Measurement of Mercury and Heavy Metals Emissions from Fossil-Fired Power Plants

30

Professional Development Hours (PDH) or

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EXECUTIVE SUMMARY

With mercury regulations pending and control technologies in the full-scale demonstration stage, measurement of mercury (Hg) in combustion flue gas is of critical importance. The ability to accurately and reliably measure mercury is fundamental to demonstrating compliance when regulations are promulgated and, in the meantime, to ensuring adequate quantification of mercury removal during the demonstration and commercialization of the various mercury control technologies.

The important issue facing electric utility industry is a short compliance timeline: by January 1, 2009, certified continuous mercury monitors (CMM) need to be installed. Following certification, a certified CMM should collect 12 months of mercury emissions data. Reporting of data for compliance monitoring would start on January 1, 2010. This gives two years for CMM installation and certification, and three years until mandatory reporting for emissions compliance, Figure E-1.

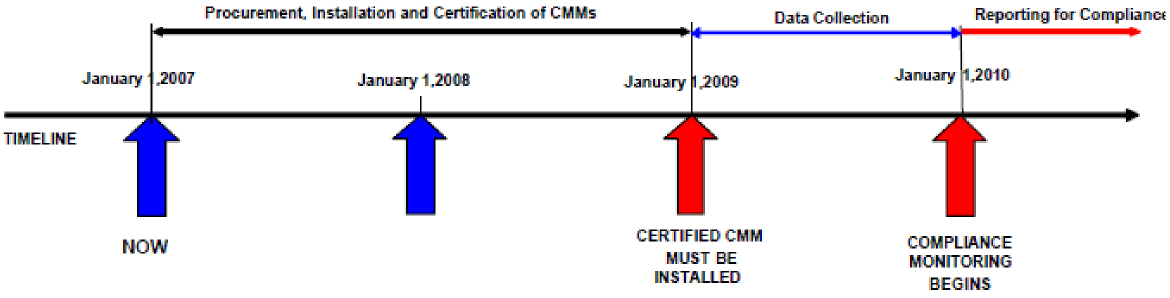


Figure E-1: Mercury Compliance Timeline

Collecting a representative flue gas sample for Hg analysis from coal combustion flue gas produces many challenges. The complexity of flue gas chemistry, relatively high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct or stack. In addition to measuring total mercury accurately, the identification and quantification of species of mercury is also very important. Mercury emissions from anthropogenic sources occur in three forms: solid particulate-associated mercury Hg(p); gaseous divalent mercury, Hg2+; and gaseous elemental mercury, Hg0.

Continuous monitoring of mercury emissions will be needed for all stationary sources where annual Hg emissions exceed 29 pounds of Hg. The Ontario Hydro wet chemistry method (OHM) and dry sorbent trap methods provide good results for total and speciated mercury measurements. However, these methods are not designed to provide the real-time data often necessary for environmental compliance.

Hg CEMs are similar to other combustion system CEMs in that a sample is extracted from the gas stream, conditioned, and sent to a remote analyzer for detection. However, as stated earlier, mercury is present in three different forms (Hgp, Hg2+, and Hg0), which greatly complicates the measurement process. As they are currently configured and utilized, Hg CEMs possess several challenges to long-term, lowmaintenance continuous operation for flue gas mercury monitoring. The two main challenges include the areas of sample collection and flue gas conditioning. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas is not an easy task.

With the support from the U.S. EPA, EPRI, U.S. electrical utility companies, and the Italian Ministry of Economic Development, The Institute for Environment and Sustainability of the Joint Research Centre, and with great help from Allegheny Energy, the ERC organized a field test where the commercially available Hg CEMs and sorbent trap methods were field-tested at Allegheny Energy's Armstrong Generating Station and compared to the reference method.

The main project objectives included:

- Testing of mercury CEMs under field conditions and comparison against the reference method (OHM).
- Testing of the Appendix K sorbent trap methods under field conditions and comparison against the reference method (OHM).
- Field-testing of the EPA Instrumental Reference Method (IRM) for mercury.
- Comparison of the reference methods and test equipment for Hg measurement developed in the U.S. and EU.
- Comparison of the reference methods for heavy metals, PM2.5, and PM10 measurement developed in the U.S. and EU.

The sorbent trap testing was conducted in parallel to the OHM tests. The start and end times for the OHM and sorbent trap tests were coordinated to allow direct comparison of the results. The Hg CEM and sorbent trap method results were compared to the mercury concentrations measured by OHM. Collected OHM samples were analyzed on-site.

A total of 72 OHM tests were performed. In addition, 36 samples were obtained by the EU reference Method. The total number of sorbent trap tests, performed by all test teams, was 186. Based on the number of the performed tests, the Armstrong field test represents one of the most comprehensive field test efforts in the mercury measurement area conducted in the U.S.

Also, as part of the Armstrong project, the U.S. EPA, in association with Arcadis, performed a first field test of the new Instrumental Reference Method (IRM).

Field testing was performed in July 2006 by a joint U.S. and EU team at the Allegheny Energy Armstrong Generating Station, located northeast of Pittsburgh, Pennsylvania. For the first part of the test, the plant was firing bituminous coals with high and varying mercury content from local mines. For the second part of the test, a low-Hg coal from Virginia was fired.

This report is divided into two parts. Project objectives, technical approach, test site, test equipment and methods, and Hg CEMs are described in Part 1 of the report. Test results are presented in Part 2.

A comparison of the gas-phase mercury concentration measured by the Hg CEMs and OHM shows a very good agreement between the mercury concentrations measured by both methods, Figure E-2. Also, the inter-comparison between different Hg CEMs is very good, especially for the low-Hg coal.

A comparison of the total mercury HgT measured by the sorbent trap methods and OHM, presented in Figure E-3, also shows a very good agreement of results obtained by both methods.

The average bias error B in the gas-phase Hg concentration measured at Armstrong by the Hg CEMs and OHM ranges from -4.2 to + 10.5 percent. The bias error for the high-Hg coal is in the -3.1 to 10.5 percent range, while for the low-Hg coal the value of B is in the -10.4 to 4.6 percent range. The values of bias error for Hg CEMs tested at Armstrong are presented in Figure E-4.

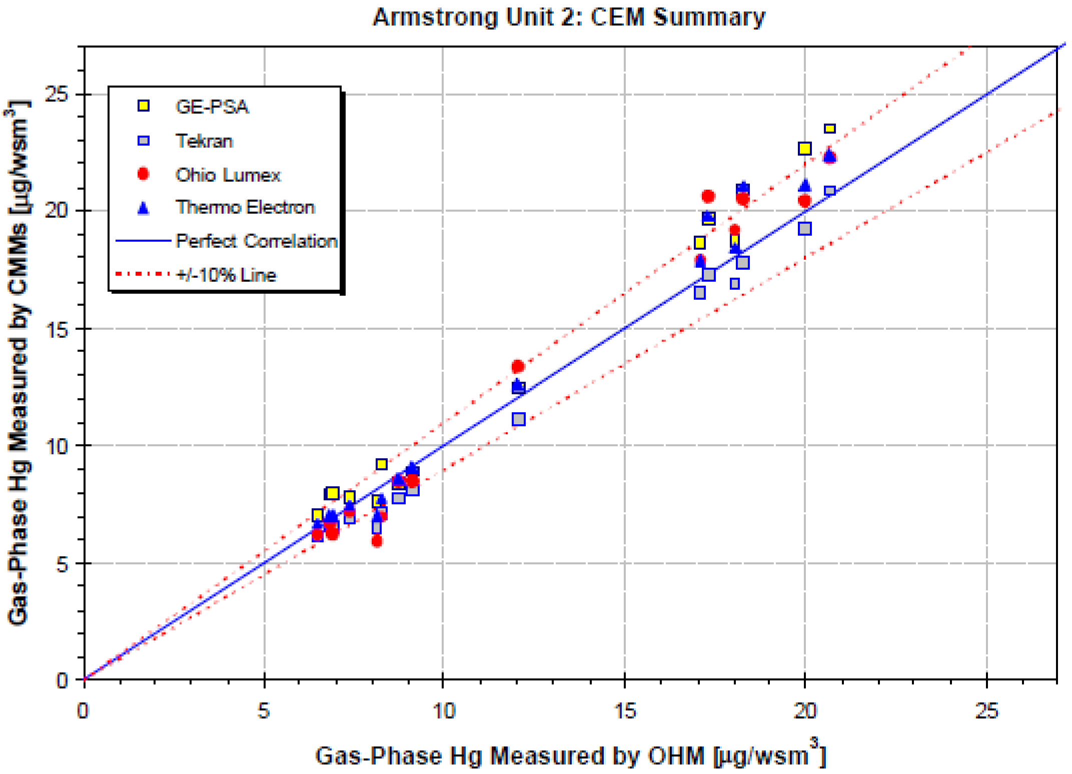


Figure E-2: Comparison of Gas-Phase Hg Concentration Measured By Hg CEMs and OHM

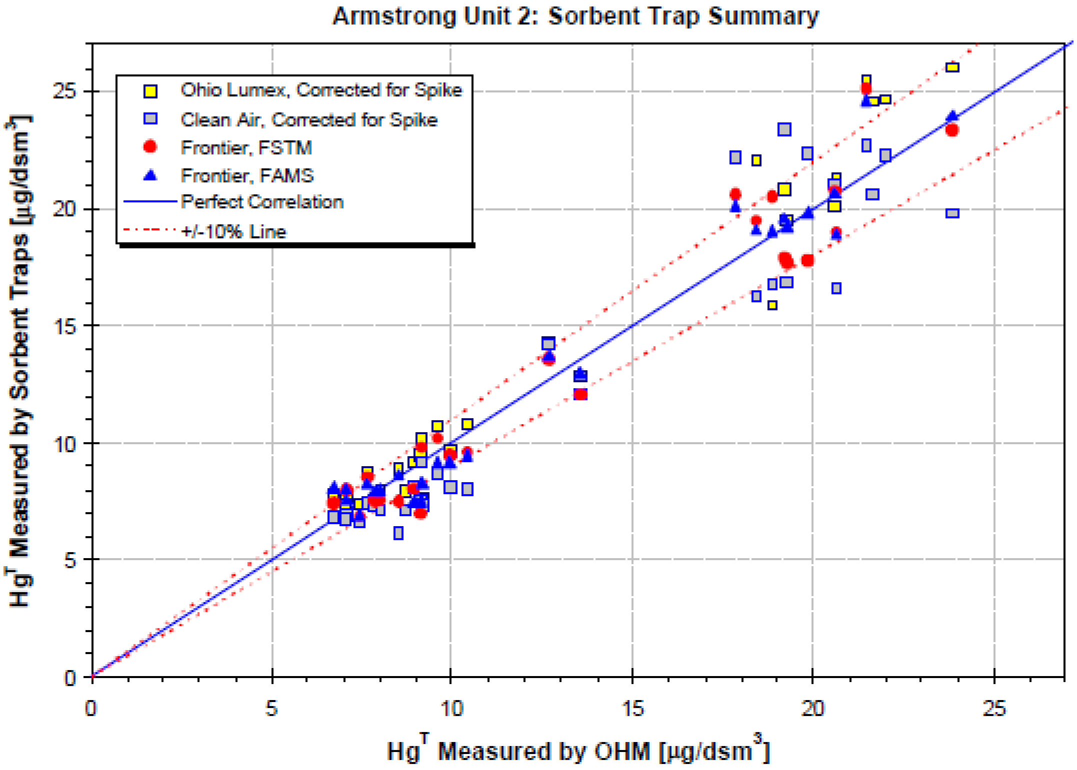


Figure E-3: Comparison of HgT Concentration Measured By Sorbent Traps and OHM

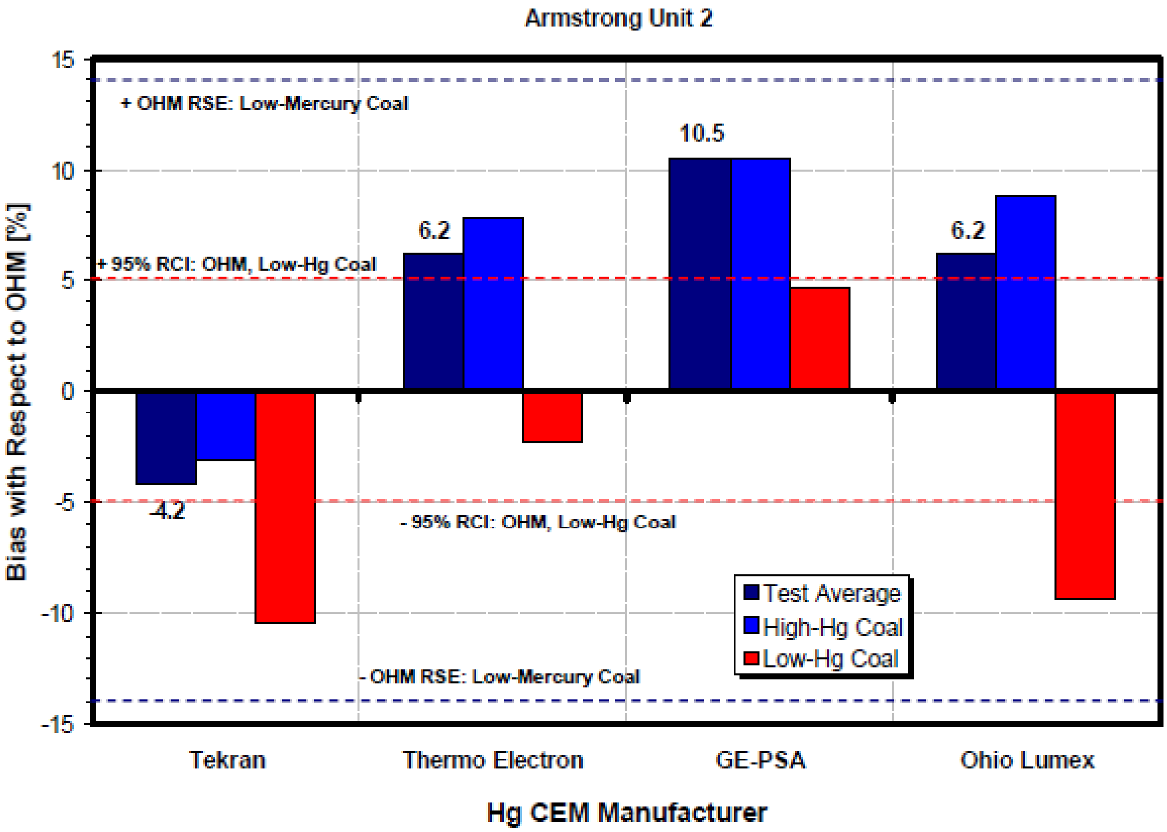


Figure E-4: Hg CEM Bias Error With Respect To OHM

The results of a statistical analysis involving comparison of the interval estimates show that the bias between the OHM, GE -PSA CMM and Ohio Lumex Hg CEM results for the high-Hg coals fired at Armstrong is statistically significant. For the low-Hg coals, the analysis shows that the bias between the OHM, Tekran CMM and Ohio Lumex CEM is statistically significant.

The average bias error in HgT concentration, measured by the sorbent trap methods and OHM, ranges from –4.7 to 11.3 percent. The bias error for the high-Hg coal is within the -1 to 13.3 percent range, while for the low-Hg coal B is within the -12 to 7.9 percent range. The values of bias error, for sorbent trap methods tested at Armstrong, are presented in Figure E-5.

For the sorbent trap results obtained by the Ohio Lumex – Apex Instruments test team, not correcting the results for spike resulted in an increase in the bias error; for the CleanAir Engineering - CONSOL results, the bias error for the uncorrected results decreased. The lowest bias error was achieved by the Frontier Geosciences' FSTM and FAMS methods.

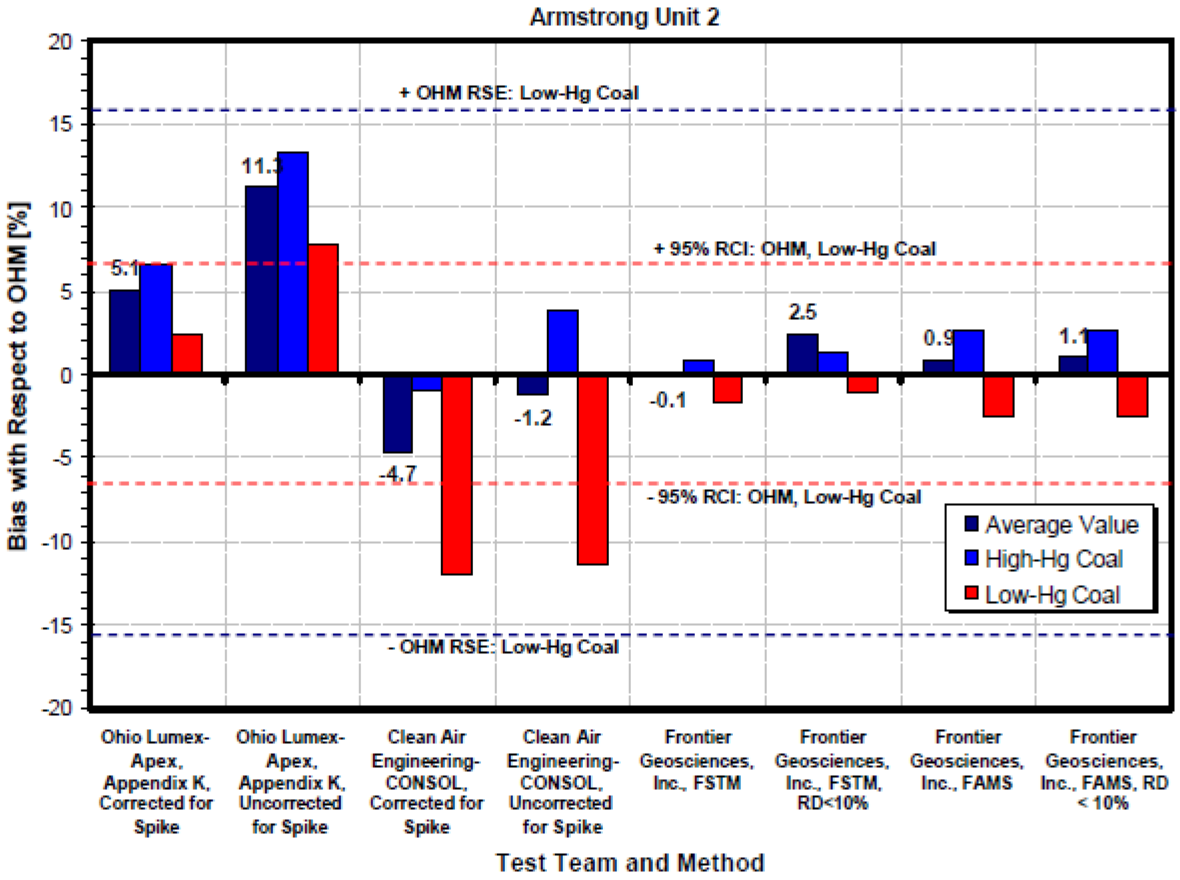


Figure E-5: Sorbent Trap Bias Error With Respect To OHM

The results of a statistical analysis involving comparison of the interval estimates show that the bias between the OHM uncorrected Ohio Lumex and Clean Air Engineering results for the high-Hg coals fired at Armstrong is statistically significant. For the low-Hg coal fired at Armstrong, the bias between the OHM and uncorrected Ohio Lumex results is statistically significant.

