

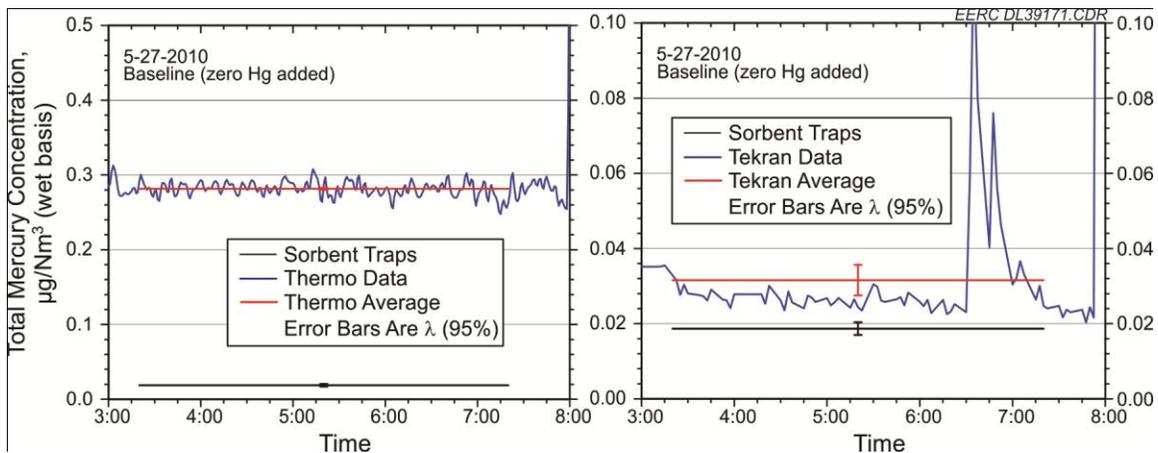


Figure B-15. Comparison of mercury measurement methods under baseline conditions for the second natural gas test (5-27-10).

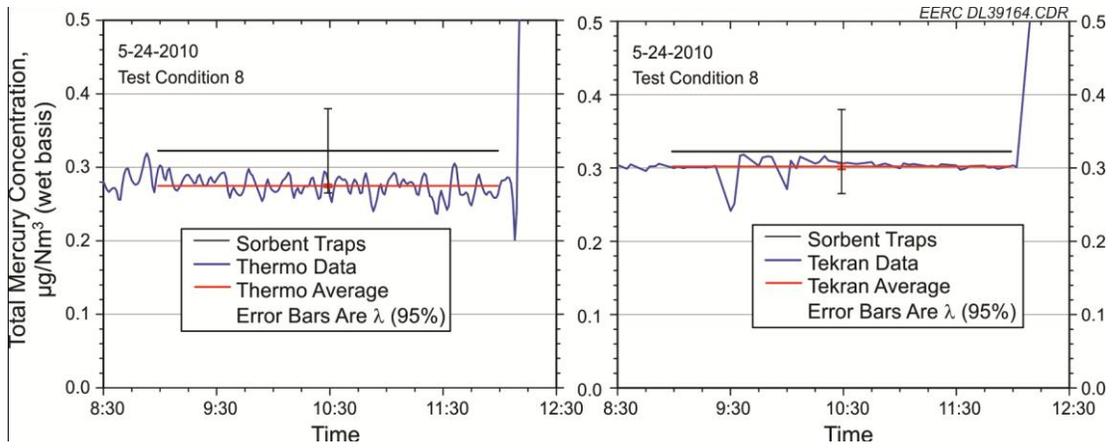


Figure B-16. Comparison of mercury measurement methods for Test Condition 8 for the second natural gas test.

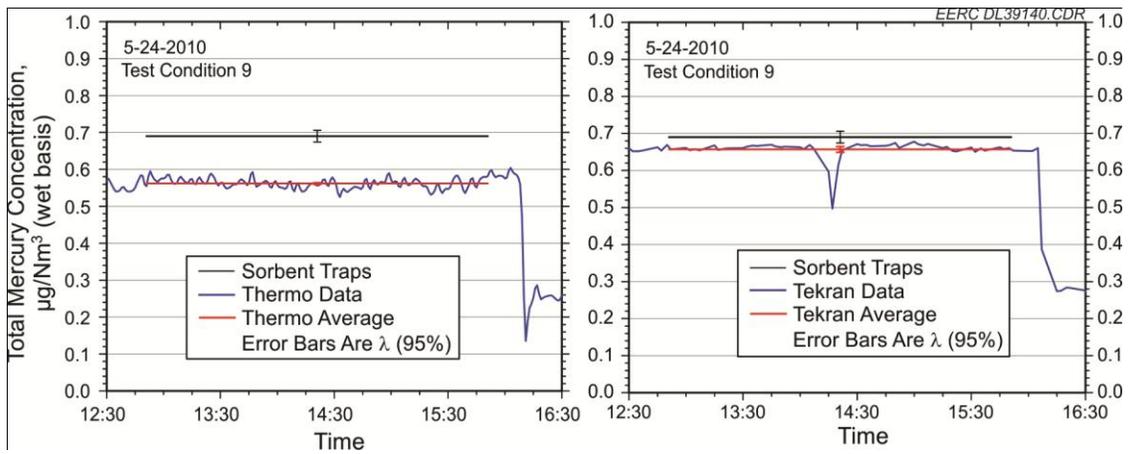


Figure B-17. Comparison of mercury measurement methods for Test Condition 9 for the second natural gas test.

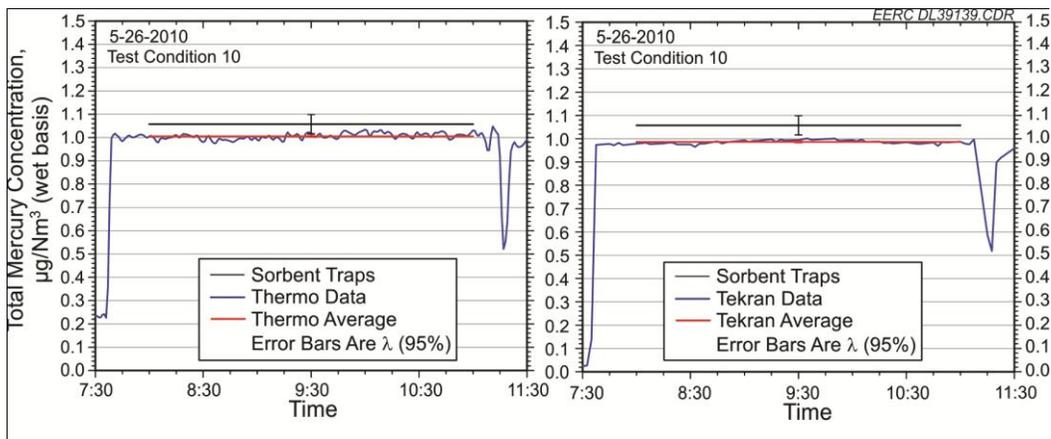


Figure B-18. Comparison of mercury measurement methods for Test Condition 10 for the second natural gas test.

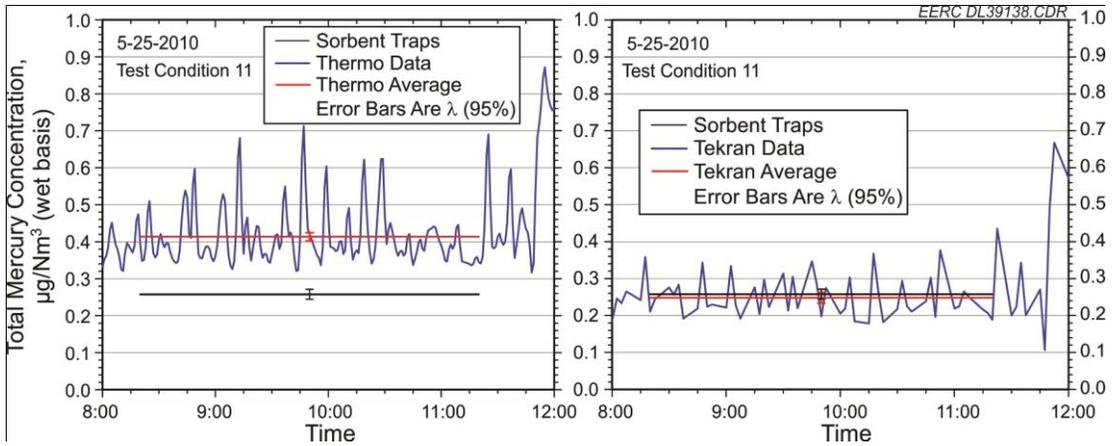


Figure B-19. Comparison of mercury measurement methods for Test Condition 11 for the second natural gas test.