The precision of the corrected and uncorrected for spike Appendix K method results was used to determine the effect of spike correction. The results show that spike correction has a very small and inconsistent effect on the precision of the Appendix K results obtained at Armstrong.

A comparison of the HgT concentration values measured by EN-13211 and OHM shows a very good correlation between the two EU and U.S. Reference Methods for HgT measurement. In summary, EN-13211 performed very well and, on average, produced almost identical values compared to OHM. This means that Hg emission rates measured by the Reference Methods in the USA and European Union are, from the practical point of view, identical and Global trading (if it ever becomes a reality), would be fair and unbiased, as far as measurement accuracy is concerned.

The results from the Armstrong field test show there is a good agreement between the Reference Method (OHM), Hg CEMs, and sorbent trap method results. The maximum bias, calculated for the Armstrong data, is in the 10 percent range. Also, the precision of the OHM results obtained at Armstrong was comparable to the results obtained at other sites.

Based on the obtained results and experience with the test equipment and Hg monitors, recommendations are provided for the dry stacks concerning the automation of the OHM, application of the sorbent trap methods, Instrumental Reference Method hardware, and methods for Hg stratification measurement.

1. INTRODUCTION

As the U.S. and world population grows, energy use increases. Increased energy usage requires an increase in electric power generation, which constitutes one of the major components of the total energy needs. Increased power generation from fossil-fired power plants also results in increased emissions of pollutants, such as NOx, SOx, Hg, heavy metals and particulate matter (PM).

Pollution emissions are regulated by Government rules and regulations, which typically require continuous measurement of emissions and periodic calibration of the continuous emission monitoring system (CEMs) using approved reference methods. Instrumentation, techniques, and reference methods for the measurement of NOx and SOx emissions are mature technologies, with well established procedures, accuracy and reliability.

Of the 189 substances designated hazardous air pollutants by the U.S. Environmental Protection Agency (EPA), mercury (Hg) has attracted significant attention in the world due to its increased levels in the environment and welldocumented food chain transport and bio-accumulation. As a consequence, on March 15, 2005, the EPA issued the Clean Air Mercury Rules (CAMR), which mandate national Hg reductions from coal-fired power plants through a “Cap and Trade” Program of 23 percent in 2010 (Phase I, based SO2 and NOx co-benefit controls) and 69 percent by 2018 (Phase II). As a consequence of these Hg regulations, research and development of cost-effective techniques for measurement and control of mercury emissions from coal-fired boilers has become an urgent issue for the power generation industry.

However, instrumentation, techniques, and reference methods for the measurement of heavy metals and PMs are still in the development or field testing stages. The only reference method currently approved in the U.S. for Hg is ASTM D6784-02, Standard Test Method for Elemental, Oxidized Particle -bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (also known as the Ontario Hydro Method).

The Ontario Hydro Method (OHM) is a wet chemistry method developed for measuring total and elemental mercury at power plant stack operating conditions. Although very accurate, the OHM is time-consuming, man-power intensive and expensive. Typically, three good OHM readings can be obtained per day by a well trained and experienced test crew, assuming no equipment problems, such as leakage or sample contamination, and no tests need to be repeated. Since the EPA regulations require nine good repeat tests at full-load per RATA, mercury RATAs could be very time-consuming and expensive.

The other important issue, facing the electric utility industry, is a short compliance timeline: by January 1, 2009, certified continuous mercury monitors (CMM) need to be installed. Following certification, a certified CMM should collect 12 months of mercury emissions data. Reporting of data for compliance monitoring would start on January 1, 2010. This gives two years for CMM installation and certification, and three years until mandatory reporting for emissions compliance, Figure 1-1.

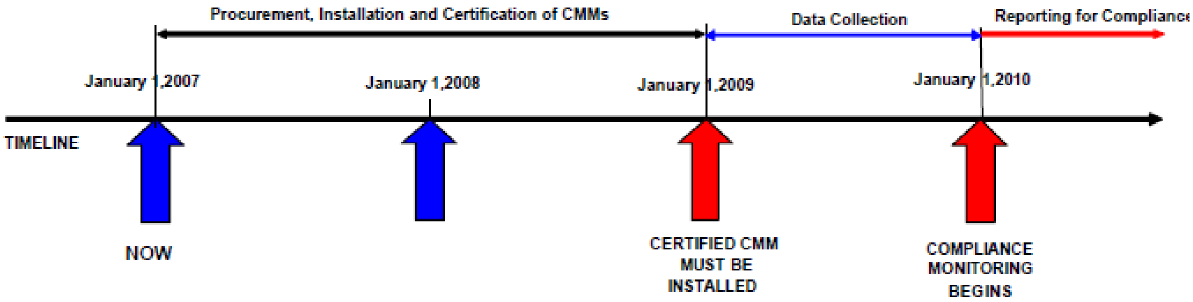


Figure 1-1: Mercury Compliance Timeline

Mercury emissions from U.S. power plants are presented in Figure 1-2. Under the Clean Air Mercury Rule (CAMR), mercury reduction of 21 percent would be required in Phase I by 2010. This would reduce annual mercury emissions by 10 tons. A 69 percent mercury reduction would be required in Phase II by 2018. This would result in an annual mercury emissions reduction of 38 tons.

Some states are pushing mercury compliance deadlines forward, reducing the time available for emission compliance, and also requiring larger mercury reductions than Federal regulations.

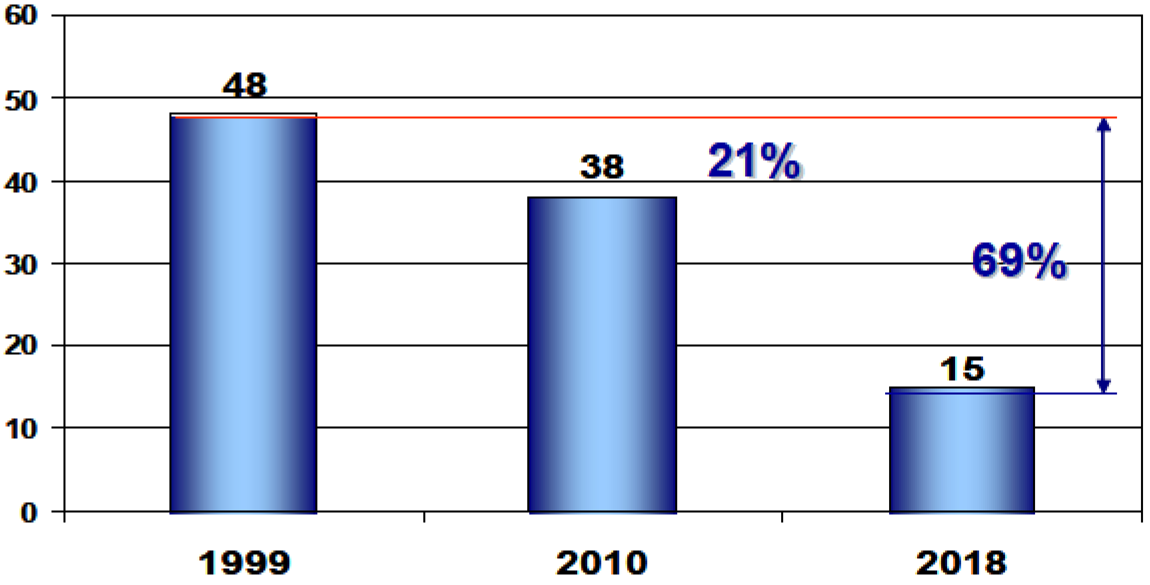


Figure 1-2: Mercury Emissions from U.S. Power Plants under Clean Air Mercury Rule (CAMR), In Tons per Year

Given a short time-line for mercury emissions compliance, commercial availability of CMMs in terms of accuracy, repeatability, and reliability is of extreme interest to the electric utility industry. Also, there is a serious concern as to whether or not enough trained test personnel will be available to perform mercury RATA tests. There is an urgent need for quicker, less man-power intensive and less expensive reference methods for Hg measurement.

With the support from the U.S. EPA, EPRI, U.S. Electrical Utility Companies, and the European Commission, the Lehigh University Energy Research Center (ERC) with great help from Allegheny Energy, organized a field test in which three continuous and two semi-continuous CMMs, currently commercially available in the U.S., were installed and field -tested at Allegheny Energy's Armstrong Generating Station. The continuous mercury CEMs were provided by Thermo Electron, Tekran, and PS Analytical. The semi-continuous mercury CEMs were provided by Ohio Lumex and Horiba.

The CMM results were compared to the mercury concentrations measured by the Reference Methods (RM) for mercury, developed in the United States (U.S.) and European Union (EU). The Ontario Hydro method (OHM) was used as a "gold" reference or standard for all measurements. On-site analysis of collected OHM samples was performed by Western Kentucky University (WKU), using their mobile test laboratory.

In addition, mercury emissions were also measured by the Sorbent Trap Method (Appendix K). Sorbent tubes and test equipment were provided by three manufacturers: Frontier GeoSciences, CleanAir & CONSOL, and Ohio Lumex & Apex.

Measurement of heavy metals and PMs was also performed by using RMs, developed in the U.S. and the European Union (EU). Comparison of the results was performed.

Field testing was performed in July 2006 by a joint U.S. and EU team at the Allegheny Energy Armstrong Generating Station, located northeast of Pittsburgh, Pennsylvania. The plant is firing bitumi nous coals with varying mercury content.

Also, as part of the Armstrong project, the U.S. EPA in association with Arcadis performed a first field test of the new Instrumental Reference Method (IRM). IRM results are presented in the Appendix. The CMMs provided by Tekran, Thermo Electron, GE & PS Analytical, and Ohio Lumex were used for the IRM tests.

2. PROJECT OBJECTIVES

The main objectives of the Armstrong project were the following:

- Test continuous and semi-continuous CMMs under field conditions and compare readings against the reference method (OHM) to determine CMM accuracy and repeatability.
- Test Appendix K (Part 75) Sorbent Trap (ST) method under field conditions and compare results against the reference method (OHM). The results of this comparison provided evidence as to whether or not the ST method could be considered as a potential reference method for mercury.
- Compare mercury concentrations measured by the CMMs and ST. Theresults provided information on the potential bias between CMMs and STs.
- Field-test EPA Instrumental Reference Method (IRM) for mercury. The IRM is designed as an alternative to OHM with the intent to provide an additional RM for mercury RATAs.
- Compare reference methods for Hg developed by the European Union (EU) and the United States (U.S.).
- Determine whether there is a bias in pollutant emissions measured by the RMs developed in the U.S. and EU. To our knowledge, such a comparison has never been done.
- The absence of a direct comparison of RMs makes a comparison of toxic inventories in the world uncertain, and fair global trading impossible. The direct comparison between the U.S. and EU reference methods will allow a direct comparison of emission levels measured in the U.S. and the EU.
- Compare all reference and other methods for mercury measurement under the same test conditions. · Compare RMs for heavy metals, and PM2.5, and PM10 developed in the U.S. and EU.

3. TECHNICAL APPROACH

A side-to-side comparison of the three continuous and two semi-continuous mercury CEMs, and Sorbent Traps to the RM (OHM) was performed under field conditions. The continuous CMMs were located on the ground level. The flue gas samples, extracted from the stack and conditioned by the sample extraction probes, were delivered to the Hg analyzers via 450 ft long heated umbilical lines. The semicontinuous mercury CEMs were located at the stack CEM platform, 350 ft above the ground and utilized very short heated umbilical cords.

The Ontario Hydro Method (OHM) was used to obtain samples in accordance with ASTM D6784-02 - Standard Test Method for Elemental, Oxidized Particle-bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources. The OHM testing was performed by Western Kentucky University (WKU) test crew using two paired OHM sampling trains.

Two EU computer-controlled automated isokinetic sampling trains were used to obtain samples in accordance with EN-1321 method for mercury measurement. The samples, collected by the OHM and EU trains, were analyzed on site by using the WKU mobile chemical analysis laboratory. Sample analysis was performed by the second WKU crew overnight, and results from the previous test day were available next morning.

Sorbent trap testing was conducted in parallel to the OHM tests. The start and end times for the OHM and ST test were coordinated to allow direct comparison of the results.

Since Armstrong Generating Station needed to participate in frequency control (Area Grid Regulation, AGR) during the test period, the station personnel and power dispatcher reached an agreement to provide two 2-hour test periods of consta nt load each day. The first constant load period was in the morning, while the second one was in the afternoon. This limited the number of tests that could be conducted to two per day, Figure 3-1. Duration of the test period corresponded to duration of the OHM test (typically 2 hours).

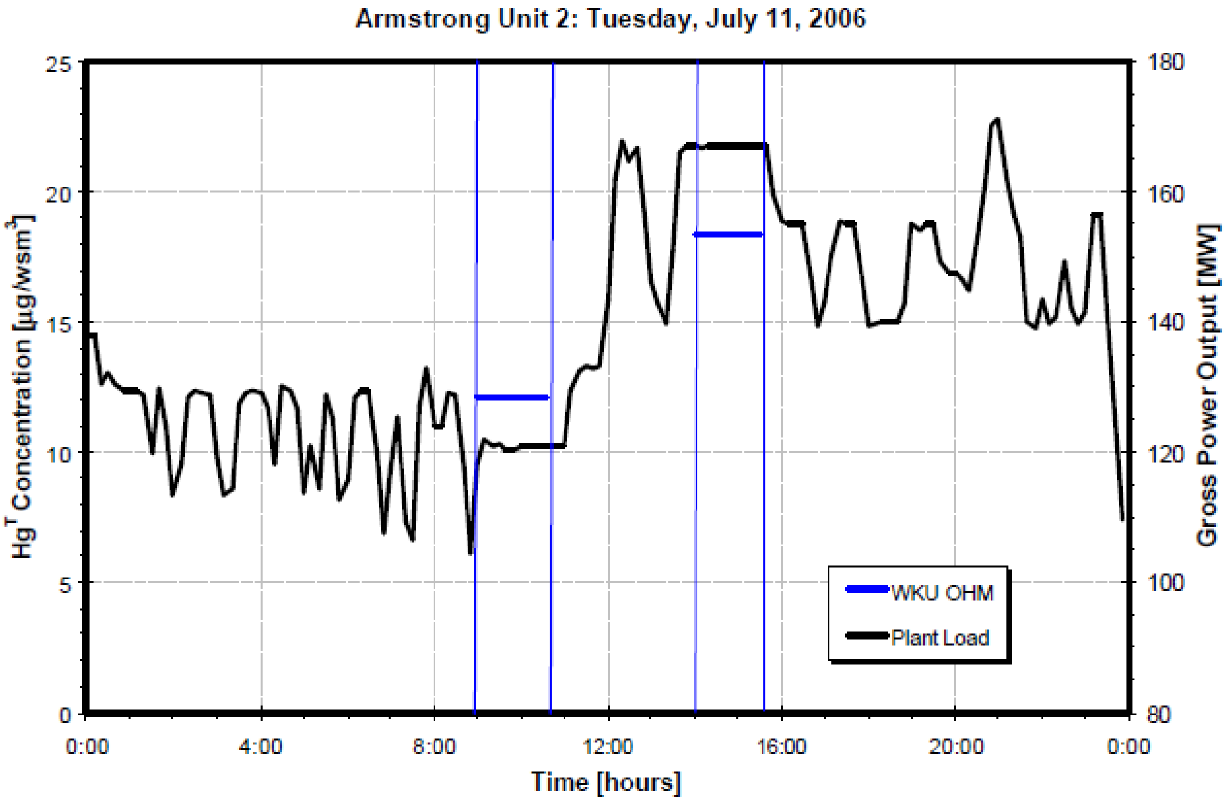


Figure 3-1: The AM and PM Constant Load Test Period. Duration of Test Period Corresponds to the OHM Test Duration.

Fly ash and coal samples were collected at least three times per day to determine mercury concentration and stability in the ash. Coal samples were collected from the coal mills, Figure 3-2, while fly ash samples were collected from the Electrostatic Precipitator (ESP) hoppers, Figure 3-3.

Major, minor and trace constituents in the ash were determined using ASTM Methods D 6349 (ICP-AES), D 4326 (XRF) and D 6357 (ICP/MS). The “loss on ignition” of ash was determined using ASTM Method D 5142. The ultimate analysis for carbon and sulfur was determined using ASTM Methods D 5373 and D 4239. The stability of Hg was determined using TCLP: SW-846 method 1311. Coal ultimate analysis was also performed.

Test coordination, test planning and execution were performed by the ERC and Allegheny Energy engineers. Unit operating conditions, such as load output, excess O2 level, mill firing arrangement, and other combustion settings were monitored and controlled during the test by the Allegheny Energy engineer. Sootblowing was put on hold during the test to avoid interference with the measurements.

Figure 3-2: Collection of Coal Samples from Mill Feeders

Figure 3-3: Collection of Ash Samples from the ESP Hoppers

3.1. Test Participants and Their Responsibilities

ERC. The ERC test team organized, coordinated, and supervised field testing. During the testing, the ERC engineer was in constant communication with Allegheny Power engineer or operating staff to ensure plant operating conditions met the required test conditions.

The ERC was also responsible for the analysis of raw test data and writing of interim and final reports to project sponsors. With help from U.S. EPA, ERC organized a results meeting and presented test results to project sponsors in October 2006.

EPA & Arcadis. The EPA provided personnel and equipment to implement and field-test IRM. The EPA contractor (Arcadis) personnel were responsible for the injection of gaseous Hg standards (Hg0 and Hg+2) to the continuous and semicontinuous mercury CEMs participating in the IRM test. The EPA also provided the necessary gas standards and ancillary support equipment. The EPA activities were timed so as to minimize impact on Reference Methods sampling activities (e.g., prior to/after runs, in-between train changes). A significant portion of the IRM testing was performed at night to avoid interference with CMM tests.

Mercury CEM Vendors. The instrument vendors: Tekran, Thermo Electron, and GE & PS Analytical have provided continuous mercury CEMs for the project. Ohio Lumex and Horiba supplied semi-continuous mercury CEMs.

Installation and calibration of the mercury CEMs was performed by the instrument vendors under supervision of an Allegheny Energy engineer. The continuous mercury CEMs were operated continuously during the time period preceding and following the test program. The semi-continuous mercury CEMs were operated only during the time interval corresponding to the individual test points.

Each instrument vendor provided a dedicated technician, or a representative, familiar with the test instrumentation and equipment, to ensure proper operation of the mercury CEM, and assist with data collection.

Western Kentucky University (WKU). The WKU test team performed OHM testing by using two paired OHM trains. Two measurements of heavy metals and PMs in stack flue gas were also performed. The WKU personnel analyzed all OHM and EU test samples on site, using the WKU mobile test laboratory, and provided raw test data to the ERC next morning after the test. After the system losses were determined, WKU provided final test results to the ERC.

CESI RICERCA Research. The CESI RICERCA Research test team has performed measurements of mercury, heavy metals and PMs using EU-developed methods, standards, and equipment. CESI RICERCA Research provided raw and final test data to the ERC.

Frontier GeoSciences. Frontier GeoSciences supplied sorbent traps and sampling equipment required for the test. Their test personnel performed sorbent trap testing according to Appendix K, and has performed mercury stratification measurements using specially designed probes. Collected samples were analyzed by the Frontier GeoSciences laboratory in California. Final test results were provided to

ERC.

CleanAir & CONSOL. The CleanAir & CONSOL supplied sorbent traps and sampling equipment needed for the test. Their test personnel performed sorbent trap testing according to Appendix K, and also analyzed collected test samples in their laboratory in Pennsylvania. CleanAir provided final test results to ERC.

Ohio Lumex & Apex. Ohio Lumex & Apex Testing supplied sorbent traps and sampling equipment needed for the test. The Apex test personnel performed sorbent trap testing according to Appendix K. The Ohio Lumex engineer analyzed collected test samples on site and provided raw and final test results to ERC.

3.2. Test Schedule

Field testing at Armstrong was conducted during the time period from July 8 to July 17, 2006. Pre-test, test, and post-test activities are summarized in Table 3-1.

Table 3-1 Pre-Test, Test, and Post-Test Activities at Armstrong

DATE/TIME PERIOD	ACTIVITY	COMMENT
November 2005	▪ First project Meeting at Lehigh University, Bethlehem, PA	
April 11, 2006	▪ Second Project Meeting at Greensburg Corporate Center, Greensburg, PA	
April 12, 2006	▪ Visit to Armstrong GS	
Late April 2006	▪ Umbilical cords arrive at Armstrong	▪ Cords and utilities installed by the contractor
May and June 2006	▪ Mercury CEMs arrive at Armstrong. ▪ Mercury CEMs installed, calibrated and placed in continuous operation	▪ CEM Installation supervised by Mr. Mark Seibel.
Late June through early July 2006	• CEM Pre-certification • Pre-IRM tests • Setup: WKU, CESI RICERCA Research, Frontier GeoScience, Clean Air & Consol, Ohio Lumex & Apex Instruments	• Central DAS installed to record CEMs data. Also used as a backup. • Meeting with plant operating staff
July 8 to 17, 2006	• **Field Test:** • CMMs in continuous operation • Semi-continuous Hg CEMs operated during test intervals • Paired OHM testing • Paired EU testing • Heavy metals testing • $PM_{2.5}$ and PM_{10} testing • Sorbent Trap testing • Hg CEM drift testing conducted at night to avoid interference with the other test activities.	• Collect ash and coal samples 3 times daily • Recorded Hg CEM output provided to Allegheny Energy and ERC in electronic form on daily basis • Plant operating data provided to ERC in electronic form on daily basis • All test teams provide raw test data to ERC • Cleanup and demobilization
July 17 to the end of July 2006	▪ Final IRM testing.	
August 2006	▪ Tekran and Thermo Electron CMMs continue to operate. ▪ Other equipment removed from test site	
August through October 2006	▪ ERC provides project updates and results to project sponsors as they become available.	
October 10, 2006	▪ Third (results) project meeting at EPA's Main Campus at RTP, Durham, NC	▪ Project results presented and discussed with project sponsors and EPA personnel.
February 2007	▪ Final report issued to project sponsors	

3.3. Description of Host Unit and Stack Measurement Location

Armstrong Generating station is comprised at two units rated at approximately 190 MW gross, each. The station receives coal by truck from a number of local mines, and also fires Virginia coal that is delivered by rail. Two Electrostatic Precipitators (ESPs) in a serial arrangement, Figure 3-4, are used for particulate emissions control. As a result, opacity at the stack is very low, typically in the 3 percent range. Although Armstrong is typically a base-loaded unit, it participates in the frequency (AGR) control.

Units 1 and 2 at Armstrong discharge flue gas into the atmosphere through two steel stacks. The stacks are contained in a common 1,000 ft high concrete liner. Stack breechings are shown in Figure 3-5. The abounded Unit 1 and 2 stacks are shown in the back.

Stack diameter is 14.5 ft, which gives average flue gas velocity of approximately 75 ft/s at full-load. The main CEM platform is located approximately 350 ft above ground level, Figure 3-6, and is accessible by elevator. The elevator was serviced in advance of the test and used extensively during the setup and test.

Figure 3-4: ESPs at Armstrong Unit 3

Figure 3-5: Stack Breechings

The CEM platform has three elevations, as presented in Figure 3-7. A number of ports are available at each platform elevation, which makes Armstrong a perfect test site. Five ports on the main CEM platform were used for sampling probes delivering flue gas samples to Tekran, Thermo Electron, GE & PS Analytical, Ohio Lumex and Horiba mercury analyzers. The four ports in the cross arrangement were used by the two paired OHM trains and two single EU sampling trains.

As discussed earlier, Tekran, Thermo Electron, and GE & PS Analytical analyzers were located in the CEM shelters at the ground level and were receiving flue gas samples via 450 ft long heated umbilical lines.

Figure 3-6: Location of the CEM Platform

The semi-continuous mercury CEMs, Ohio Lumex and Horiba, were located at the main CEM platform, close to the sampling probe. The sample from the probe was delivered to the analyzer via short heated umbilical cords. Arrangement of the continuous and semi-continuous mercury CEMs is presented in Figure 3-8. The photographs depict sampling probes and semi-continuous analyzers.

The arrangement of ports used for OHM sampling is presented in Figure 3-9. The OHM sampling trains, operated by the WKU test personnel, used Ports 1 and 4 (The ports were numbered in a clockwise direction, with a 12 o'clock port being numbered Port 1). The EU sampling trains, operated by the CESI RICERCA Research personnel, used Ports 2 and 3. Halfway through the test, WKU and CESI RICERCA teams switched ports to eliminate any possible bias in measurements due to potential mercury stratification within the stack.

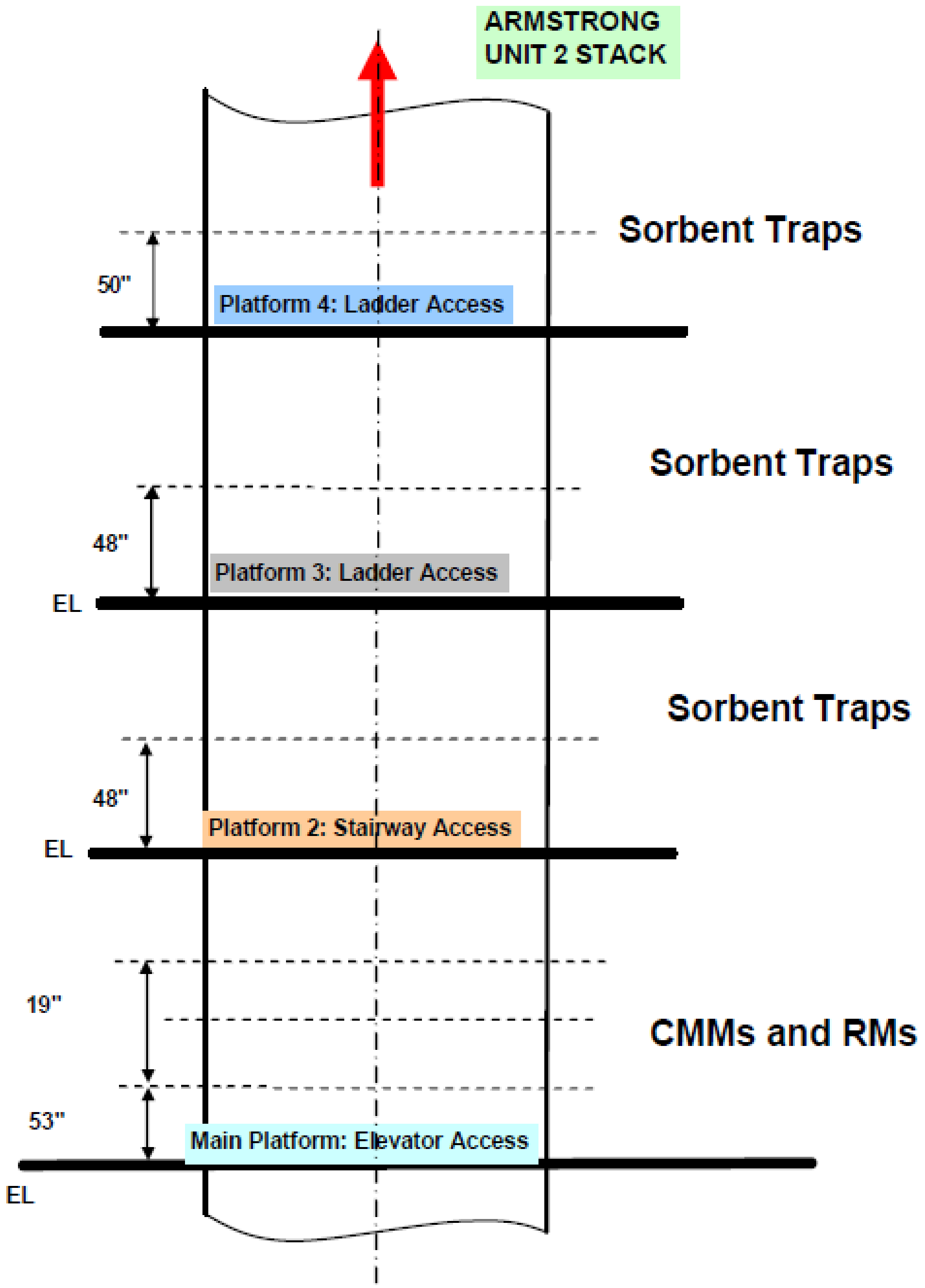


Figure 3-7: Main CEM Platform and Three Platform Elevations

The Appendix K equipment for mercury measurement was located on the second, third, and fourth platforms, as shown in Figure 3-7. Detailed arrangement of the equipment is presented in Figures 3 -10, 3-11, and 3-12.

The Ohio Lumex/Apex Instrument probe and sampler and one of the Frontier GeoScience probes were located on the second CEM platform, as shown in Figure 3- 10. The photographs depict Ohio Lumex/Apex Instruments sampling probe and a sampler.