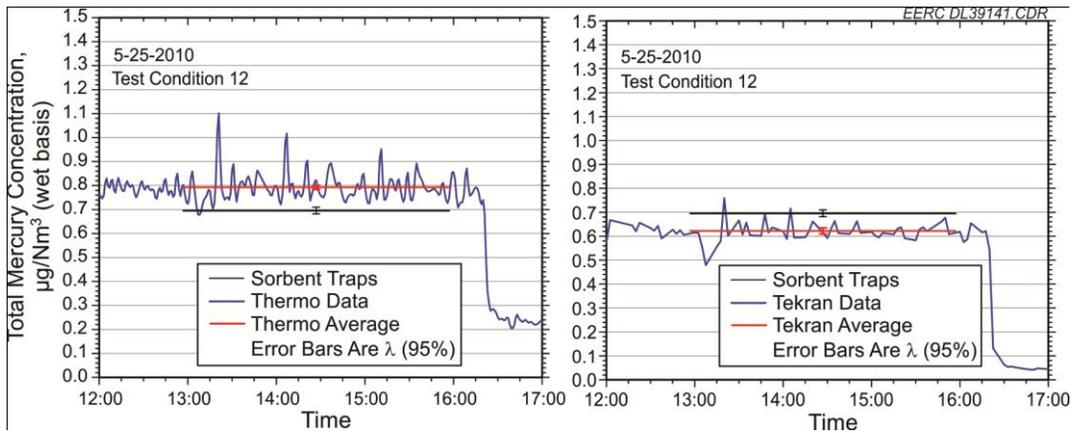


Figure B-20. Comparison of mercury measurement methods for Test Condition 12 for the second natural gas test.

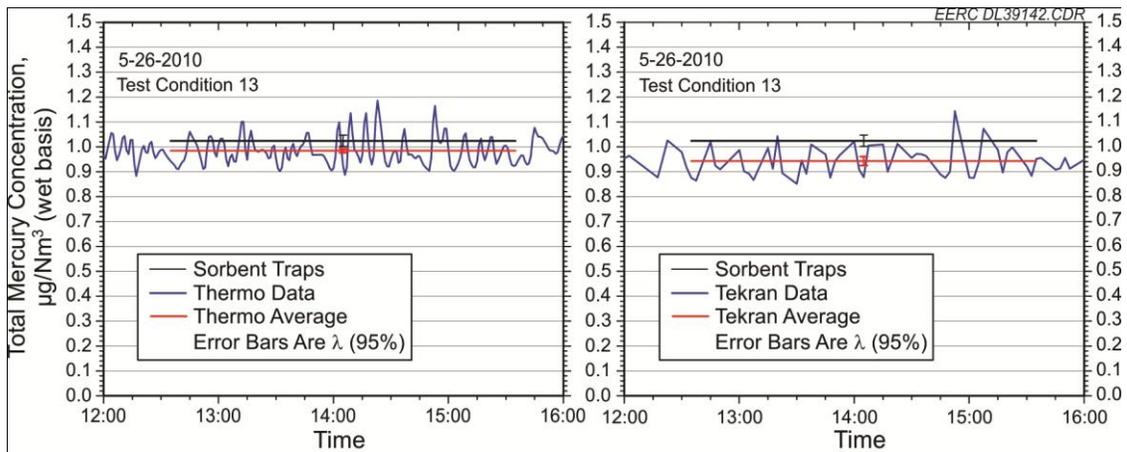


Figure B-21. Comparison of mercury measurement methods for Test Condition 13 for the second natural gas test.