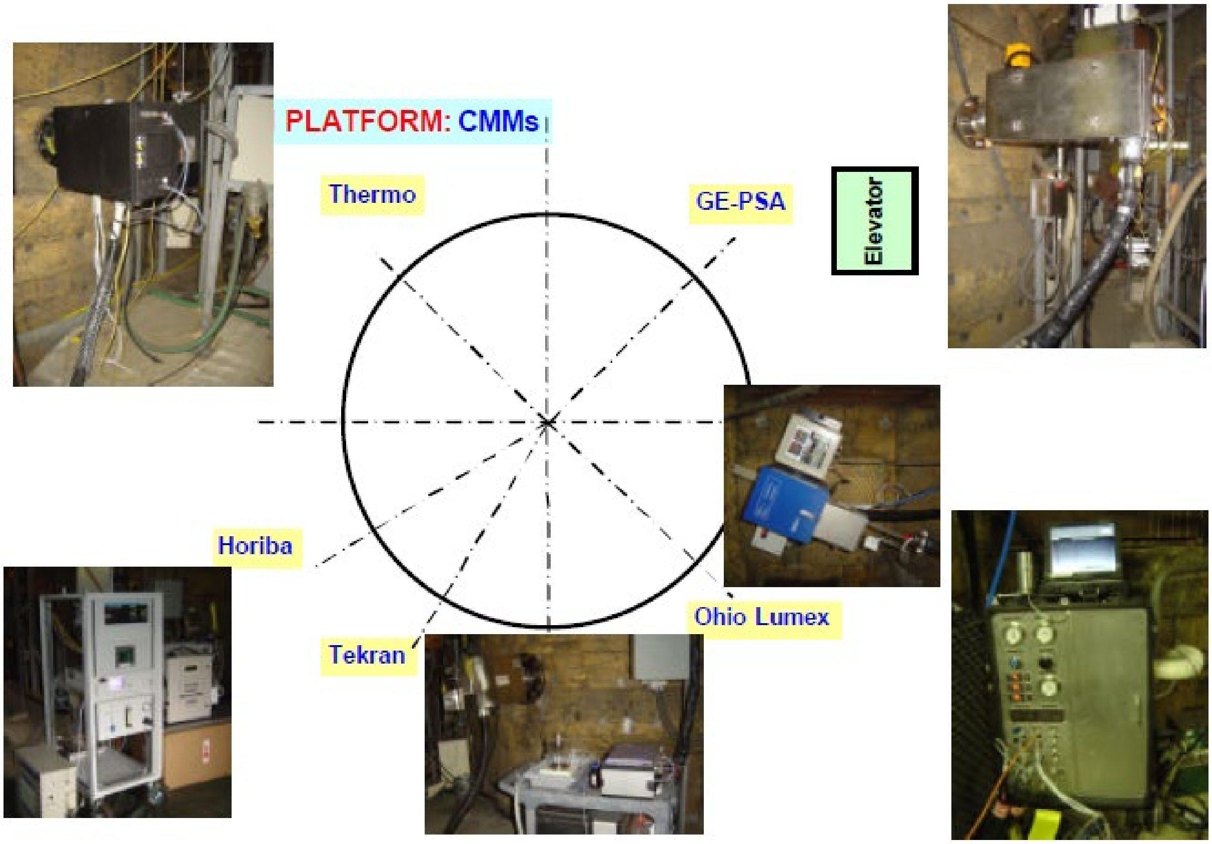


Figure 3-8: Mercury CEM Equipment Arrangement on the Main CEM Platform

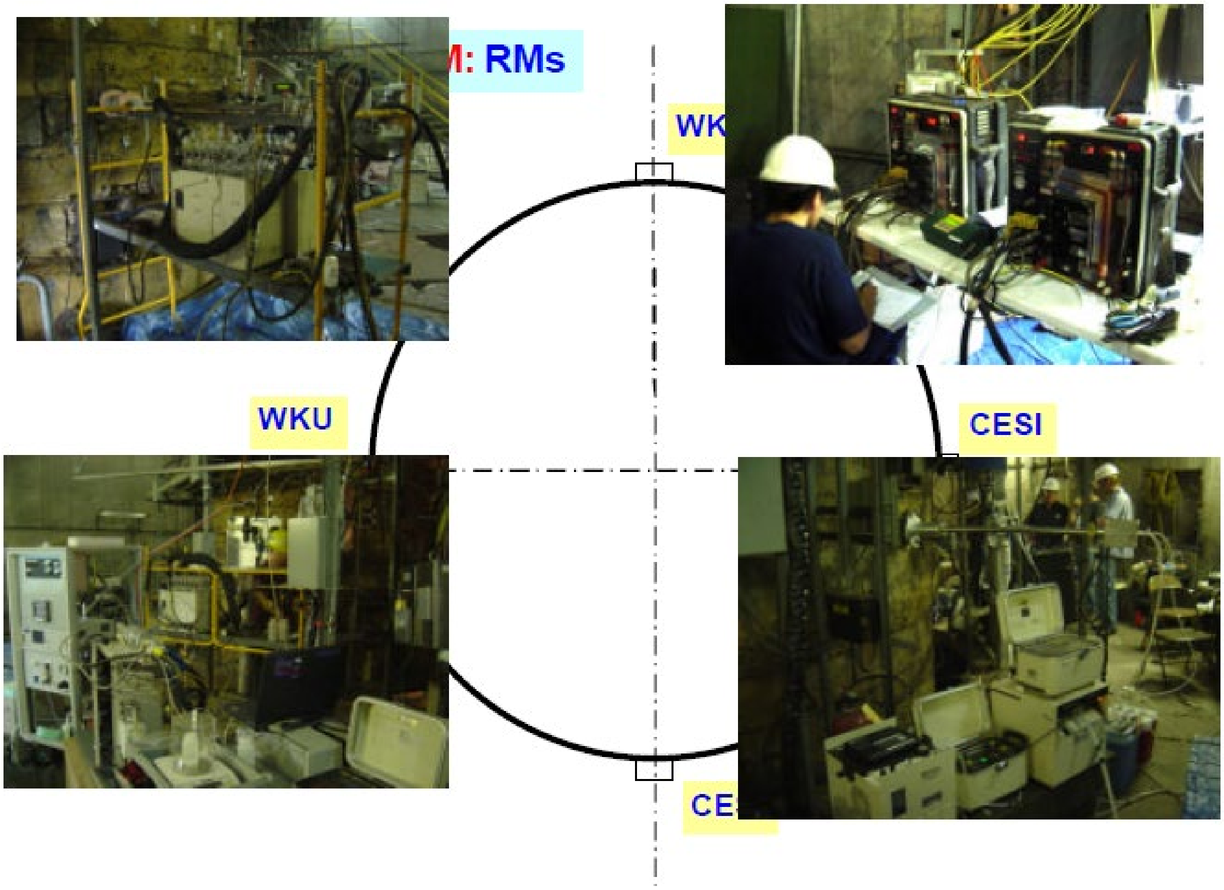


Figure 3-9: Arrangement of Sampling Ports for OHM and EU Sampling Trains

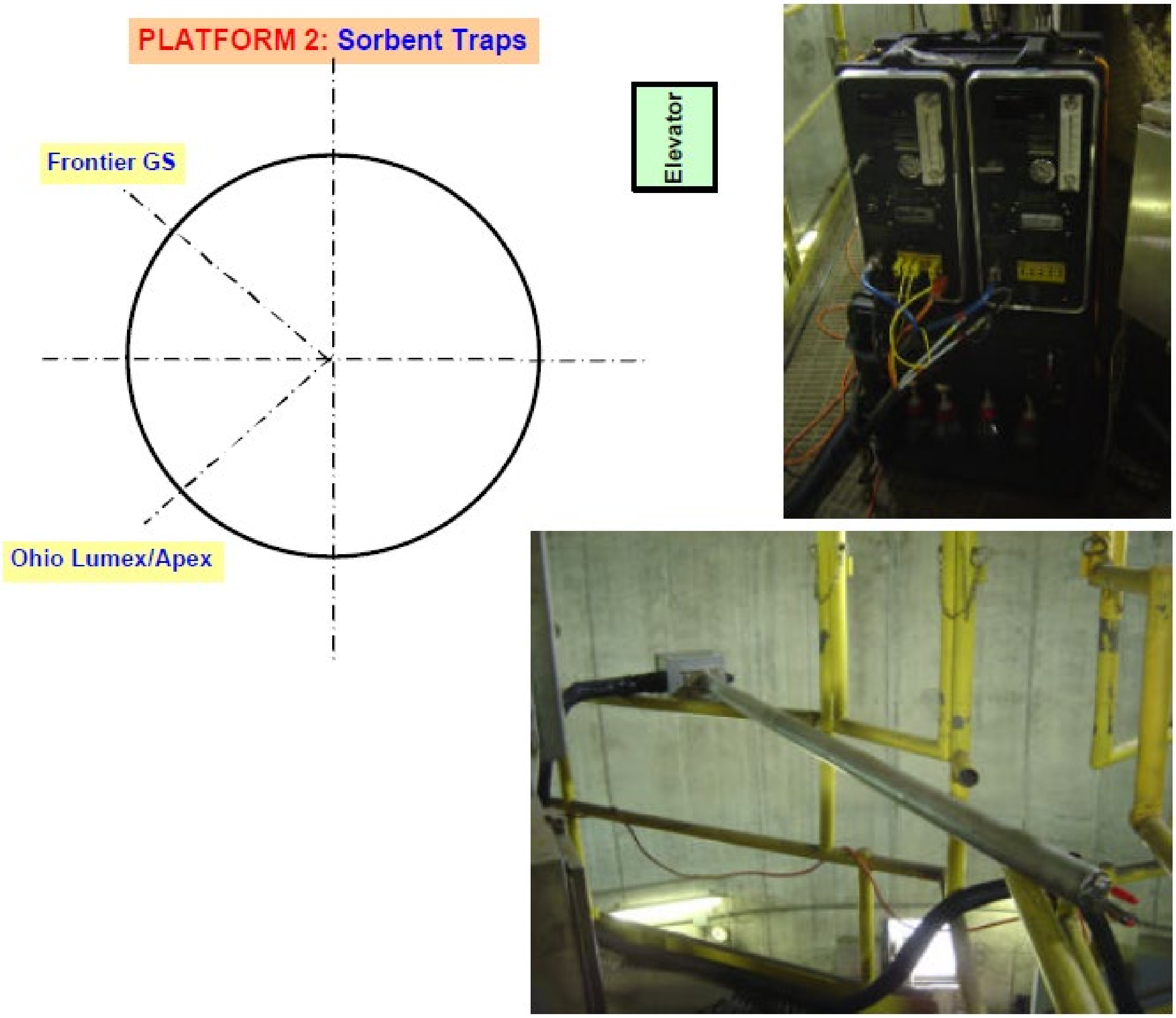


Figure 3 -10: Ohio Lumex/Apex Instruments and Frontier GeoScience Equipment for Hg Measurement According to Appendix K Sorbent Trap Method, Located on the 2nd CEM Platform

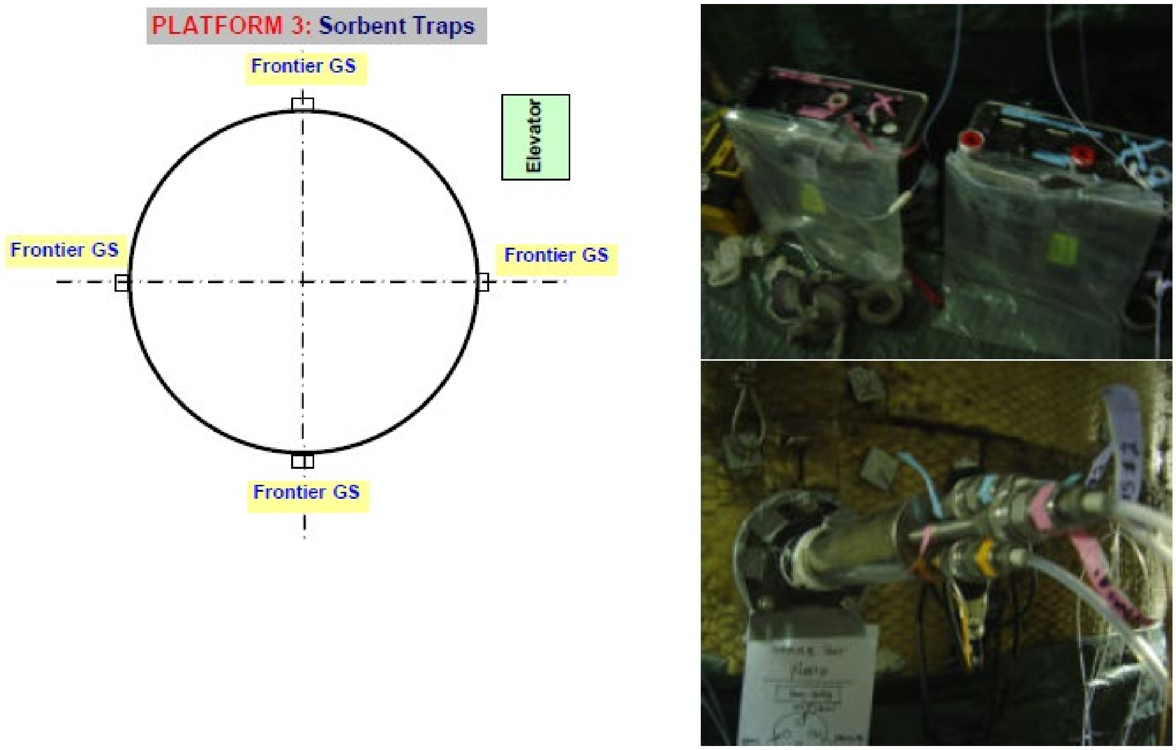


Figure 3-11: Frontier GeoScience Equipment for Hg Measurement According to Appendix K Sorbent Trap Method, Located on the 3rd CEM Platform

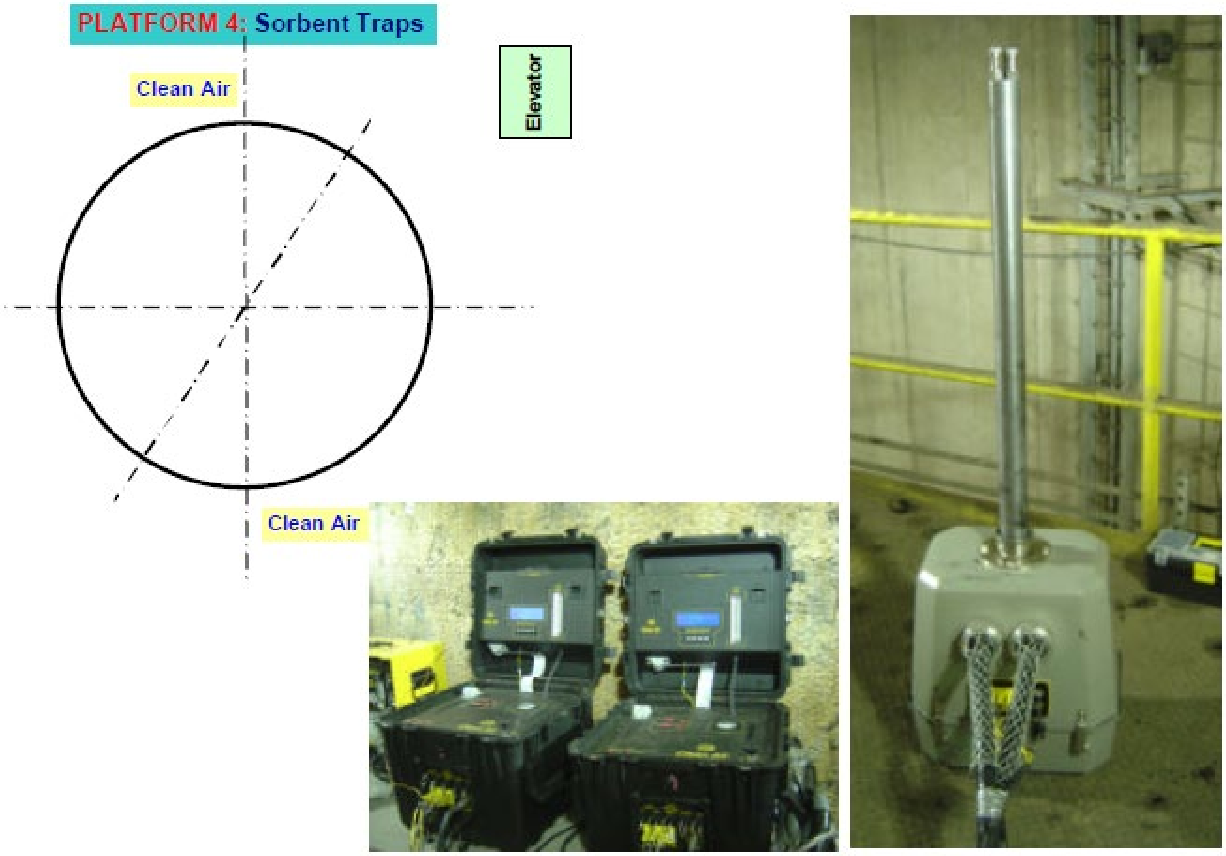


Figure 3-12: CleanAir/CONSOL Equipment for Hg Measurement According to Appendix K Sorbent Trap Method, Located on the 4th CEM Platform

As presented in Figure 3-11, most of the Frontier GeoScience equipment was located on the 3rd CEM Platform. Frontier used four sampling probes and four samplers to obtain mercury flue gas concentration measurements from four mutually perpendicular sampling ports. This measurement location was used to perform mercury stratification measurements, which were conducted by using sampling probes specially designed by Frontier for the Armstrong test.

The CleanAir/CONSOL equipment for Hg flue gas concentration measurement according to the sorbent trap method was located on the 4th, and hottest, CEM platform.

The average ambient temperature at the main CEM platform throughout the test was approximately 100°F. It increased by approximately 5°F per platform elevation, resulting in an ambient temperature at the 4th CEM platform of approximately 115°F. Despite high ambient temperature, sampling equipment was working properly and no electronics-related problems were encountered during the test.

3.4. CMM Commissioning, Installation and Calibration

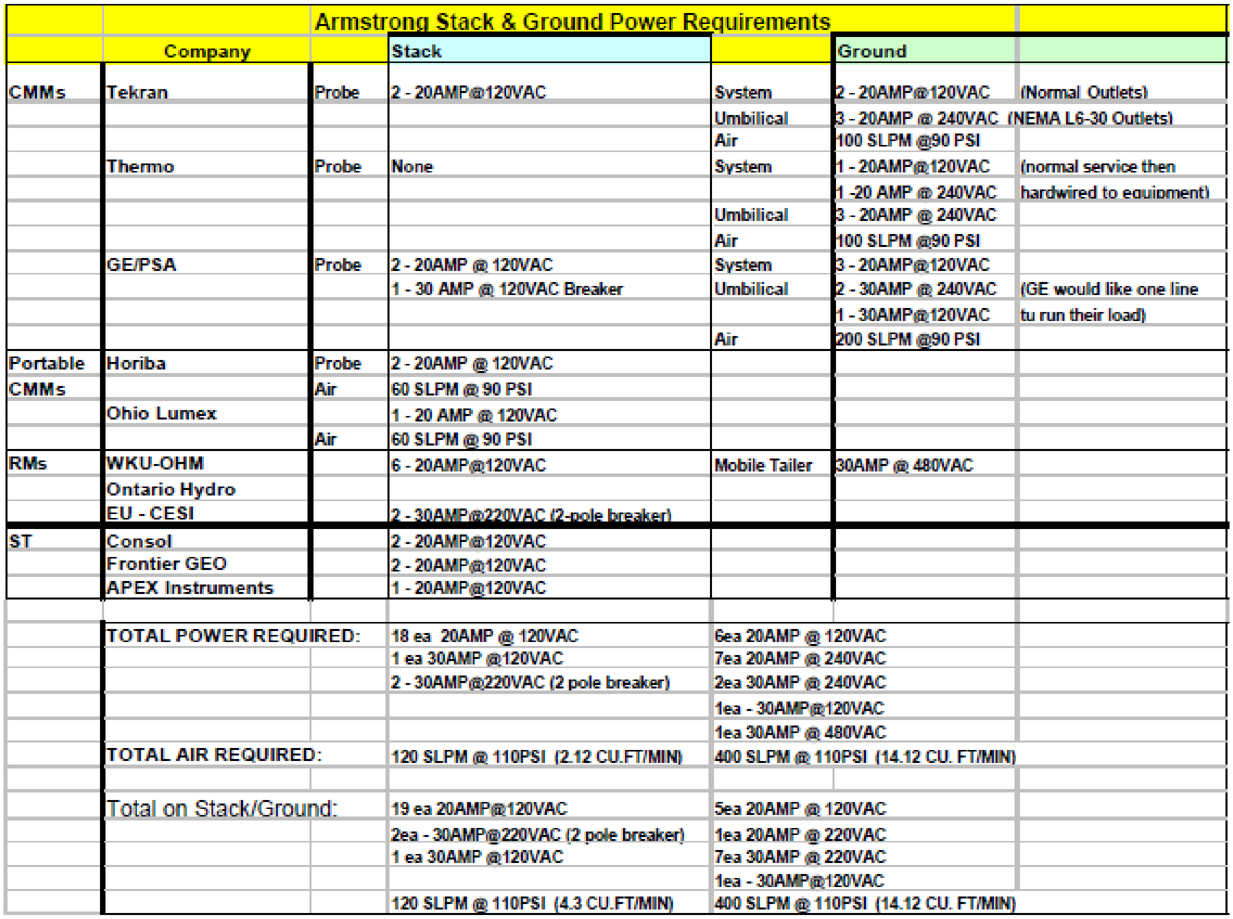
Mercury CMM commissioning, installation and calibration activities were organized and supervised by Mr. Mark Seibel and Allegheny Energy. The activities were divided into five phases:

1. Design
2. Procurement
3. Installation
4. Startup
5. Calibration and Testing

Mercury CMMs were ordered in early February for delivery in mid April. The initial plan was to locate all mercury CMMs in a shelter at the stack CEM platform. This was decided against for the following reasons: (a) difficulty in lifting shelters and mercury CMMs to a 350 ft high CEM platform, (b) the expense and difficulty of supplying required power, compressed air, and other utilities to the CEM platform elevation, (c) the need to test long umbilical lines (cords) for losses, installation difficulties, and response time, and (d) lack of space on the CEM platform.

Required electrical power and compressed air for the Armstrong project are presented in Table 3-2. The requirements are divided into stack and ground requirements, i.e., the power and compressed air required to operate equipment at the CEM platform and equipment on the ground, at the base of the stack. Power and compressed air requirements for individual mercury measurement systems are presented as well.

Table 3-2
Electrical Power and Compressed Air Requirements



		Armstrong Stack & Ground Power Requirements				
	Company		Stack		Ground	
CMMs	Tekran	Probe	2 - 20AMP@120VAC	System	2 - 20AMP@120VAC	(Normal Outlets)
				Umbilical	3 - 20AMP @ 240VAC (NEMA L6-30 Outlets)	
				Air	100 SLPM @90 PSI	
	Thermo	Probe	None	System	1 - 20AMP@120VAC	(normal service then
					1 -20 AMP @ 240VAC	hardwired to equipment)
				Umbilical	3 - 20AMP @ 240VAC	
				Air	100 SLPM @90 PSI	
	GE/PSA	Probe	2 - 20AMP @ 120VAC	System	3 - 20AMP@120VAC	
			1 - 30 AMP @ 120VAC Breaker	Umbilical	2 - 30AMP @ 240VAC	(GE would like one line
					1 - 30AMP@120VAC	tu run their load)
				Air	200 SLPM @90 PSI	
Portable	Horiba	Probe	2 - 20AMP @ 120VAC			
CMMs		Air	60 SLPM @ 90 PSI			
	Ohio Lumex		1 - 20 AMP @ 120VAC			
		Air	60 SLPM @ 90 PSI			
RMs	WKU-OHM		6 - 20AMP@120VAC	Mobile Tailer	30AMP @ 480VAC	
	Ontario Hydro					
	EU - CESI		2 - 30AMP@220VAC (2-pole breaker)			
ST	Consol		2 - 20AMP@120VAC			
	Frontier GEO		2 - 20AMP@120VAC			
	APEX Instruments		1 - 20AMP@120VAC			
	TOTAL POWER REQUIRED:		18 ea 20AMP @ 120VAC	6ea 20AMP @ 120VAC		
			1 ea 30AMP @120VAC	7ea 20AMP @ 240VAC		
			2 - 30AMP@220VAC (2 pole breaker)	2ea 30AMP @ 240VAC		
				1ea - 30AMP@120VAC		
				1ea 30AMP @ 480VAC		
	TOTAL AIR REQUIRED:		120 SLPM @ 110PSI (2.12 CU.FT/MIN)	400 SLPM @ 110PSI (14.12 CU. FT/MIN)		
	Total on Stack/Ground:		19 ea 20AMP@120VAC	5ea 20AMP @ 120VAC		
			2ea - 30AMP@220VAC (2 pole breaker)	1ea 20AMP @ 220VAC		
			1 ea 30AMP @120VAC	7ea 30AMP @ 220VAC		
				1ea - 30AMP@120VAC		
			120 SLPM @ 110PSI (4.3 CU.FT/MIN)	400 SLPM @ 110PSI (14.12 CU. FT/MIN)		

Initially $200,000 was budgeted for installation of mercury CEMs. The costs included:

- Two 8'x8'x8' CEM shelters at base of the stack (shelters were obtained from another Allegheny Energy station, which saved $45,000 in installation costs).
- Pulling and securing three 450 ft long umbilical lines (cords).
- Building, installing, and hooking up three power packs (two on the ground level, and one on the CEM platform).
- Running additional power lines to the CEM platform elevation and accessing existing service panels.
- Running instrument air to the CEM platform and CEM shelters and installing hookups for the air.
- Running water to the shelters and to the WKU mobile chemical laboratory trailer.
- Installing communication lines between the shelters and CEM platform, phone service lines, and data lines for the central DAS.

3.4.1. Heated Line Installation

Two 450 ft and one 400 ft heated umbilical lines were pulled for the Hg CMMs using a tugger and a heavy rope. Each umbilical was attached to a stranded steel cable using kellum grips. Two sock-type grips were installed on the pulling end of the umbilical line for extra support and one threaded type grip was installed every 25 ft. It is recommended the sock-type grips be used. Those should be prepared by compressing them with wire ties (this would save time and be stronger). There are different grades of kellums, the heavier grade is worth the additional costs.

Installation time for all three lines took one week, with four workers. This could have been shortened with better planning. It was debated weather lines could be run with flat spots or bellies. The general consensus was that with 180°C line heaters and a diluted sample it did not matter. Line heaters were terminated at the ground level. Because of the high power requirements new power packs were needed. The running amperage of each line was approximately 42 Amps @ 240VAC.

Umbilical line costs ranged from \$18,000 to \$36,000 for 450 ft long umbilical line. The cost was dependent on the line specifications and manufacturer. Three different line manufacturers were used at Armstrong. Lines made with extra insulation provided more stiffness and this made the pulling much easier. Installation cost was approximately \$20,000 for three lines. However, these were not permanent installations, which would cost 50-100 percent more. Installed umbilical lines are presented in Figure 3 - 13.

Figure 3-13: Installed Heated Umbilical Lines

3.4.2. CEM Shelters

Two CEM shelters were installed at the base of the stack as directly below the probes as possible, Figure 3-14, 3-15, and 3-16. An air line, water line and a 120VAC service panel were installed for each CEM. For two of the CMM systems, line heater connections were installed in the shelter; the third system was terminated outside. These line heaters were supplied with either two 30 Amp circuits or three 20 Amp circuits.

Two Hg CMMs were placed in one shelter, Thermo Electron and GE-PSA, while the second shelter housed the Tekran Hg CMM and Arcadis DAS communications setup. Gas cylinder racks were located on the outside of the shelters for Argon, Nitrogen and other gases used by the vendors for calibration and probe flow rates. The GE thermal converter was placed outside the CEM shelter, Figure 3-16.

Figure 3-14: CEM Shelters

Figure 3 -15: Thermo Electron and Tekran CMMs Located in CEM Shelters at Armstrong

Figure 3-16: GE/PSA CMM Analyzer Located in the CEM Shelter. Its Thermal Converter is Located Outside of the Shelter

3.4.3. Hg CMM Installation and Calibration

The installation schedule was as follows:

- One month for preparation, CEM shelter installation, getting bids and work specifications from contractors.
- Two weeks for umbilical lines, power, air and water installation.
- One week for the Hg CMM installation.
- 3–4 weeks for CEMS startup and calibration.
- 2 weeks for Instrument Reference Method checkout (pre-IRM activities).

Two of the Hg CMM systems (Tekran and Thermo Electron) were delivered on schedule, packaged for the plug-and-play startup. These were installed in one week. A third CMM system (GE/PSA) was delivered later and assembled on site.

Two semi-continuous Hg CEMs (Horiba and Ohio Lumex) were installed on the stack platform level. These were fairly simple installations because of the reduced amount and size of the equipment.

Problems encountered with the installations included difficulties with probe supports, incorrect probe internal parts, wiring in the shelters needing rerouting, and proper routing of the umbilical lines.

One Hg CMM system was brought on-line with no major problems, calibrated, and put into service. A second CMM system was started but could not be calibrated properly. It took four work days and a visit from a senior engineer to get the CMM started. After running for two days, the CMM system went down and it took another three days to get it back on-line. The majority of the problems with this CMM system were in the probe (improper flow rates, valves, etc).

The third CMM system (GE/PSA analytical) took several weeks to get started and was not properly calibrated and giving accurate readings until just before the testing started.

In conclusion, one CMM system had 5-week run time before the test began. A second CMM system had 3-week run time. Both systems passed calibrations consistently but not with good margins ; there was a good deal of drift with calibrations being off by 8% or more.

Overall, the startups went better than expected and the working quality of any of the systems was dependent on one common factor: the quality and level of training of the service person on site.

The two semi-continuous Hg CEMs (Horiba and Ohio Lumex) took a couple of weeks to get working properly, but systems calibrated well. The Horiba system became contaminated half way through the test and had to pull out. The Ohio Lumex system performed accurately, especially as a potential reference method system.

3.4.4. Sorbent Trap System Installation, Startup, and Calibration

Three sorbent trap (Appendix K) sampling systems were installed: Frontier GeoScience, CleanAir/CONSOL, and Ohio Lumex/Apex Instruments. Frontier GeoScience system used two two-point dual trains. A specially designed four-point dual sampling train system was used for Hg stratification testing.

Sorbent trap system installations were very simple, with the longest taking less than one day to set up and prepare for sampling . No major problems occurred during the test. The worst problem encountered was caused by a probe which had a burr on the end causing breakage of two sample traps.

4. METHODS AND INSTRUMENTATION

4.1. U.S. Reference Methods

The following U.S. reference methods were used at Armstrong:

Mercury: Ontario Hydro, ASTM D6784-02 -- Standard Test Method for Elemental, Oxidized Particle-bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources. Paired OHM trains were used.

Heavy Metals: EPA Method 29. The measured metals included Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr),Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel, (Ni), Phosphorus (P), Selenium (Se), Silver (Ag), Thallium (Tl), and Zinc (Zn).

PM 2.5 and PM10: EPA Method 5B.

4.1.1. Ontario Hydro Method (ASTM D6784-02)

The Ontario Hydro method (OHM) was developed by Dr. Keith Curtis and other researchers at Ontario Hydro Technologies, Toronto, Ontario, Canada, in late 1994 from an old VDI method for heavy metals. The OHM has been developed specifically for the measurement of total and speciated mercury emissions from coal-fired combustion sources. The OHM was initially developed to support EPA's information collection request to characterize and inventory mercury emissions from the nation's coal-fired power plants. (The Hg emission data collected for the Part III EPA Information Collection Request (ICR) were measured using the OHM.). This method was ultimately submitted to the American Society for Testing and Materials (ASTM) and, following several revisions, is now finalized as an ASTM standard test method (ASTM Method D 6784-02).

Since its acceptance as an ASTM test method, the method has been used by EPA and other research organizations as both a research and potential compliance tool. OHM has been adopted by EPA as a reference method for total mercury in the recently proposed regulatory actions for the utility industry [1].

Figure 4-1 shows a diagram of a sampling train used for the OHM. Generally, all sampling trains consist of the same sampling components: a nozzle and probe operated isokinetically for extracting a representative sample from the stack or duct, a filter to collect particulate matter, and a liquid solution(s) and/or reagent(s) to capture gas-phase Hg. The impinger box and reagents are presented in Figure 4-2. Sampling train components are also presented in Table 4-1. After sampling, the filter and sorption media are prepared and analyzed for Hg in a laboratory.

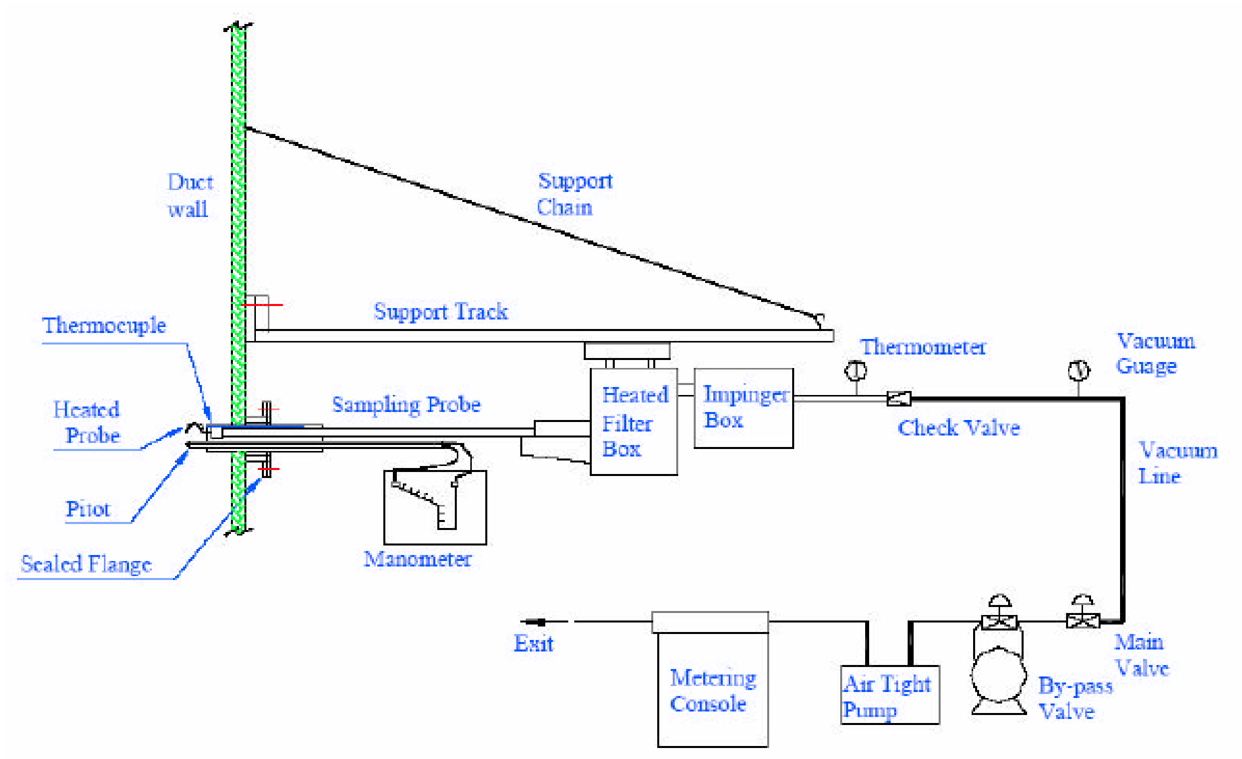


Figure 4-1: Diagram of the OHM Sampling Train

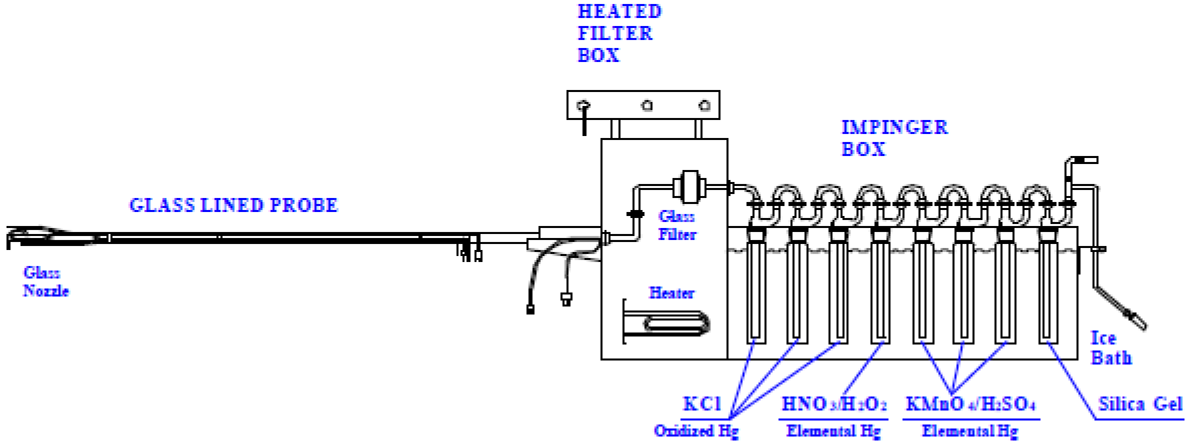
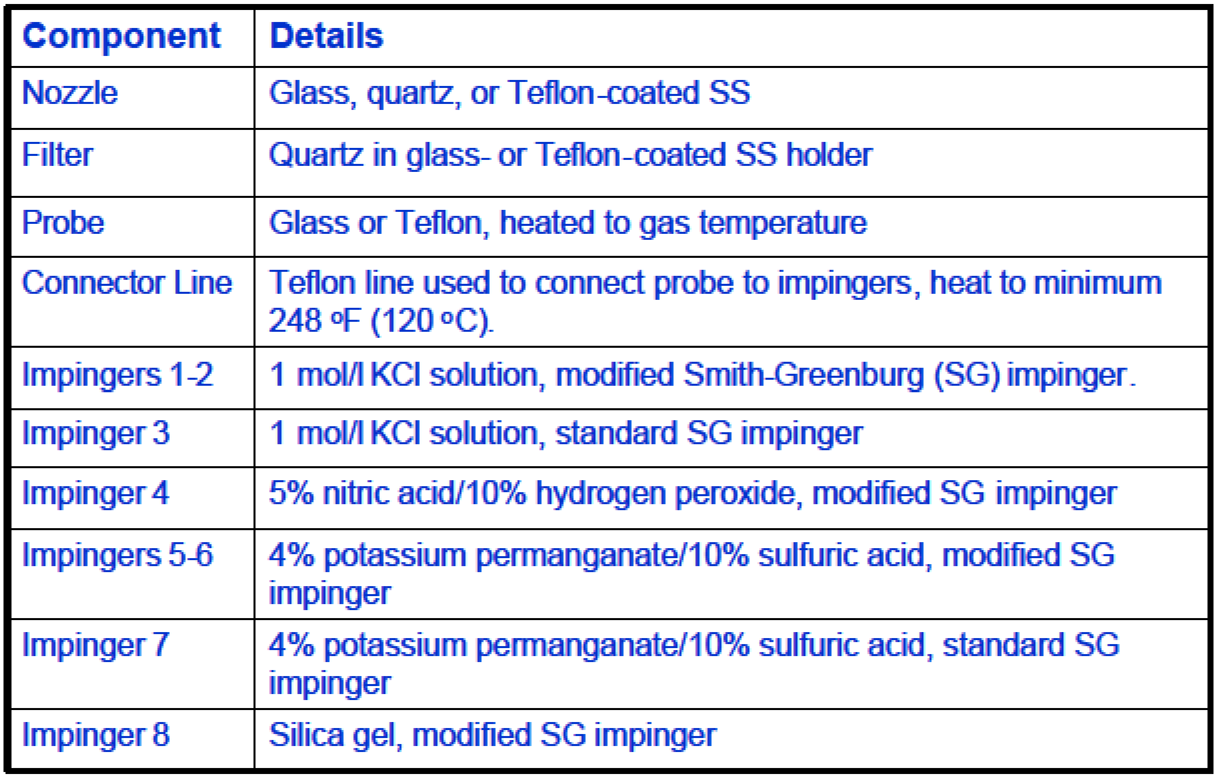