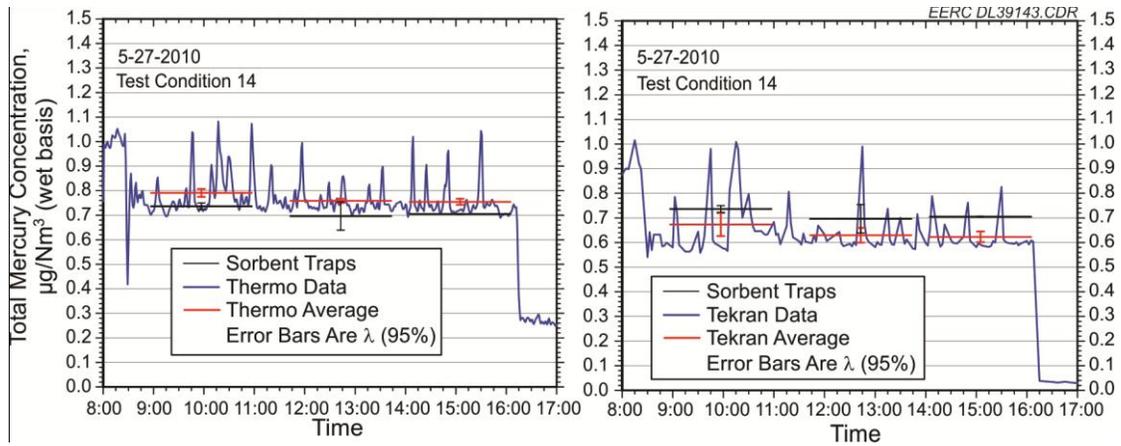


Figure B-22. Comparison of mercury measurement methods for Test Condition 14 for the second natural gas test.

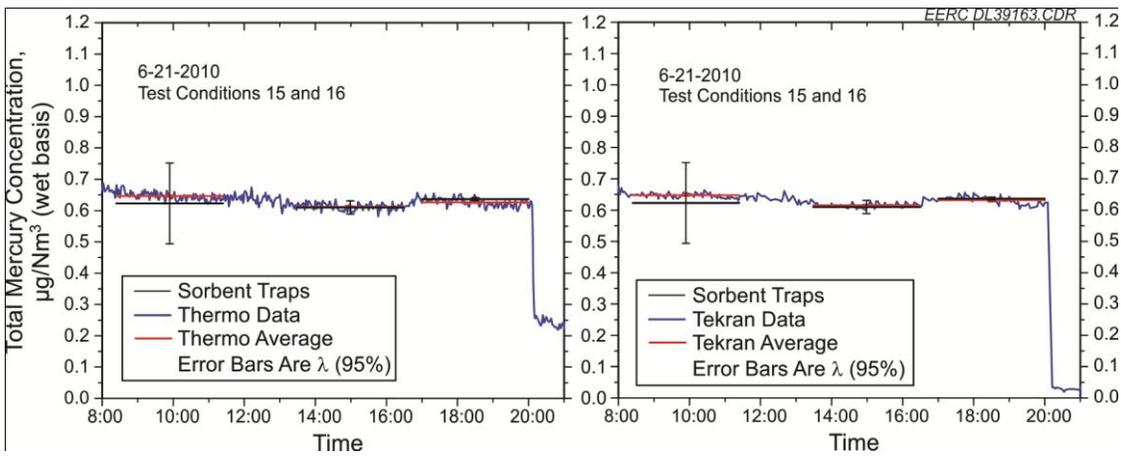


Figure B-23. Comparison of mercury measurement methods for Test Condition 15 and Test Condition 16.

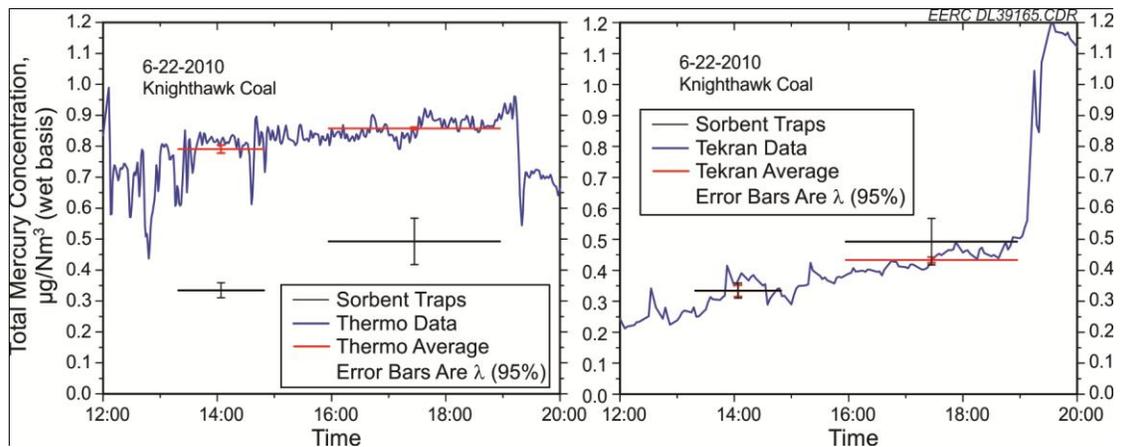


Figure B-24. Comparison of mercury measurement methods for coal test (6-22-10).