Figure 4-2: Impinger Box and Reagents

Table 4-1 Components of the OHM Sampling Train



Component	Details
Nozzle	Glass, quartz, or Teflon-coated SS
Filter	Quartz in glass- or Teflon-coated SS holder
Probe	Glass or Teflon, heated to gas temperature
Connector Line	Teflon line used to connect probe to impingers, heat to minimum 248 ^{o}F (120 ^{o}C).
Impingers 1-2	1 mol/l KCl solution, modified Smith-Greenburg (SG) impinger.
Impinger 3	1 mol/l KCl solution, standard SG impinger
Impinger 4	5% nitric acid/10% hydrogen peroxide, modified SG impinger
Impingers 5-6	4% potassium permanganate/10% sulfuric acid, modified SG impinger
Impinger 7	4% potassium permanganate/10% sulfuric acid, standard SG impinger
Impinger 8	Silica gel, modified SG impinger

Measurement of total Hg is based on the concept that all forms of gaseous Hg can be captured with a strong oxidizing solution, such as potassium permanganate. The speciation is accomplished relying on the solubility and insolubility of the gaseous oxidized and elemental Hg species. The oxidized (Hg2+) form is considered to be readily soluble in aqueous solutions, while elemental Hg (Hg0) is essentially insoluble. To speciate gaseous Hg into the oxidized and elemental forms, multiple solutions/reagents are used. When the aqueous solutions are positioned immediately after the filter, the Hg2+ is captured and the Hg0 passes through to the oxidizing solution where it is then captured. These solutions are analyzed separately to determine the distribution of oxidized and elemental Hg within the sampling train. Experimental data support application of OHM to concentrations < 0.1 µg/Nm3, [1]

The OHM was thoroughly evaluated by the University of North Dakota as part of their research to develop and validate a speciating manual method suitable for characterization of Hg emissions from coal-fired combustion sources. Both pilot-scale and field Method 301 studies were conducted that validated the OHM for total Hg measurements. The OHM is now finalized as an ASTM standard test method, which states that the method is applicable for sampling elemental, oxidized, and particlebound Hg at the inlet and outlet of emission control devices and is suitable for measuring Hg concentrations ranging from approximately 0.5 to 100 µg/Nm3, [1]. The lower detection limit is set by the amount of reagents present in the impingers and a sample volume.

Although the ASMT method estimates the lower limit of OHM application to be approximately 0.5 µg/Nm3, laboratory testing indicates that, from an analytical perspective, Hg emissions that are ten times lower can be reliably quantified, [1].

4.1.1.1. Factors Affecting Speciation. High particulate matter (PM) concentration can bias speciation, primarily by over-reporting the level of the oxidized Hg species. The PM may posses catalytic properties whereby, at the conditions of PM filtering environments, elemental mercury can be oxidized across the PM surface. This is not an issue from a total Hg measurement standpoint. However, it may have major implications when measuring Hg in gas streams possessing high PM loadings. This bias is minimized in low PM loading gas streams, corresponding to Hg measurements downstream of the PM control equipment.

When sampling takes place upstream of PM control equipment, the sampling train filter has the potential to collect a high loading of fly ash. The speciated Hg measurement can be biased two ways. The fly ash on the filter can adsorb gaseous Hg from the flue gas as it passes through the filter. Reactive fly ashes can also oxidize gaseous Hg0 entering the filter. When adsorption and/or oxidation occur across the filter, they alter the distribution of total Hg or gaseous Hg measured. For example, if particles on the filter adsorb gaseous Hg, the filter will contain a greater amount of Hgp than if no adsorption had taken place; in this case, the method will overestimate the amount of Hgp in the flue gas and underestimate the gaseous Hg; thus, the total distribution of Hg will be altered. Alternatively, fly ash on the filter can oxidize gaseous Hg0 to Hg2+ (without adsorption) overestimating the amount of Hg2+ in the flue gas. Thus, the distribution of gaseous Hg will be altered. The rates of these transformations are dependent on the properties of the coal and resulting fly ash, the amount of fly ash, the temperature, the flue gas composition, and the sampling duration. As a result, the magnitude of these biases varies significantly and cannot be uniformly assessed. It is for this reason that ICR measurements performed at the inlet of PM control systems possess a large degree of uncertainty. Due to low PM loading at Armstrong, mercury measurements at that site were not affected by potential adsorption and/or oxidation of Hg on the sampling train filter.

Another potentially significant source of speciated Hg measurement bias takes place in the liquid phase. In combustion gases where chlorine gas (Cl2) is present, under certain conditions the Cl2 may react in the liquid phase to oxidize Hg0. Fundamental laboratory experiments determined that the hypochlorite ion (OCl-), formed during the dissociation of Cl2 in aqueous solutions, oxidizes Hg0 to soluble Hg2+. These same experiments also determined that that this problem can be mitigated by the addition of sodium thiosulfate (Na2S2O3) to selectively react with the OCl- ion. The presence of sulfur dioxide (SO2) in the combustion gas stream was determined to also mitigate this bias in a similar manner. As a result, this speciation bias is not likely to be a factor for coal combustion applications. However, the speciation bias may be factor in combustion measurement environments where Cl2 is present without sufficient levels of SO2, [1].

Measurement Precision

The precision of the OHM is a critical parameter. According to Reference 2, based on the results of validation testing, performed by EERC, the relative standard deviation (RSD) for gaseous elemental mercury and oxidized mercury was found to be less than 11 percent for mercury concentrations greater than 3 μg/Nm3 and less than 34 percent for mercury concentrations less than 3 μg/Nm3. These values are within the acceptable range, based on the criteria established in EPA Method 301 (% RDS less than 50 percent).

The OHM precision data, collected from various reports on pilot-scale and field measurement of Hg by the OHM available in the open literature and provided by EPRI, is presented in Figure 4-3 as a function of measured Hg concentration. For the most part, the data support EERC conclusions. For some test data, precision is lower, i.e., RSD is higher (close to 15 percent). From the test data, it can be concluded that measurement precision for the low, predominantly elemental, mercury concentrations is approximately three times higher compared to the RSD values for total Hg measurement.

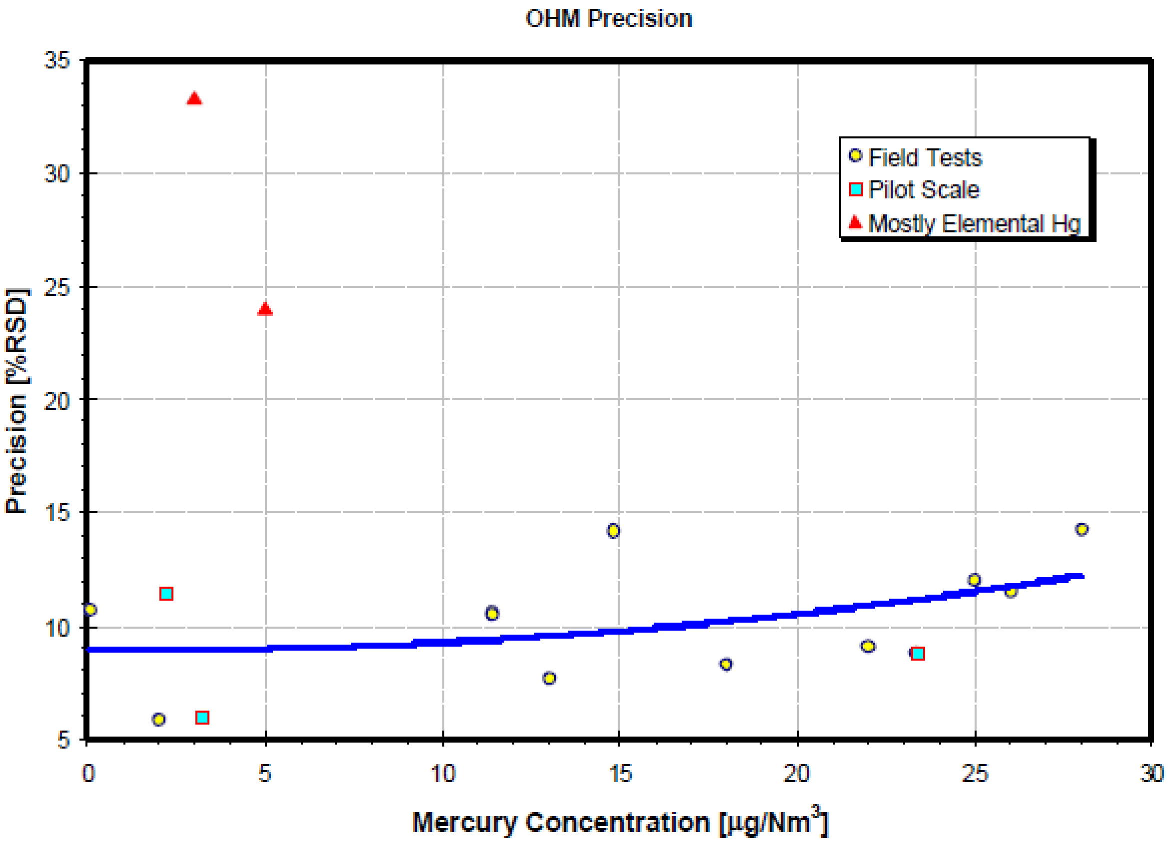


Figure 4-3: OHM Precision Versus Mercury Concentration

The precision of particle-bound, oxidized, and elemental mercury sampling method data is influenced by many factors: flue gas concentration, source, procedural and equipment variables. Strict adherence to the method is necessary to reduce the effect of these variables.

To ensure precise results are achieved, it is necessary that the system be leakfree; all indicated system components accurately calibrated; proper sampling locations selected; glassware thoroughly cleaned; and prescribed sample recovery, preparation, and analysis procedures followed.

Some of the practical limitations of the impinger-based sampling methods originate from the problems and difficulties of using complex sample trains that are composed of relatively large amounts of glassware and tubing in the field. In addition, the glass impingers contain strong oxidizing and acidic reagents which require complex sample recovery and analytical procedures.

Leakage Check

For each OHM test, a series of sampling system leakage checks were performed, including pre-test, during test and post-test leak checks.

According to EPA requirements, the pre-test and post-test leakage checks performed at the beginning and end of each OHM test followed these procedures.

1. Assemble the sampling train, including connecting the probe, console meter, vacuum pump, and impinger set (box), Figure 4 -2.
2. Balance the console meter to ensure the ?H and ?P indicators are both on 0 mm water position.
3. Introduce suction (?H) by turning on the vacuum pump. The ?H was adjusted to 15 mm water.
4. Seal the probe tip opening to see if the ?H indicator decreases back to 0 mm water, and check if the impingers stop bubbling (pre-test leakage check).
5. After desired sampling volume is reached, record the final sample gas volume and pull out the entire sampling system while the vacuum pump is still on.
6. Seal the probe tip opening again to see if the ?H indicator decreases back to 0 mm water, and check if the impingers stop bubbling (post-test leakage check).

Sample Recovery

The impinger samples were recovered into pre-cleaned glass bottles with vented Teflon-lined lids. The following sample fractions were recovered (specific rinse solutions are contained in the method):

1. The sample filter
2. The front half rinse (includes all surfaces upstream of the filter)
3. Impingers 1 through 3 (KCl impingers) and rinses
4. Impinger 4 (HNO3/H2O2 impinger) and rinses
5. Impingers 5 through 7 (KMnO4/H2SO4 impingers) and rinses

6. Impinger 8 (silica gel impinger). Note this sample is weighed for moisture determination and is not included in the mercury analysis.

Sample Preparation and Analysis

The sample fractions were prepared and analyzed as specified in the method, and are summarized below:

Ash Sample (Containers 1 and 2) – The particulate catch was analyzed using EPA Method 7043 or equivalent. If the particulate catch was less than 1 gram (as would be the case at most particulate control device outlet locations), the entire sample of the particulate collected on the filter (including the filter) was subsequently digested using EPA Method 3051, followed by analysis using EPA 7471A.

KCl Impingers (Container 3) – The impingers were prepared using H2SO4, HNO3, and KMnO4 solutions as specified in the method.

HNO3–H2O2 (Container 4) – The impinger solution was prepared using HCl and KMnO4 solutions as specified in the method.

H2SO4–KMnO4 Impingers (Container 5) – The impinger solution was prepared using hydroxylamine hydrochloride as specified in the method, see Figure 4-4

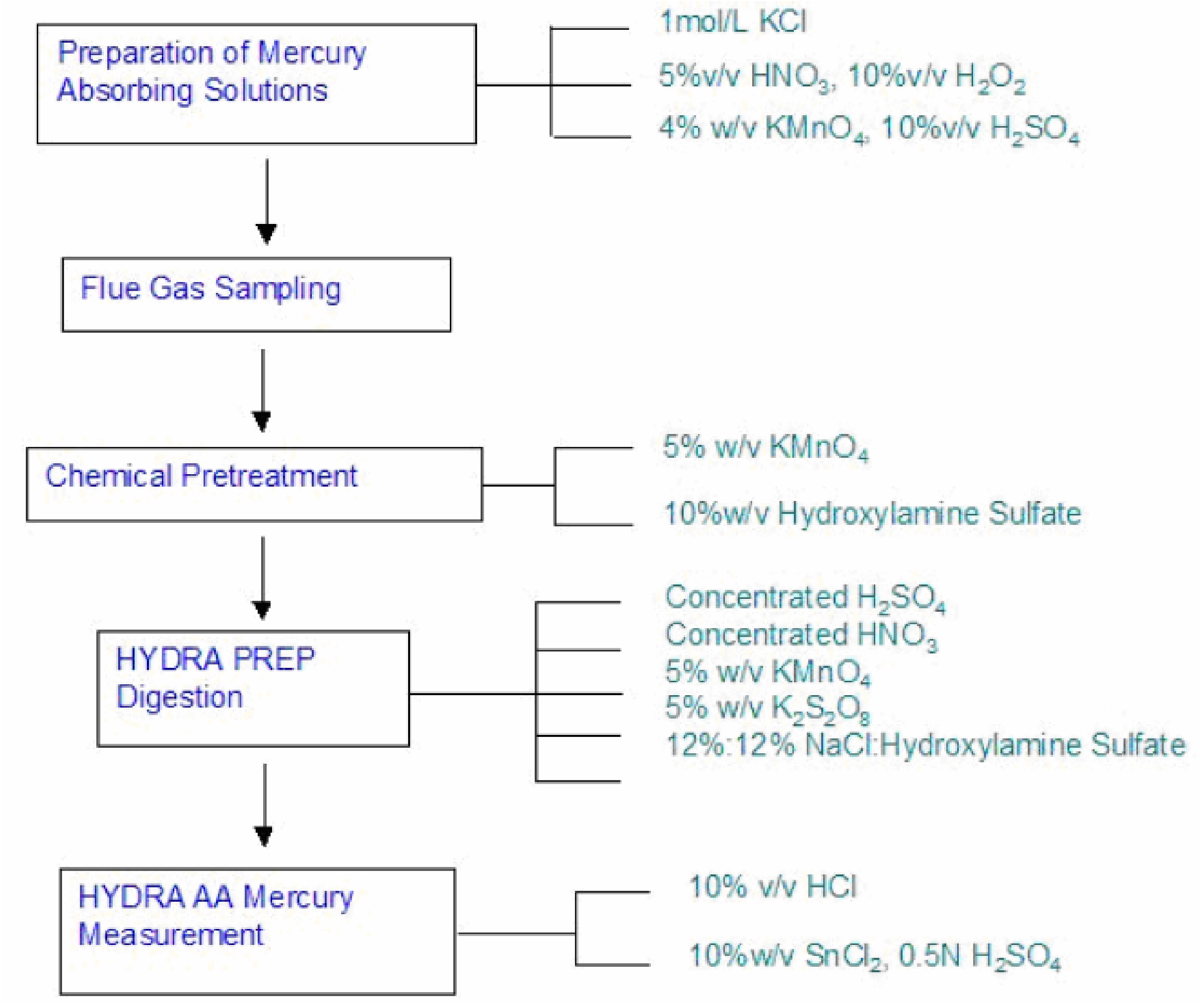


Figure 4-4: Sample Collection and RecoveryFlow Chart

Each prepared fraction was analyzed for total mercury by cold-vapor atomic absorption (CVAAS). CVAAS is a method that is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from the solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Mercury concentration is proportional to the indicated absorbance. A soda-lime trap and a magnesium perchlorate trap was used to precondition the gas before it entered the absorption cell.

The filter media consisted of quartz fiber filters. The filter holder was glass or Teflon-coated. A heated Teflon line may have been used, depending upon site-specific access limitations. An approximate 2-hour sampling time was used, with a target sample volume of 1 to 2.5 standard cubic meters.

Leeman Mercury Analyzer

The Leeman Hydra Prep was employed to replace manual solution digestion in the OHM method (Figure 4-5). After solution preparation, 4-ml aliquots of the KCl, H2O2/HNO3, and KMnO4/H2SO4 solutions used for absorbing mercury species were transferred to 15-ml digestion cups, in which 0.2 ml concentrated H2SO4, 0.1 ml concentrated HNO3, 1.2 ml 5% KMnO4, and 0.32 ml of 5% K2S2O8 were automatically added to each cup through a dispenser installed on the autosampler. The cups were set at 95°C in a water bath for two hours. After cooling, 1.333 ml of 12% NaCl hydroxylamine sulfate was added. The digested samples were then moved to the Leeman Hydra Atomic Absorption (AA) for mercury determination. Determination of mercury by the Leeman Hydra AA instrument is based upon cold vapor atomic absorption spectrometry. In the Armstrong test, 5% HNO3 was employed as the rinse solution, and 10% SnCl2:10% HCl was utilized as the reductant solution. The pump rate was controlled to be 5 ml/min, while the carrier gas was ultra high purity grade nitrogen flowing at a rate of 0.6 LPM.

Figure 4-5: Leeman AA Mercury Analyzer

Quality Control

The quality control measures are described in detail in the Ontario Hydro Method (OHM) procedures. The OHM prescribes rigorous quality control measures. Quality control for OHM starts at the beginning of the procedure. Only ACS reagent grade or ACS certified chemicals are used in the sampling solutions, reagents, and even the wash solutions. Every day, blanks are taken of the sampling solutions. Additionally, three more blanks are taken with every run: a 0.1 NHNO3 blank, a hydroxylamine solution blank, and a filter blank. A field blank is collected for every series of samples run by setting up the impinger train and letting it sit in the sampling location for the normal sampling period. OHM also outlines quality control for sample measurement. Every collected sample is analyzed twice with every tenth sample is analyzed in triplicate. The measurements of the samples must be within 10% of each other. Every eleventh sample analyzed shall be a standard. If the measured value for the standard is incorrect, then the instrument shall be recalibrated and the previous ten samples shall be analyzed again.

The paired reference method samples are required to be within 10% of the relative standard deviation of the results.

$RD = |Ca - Cb|/(Ca + Cb) \times 100\% < 10\%$

OHM Sampling at Armstrong

According to EPA Part 75 relative accuracy test audit (RATA) criteria, the OHM sampling has to be performed in paired trains, Figure 4-6. Speciated mercury samples were collected from sampling ports located at the CEM elevation at Armstrong Generating Station. Two sets of field blanks and reagent blanks were taken at each location and analyzed for QA/QC purposes. EPA Method 17 for isokinetic sampling was followed. Each impinger train was weighed before and after sampling to determine flue gas moisture.

Figure 4-6: Paired OHM Sampling Train at Armstrong

Due to space constraints on the Armstrong CEM platform and heating requirements for the OHM sampling, frequent removal of the 10 ft paired-train sampling probes in and out of the sampling ports was not practical. Therefore, modified leakage checks were performed. The sampling probes were inserted into the stack and heated to the required sampling temperature first. Instead of sealing the probe tip, the leakage check was carried out at the end of the sampling probe, starting from the opening of heated sample transport line. After the leak check, the heated line was then connected with the sampling probe, Figures 4-7 and 4-8.

The OHM is based on isokinetic sample extraction. To maintain isokinetic sampling rate, an operator is needed to make manual adjustments, Figure 4-9. Since it takes approximately 2 hours to collect sufficient sample volume, the OHM is manpower intensive and an expensive mercury measurement method.

Flue gas oxygen concentration was closely monitored (every 5 minutes) to ensure the leak-free sampling condition throughout the entire testing period (during test leakage check). The oxygen concentrations were measured to be around the 8 percent level throughout the entire test.

Figure 4-7: Impinger Boxes for Paired OHM Sampling Train

Figure 4-8: Leakage Check

Figure 4-9: Manual Adjustments to Maintain Isokinetic Sampling

Collected samples were analyzed on-site using the WKU mobile chemical laboratory, Figure 4-10.

Figure 4-10: WKU Mobile Chemical Laboratory

WKU's 53-foot mobile lab is one of the five laboratories including Philips, EERC, Consol, and Test America in North America capable of conducting continuous emission monitoring (CEM) and the Ontario-Hydro Method (OHM) for mercury emissions in power plants

4.1.2. EPA Method 29

EPA Method 29, also known as the multiple metals stack emission measurement method, was developed for measuring the solid particulate and gaseous emissions of mercury and 16 other trace elements (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, phosphorus, selenium, silver, thallium, and zinc). A schematic of the EPA Method 29 sampling train is presented in Figure 4-11.

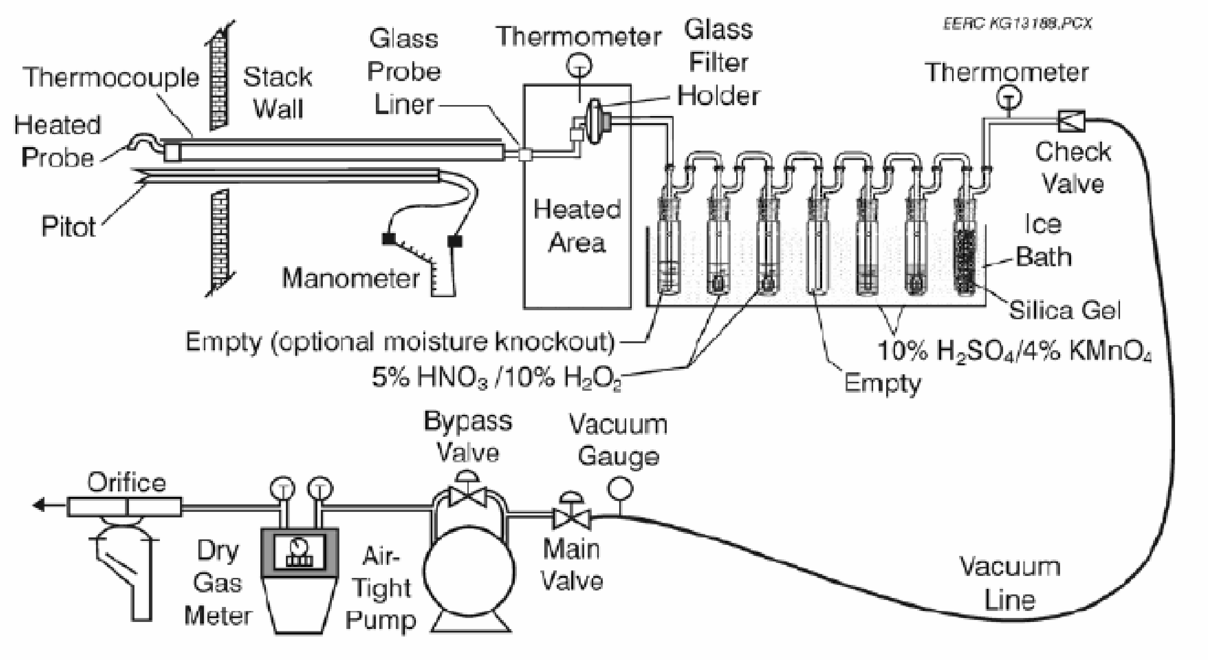


Figure 4-11: A Schematic of the EPA Method 29 Sampling Train

The EPA Method 29 sampling train consists of seven impingers. Following an optional moisture knockout impinger, gaseous mercury species are collected in two pairs of impingers connected in series containing different absorption solutions. A portion of the gaseous mercury is captured in the first pair of impingers containing aqueous solutions of 5% nitric acid (HNO3) and 10% hydrogen peroxide (H2O2), while the remainder is captured in a second pair of impingers containing aqueous solutions of 41 4% potassium permanganate (KMnO4) and 10% sulfuric acid (H2SO4). An empty impinger is located between the two sets of impingers to reduce the potential for blowback of KMnO4 into the second HNO3-H2O2 impinger during leak checks. The last impinger in both sampling trains contains silica gel to prevent contamination and entrap moisture that may otherwise travel downstream and damage the dry-gas meter and pump.

Although the EPA Method 29 sampling train was not originally designed for mercury speciation analysis, various research groups looked at the possibility of using the method for mercury speciation. Researchers surmised from the physical and chemical properties of mercury species that Hg2+ and Hg0 would be selectively absorbed in the separate acidified hydrogen peroxide (HNO3-H2O2) and acidified permanganate (H2SO4-KMnO4) solutions, respectively, used in the EPA Method 29 impinger train. However, investigation proved these assumptions are incorrect. Data from the validation tests indicated that the two different impinger solutions employed were not effective for reliably separating the Hg2+ and Hg0 forms in a chemically complex flue gas [2]. As a consequence, several groups proposed modifications to the impinger solutions used in EPA Method 29. Those included Ontario Hydro, tris buffer, and RTI methods.

EPA Method 29 was used at Armstrong to measure heavy metals concentration in flue gas.

4.1.3. EPA Method 5B: Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources

As a part of the test matrix at Armstrong, PM emissions were measured using EPA Method 5B.

Method 5B uses the Method 5 sampling train at 160°C (320°F) (Figure 4-12). This volatilizes any condensed sulfuric acid that may have been collected. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ± 14°C (320 ± 25°F). The collected sample is then heated in an oven at 160°C (320°F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

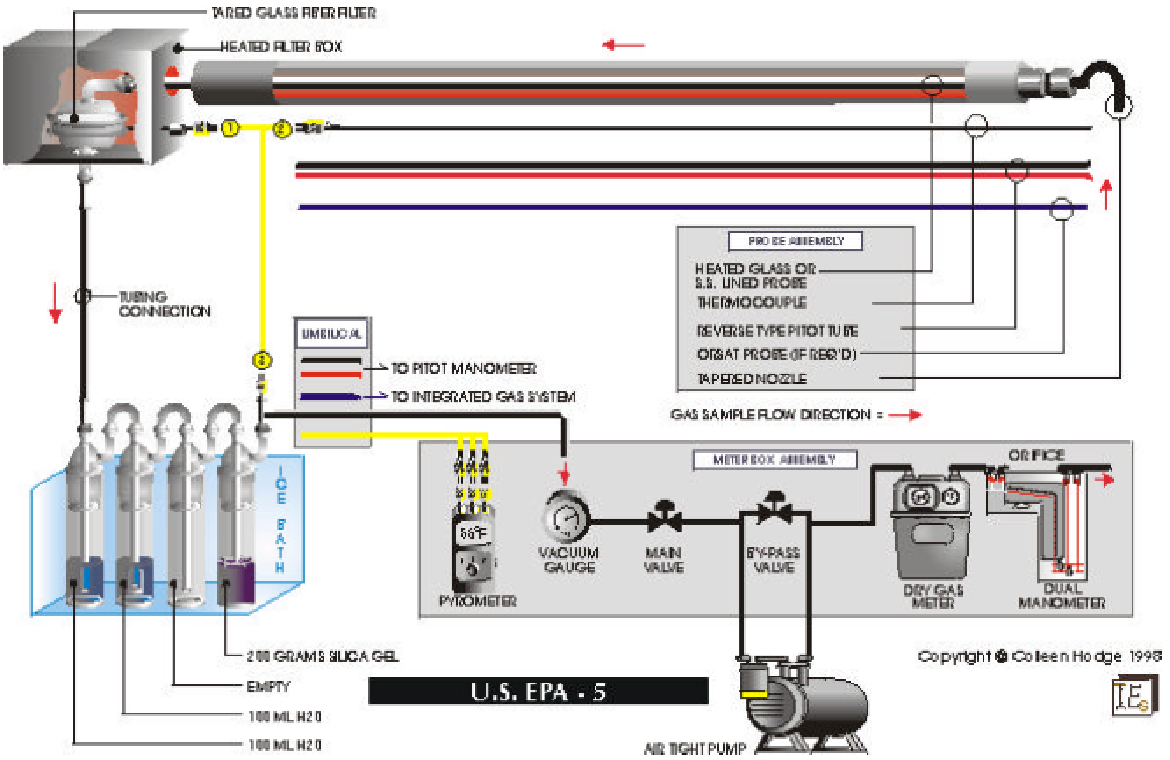


Figure 4-12: A Schematic of EPA Method 5B Sampling Train

4.2. EU Reference Methods

The following EU reference methods were used at Armstrong:

Mercury: EN-1321 for Total Mercury

Heavy Metals: EN-14385-Flux-Derived

PM 2.5 and PM10: VDI-Richtlinien 2066 (Impaction Method)

4.2.1. EN-13211 Manual Method for Total Mercury This European standard specifies a manual reference method for determination of the mass concentration of mercury in the flue gas in power plant stacks. Similar to the U.S. reference methods, sample flue gas stream is extracted isokinetically from a stack over a certain period of time with a controlled flow and known volume. Particulate matter in the sampled gas stream is collected on a filter. The particle -free flue gas stream passes through a series of impingers (absorbers), which contain solution(s) for collecting gas phase mercury. At the end of sampling period, the filter and impinger solutions are analyzed in a laboratory.

Although mercury is mainly present in the gaseous form, in can also be found in the dust phase as well as in droplets which are present in the flue gas stream downstream of the wet scrubbers.

The sampling equipment consists of a heated probe and sampling nozzle made of titanium, a filter housing for the filter, a series of impingers, a suction unit with gas metering device and a flow controller. Depending on the type of impingers used, two different sampling arrangements may be employed: main stream and side stream. In the main stream arrangement, Figure 4-13, all sampled flue gas flows through the impingers, in the side stream arrangement, Figure 4-14, only a part of the flue gas is passed through the impingers. Depending on the arrangement, one or two suction units may be used.

Two impingers, placed in the serial arrangements, are used. An empty impinger is placed downstream of the first two to serve as a liquid trap and for the protection of the downstream equipment. The sampling train should be leak tested before each sampling by sealing and starting the suction unit(s).

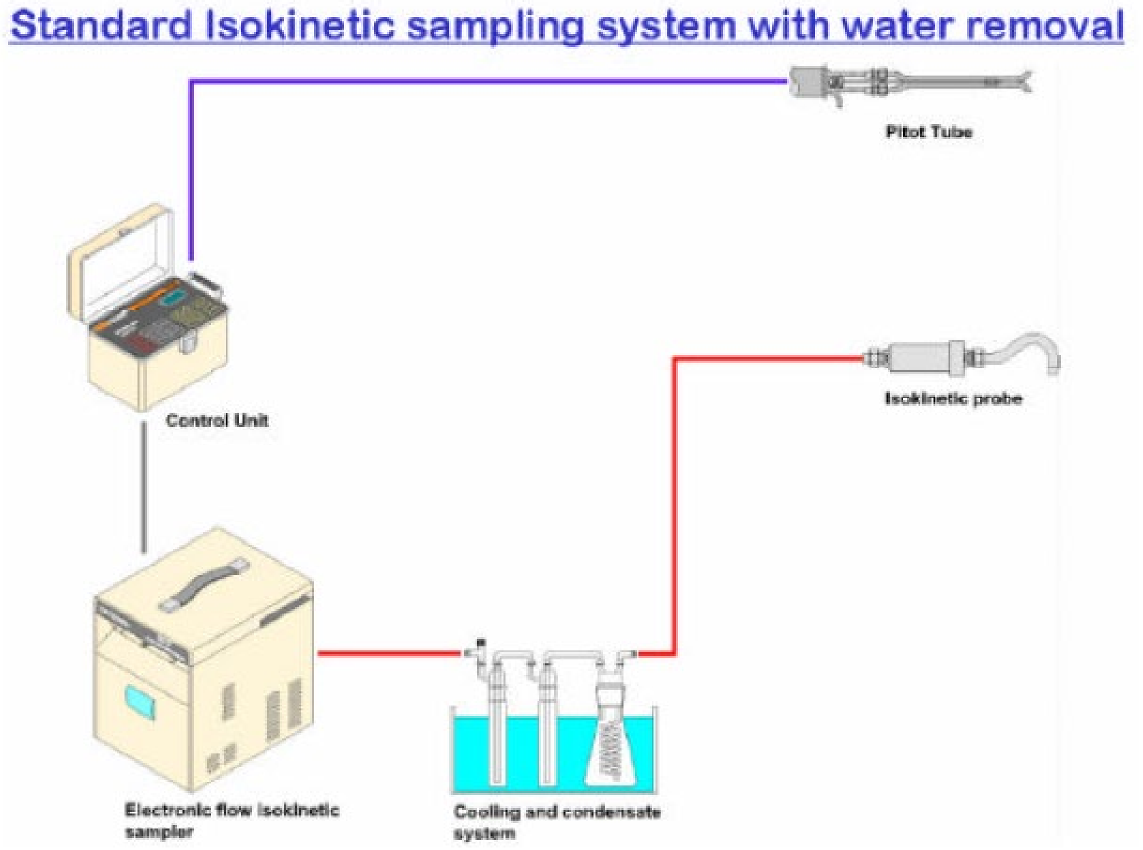


Figure 4-13: A Schematic of the EU Sampling Train: Main Stream Arrangement

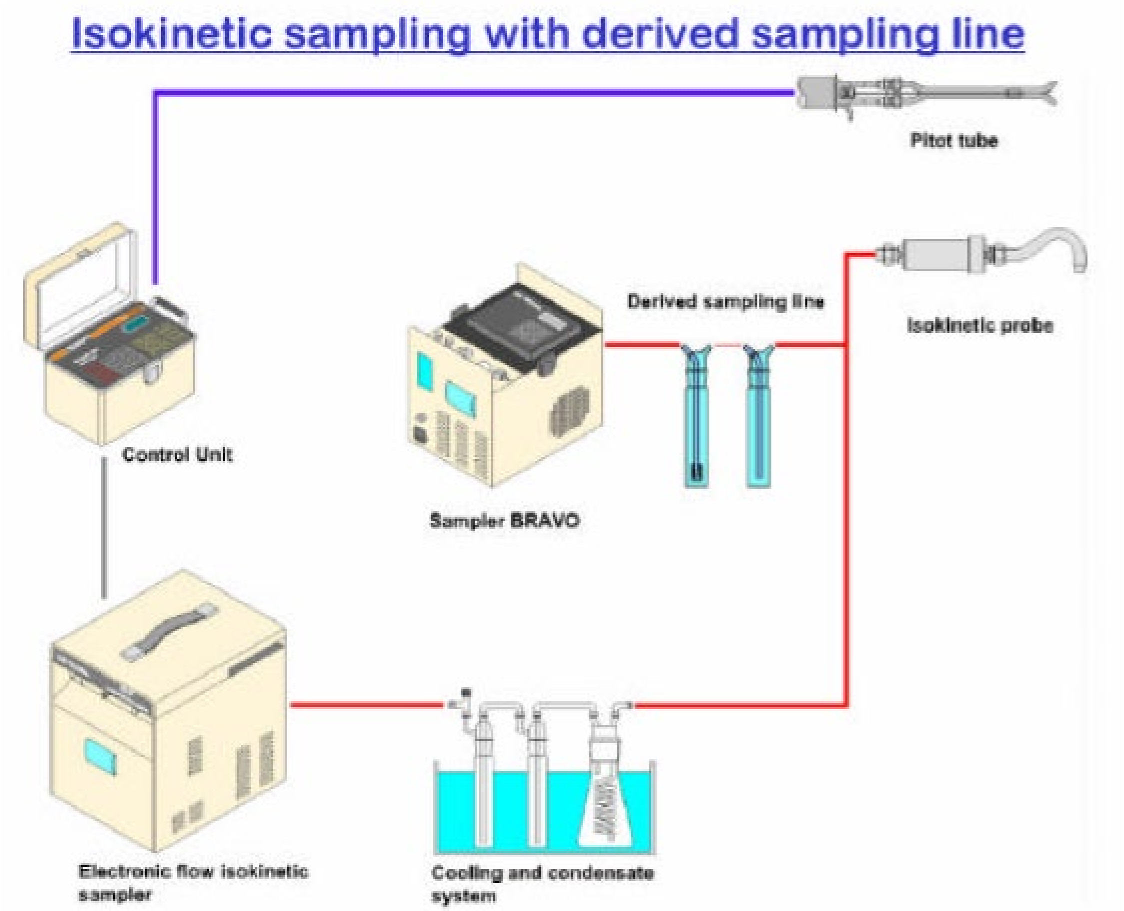


Figure 4-14: A Schematic of the EU Sampling Train: Side Stream (derived sampling line) Arrangement

Impinger solutions may include Potassium permanganate-sulfuric acid (2% m/m KMnO4 -10% m/m H2SO4), or Potassium dichromate – nitric acid (4% m/m K2Cr2O7 – 20% m/m HNO3).