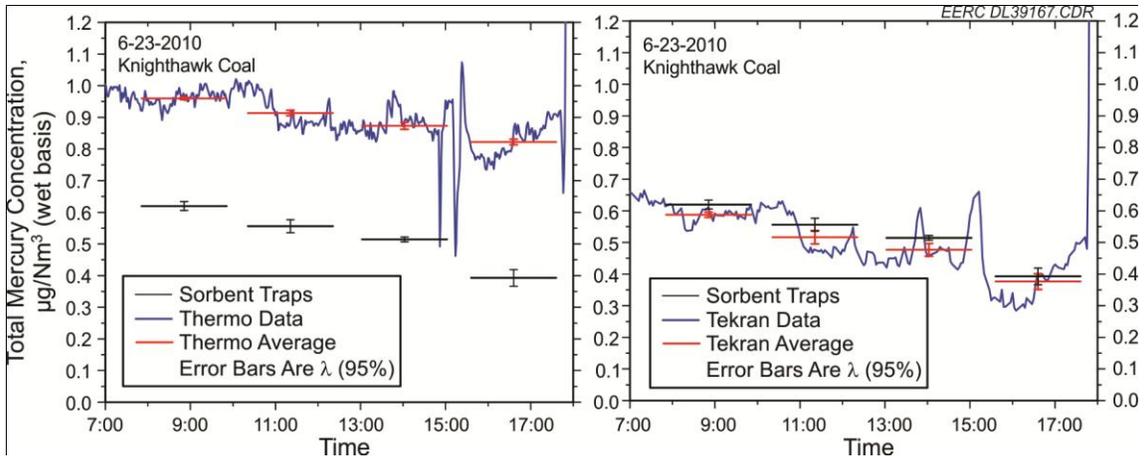


Figure B-25. Comparison of mercury measurement methods for coal test (6-23-10).

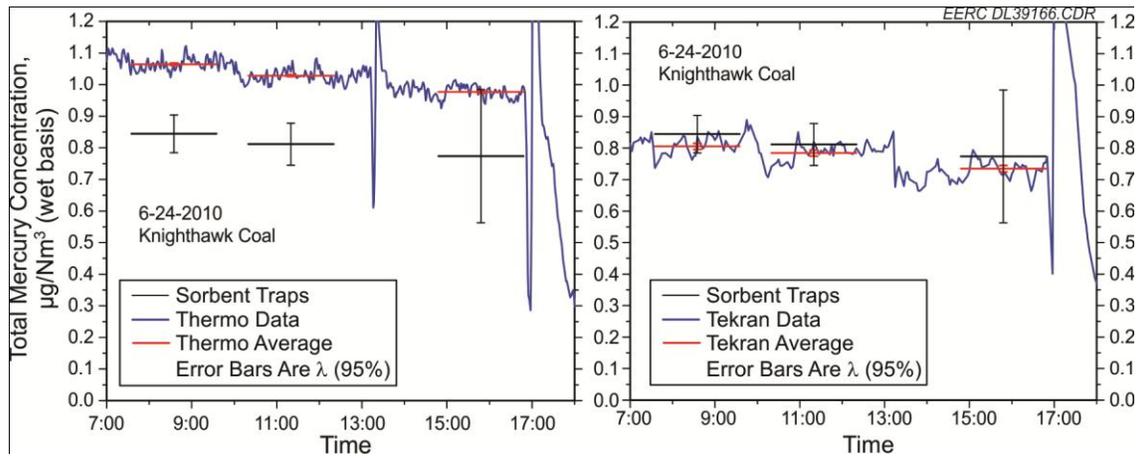


Figure B-26. Comparison of mercury measurement methods for coal test (6-24-10).