The low detection limit of EN-13211 is 0.11 mg/Nm3 for the average blank concentration of 0.05 mg/Nm3 and sampled flue gas volume of 0.05 m3. The repeatability (precision) of the measurement is ± 30% for mercury concentration in the 4-10 mg/Nm3 range. For mercury concentration in the 40-100 mg/Nm3 range, repeatability is ± 18%.

Schematic of the integrated heated titanium sampling probe is presented in Figure 4-15. The photograph of the nozzle and filter housing is given in Figure 4-16. The probe, inserted in a sampling port at Armstrong is presented in Figure 4-17. The probe is equipped with a guiding sleeve. One of the two EU sampling trains used at Armstrong is presented in Figure 4-18.

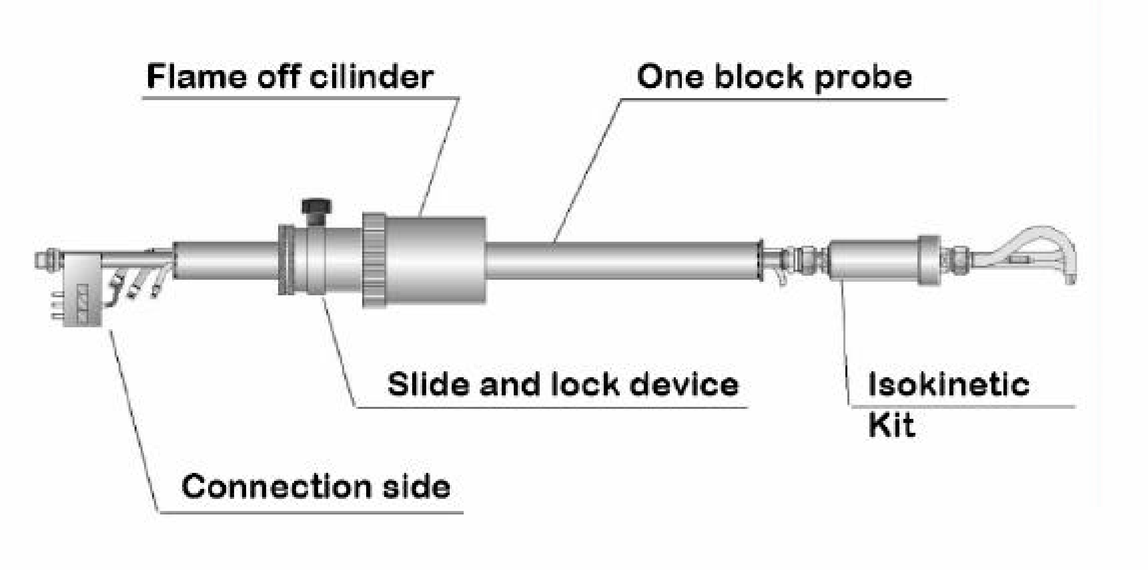


Figure 4-15: Integrated EU Sampling Probe

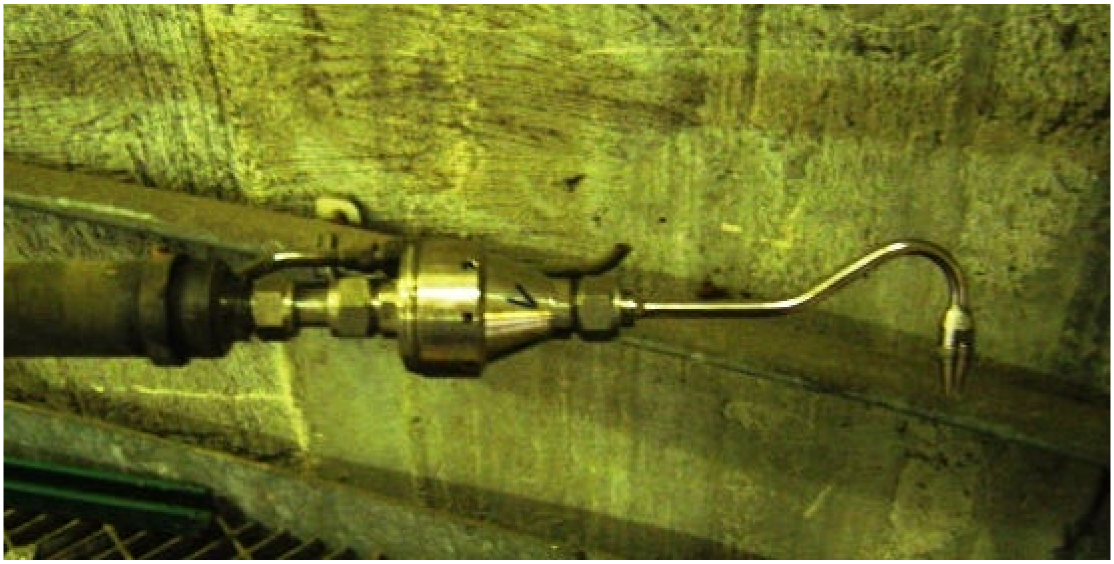


Figure 4-16: Sampling Nozzle and Filter Housing

Figure 4-17: EU Sampling Probe Inserted In a Sample Port at Armstrong

Figure 4-18: EU Sampling System at Armstrong

In summary, EN-13211 is, in many aspects, similar to the OHM. The main difference is that isokinetic rate is computer-controlled (no operator is needed), and only three impingers are used. These impingers are smaller compared to the Smith Greenburg impingers, Figure 4-19. Also, the sampling volume is smaller and sampling time is shorter compared to the OHM. These features make EN-13211 inexpensive to use.

Figure 4-19: EU Impinger (left) In Comparison to the Smith Greenburg Impinger (right)

4.2.2. EN-14385 Flux-Derived for Heavy Metals

One EU computer-controlled isokinetic sampling train, having the same arrangement as presented in Figure 4-14, was used. The measured metals included Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel, (Ni), Thallium (Tl), Vanadium (V), Sb.

4.2.3. VDA Richtlinien 2006 (Impaction Method) for PM

One EU computer-controlled isokinetic sampling train having the same arrangement as presented in Figure 4-13 was used to obtain a PM sample in parallel to the mercury measurement. The standard EU sampling probe was fitted with a filter containing PM sampling nozzles, as presented in Figures 4 -20 and 4-21.

A cross-sectional view of the PM sampling nozzles and filters is presented in Figure 4-22.

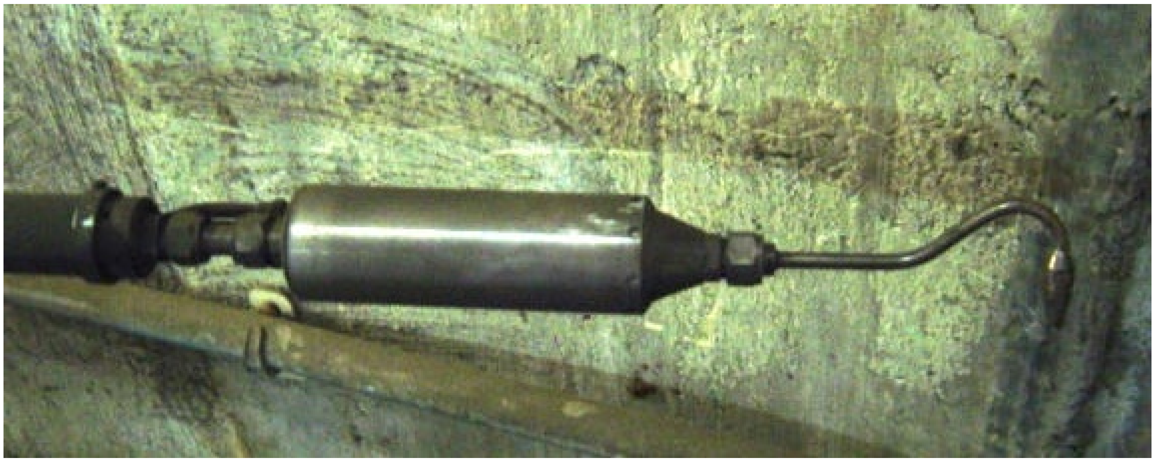


Figure 4-20: EU Sampling Probe Equipped with PM Sampling Nozzle

Figure 4-21: PM Sampling Nozzles

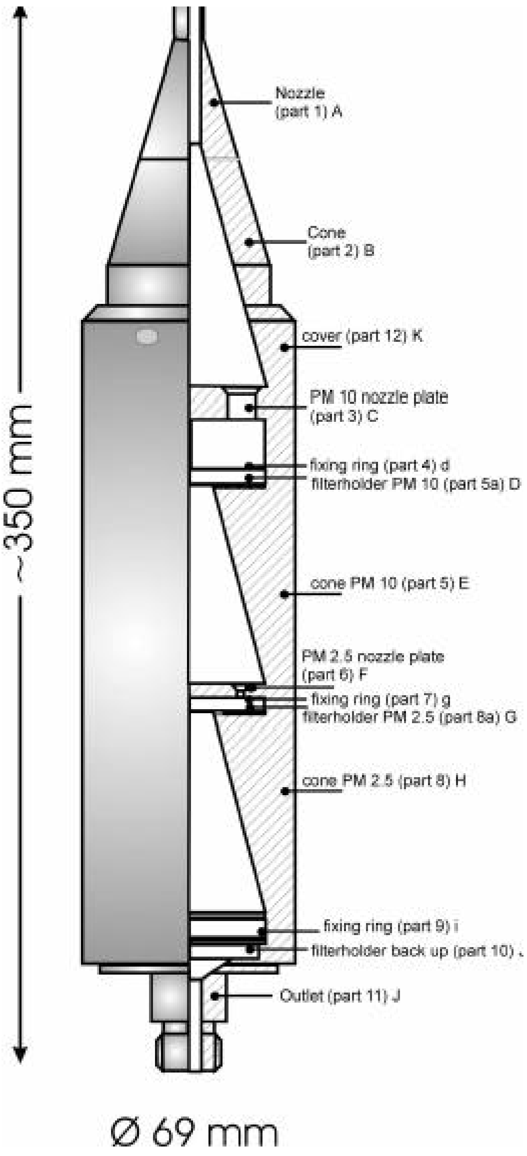


Figure 4-22: Cross-Section View of the EU PM Sampling Arrangement

4.3. Continuous Mercury Monitors

Continuous monitoring of mercury emissions will be needed for all stationary sources where annual Hg emissions exceed 29 pounds of Hg. The Ontario Hydro wet chemistry method and dry sorbent trap methods provide good results for total and speciated mercury measurements; however, these methods can fail to provide the realtime data often necessary for environmental compliance. Hg CEMs are similar to other combustion system CEMs in that a sample is extracted from the gas stream, conditioned, and sent to a remote analyzer for detection. However, as stated earlier, mercury is present in three different forms (Hgp, Hg2+, and Hg0), which greatly complicates the measurement process. Although on-line emission analyzers are expensive to purchase, install, and maintain, they offer several benefits, including the following:

- Real- or near-real-time emission data
- Operational data for process control and environmental compliance
- Evaluation of control strategies
- Greater understanding of process variability and operation
- Greater public assurance

As they are currently configured and utilized, Hg CEMs possess several challenges to long-term, low-maintenance continuous operation for flue gas mercury monitoring. The two main challenges include the areas of sample collection and flue gas conditioning. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas is very difficult. The complexity of flue gas chemistry, high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct [2].

To a great extent, heated sample lines, gas conditioning systems, and material of construction have addressed many of these issues; however, monitoring dirty locations remains difficult, especially when reactive ash is present and traditional probe filters are used. Further development and demonstration of flue gas conditioning systems is required to ensure that simple, reliable, and representative flue gas monitoring can be achieved.

In order for Hg CEMs to be considered for regulatory compliance assurance, acceptable performance will need to be demonstrated. Currently the EPA has proposed a new performance standard which outlines the requirement for mercury measurement using continuous emission monitors. This Performance Specification 12A (PS-12A) titled “Specification and Test Methods for Total Vapor-Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources” would be included in the U.S. Code of Federal Regulations (CFR) (40 CFR Part 60, Appendix B).

A summary of the PS-12A criteria is presented here as they are pertinent to defining the requirements of Hg CEMs.

- The Hg CEMs must be capable of measuring the total concentration in μg/m3 (regardless of speciation) of vapor-phase Hg and recording that concentration on a dry basis, corrected to 20°C and 7% CO2. Particulate-bound Hg is not included.
- The CEMs must include a diluent (CO2) monitor and an automatic sampling system.
- Calibration techniques and auxiliary procedures are not specified.
- Procedures for measuring Hg CEM relative accuracy, measurement error, and drift are outlined.
- Hg CEM installation and measurement location specifications and data reduction procedures are included.
- Procedures for comparison with reference methods are outlined.

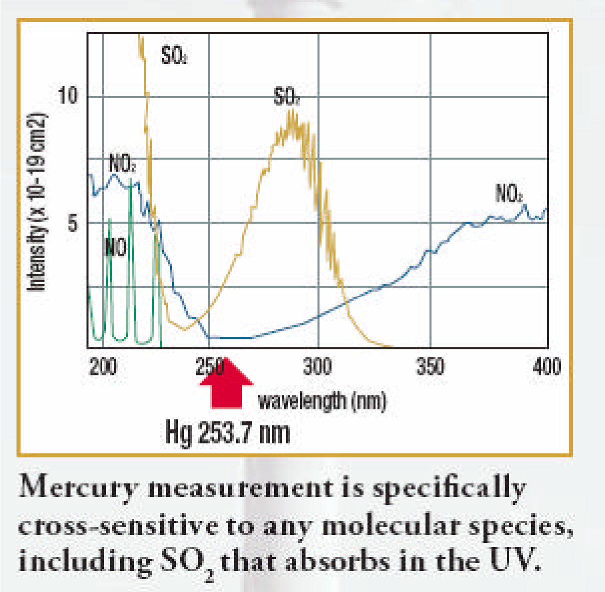
The basic steps that all Hg CEMs must accomplish in order to effectively measure mercury in a flue gas stream include:

- Filter particulate matter from the sample gas while minimizing flue gas fly ash contact.
- Transport the sample gas to a conditioning system, or condition the sample at the sampling port and transport the conditioned sample to the instrument.
- Condition the sample by reducing all forms of mercury in the sample gas to Hg0 and remove moisture form the sample gas.
- Measure the mercury in the flue gas sample.

Mercury analyzers can be distinguished by their measurement detection principle. Methods used include pre-concentration by gold amalgamation with CVAAS detection, Zeeman modulated CVAAS, pre-concentration, and gold amalgamation with CVAFS detection. Instruments are also being developed based on AES and laser technologies.

4.3.1. CVAAS Method

The Cold Vapor Atomic Absorption Spectrometry (CVAAS) method determines the mercury concentration in the gas by measuring the attenuation of the light produced by a mercury vapor lamp as it passes through a cell that contains the sample gas. The mercury atoms in the cell absorb mercury at their characteristic wavelength of 253.7 nm. Other flue gas constituents, such as SO2, absorb light across a wide spectrum including the 243.7 wavelength, thus interfering with Hg measurement, Figure 4-23. Water vapor and particulates are also broadband absorbers that must be dealt with in CVAAS measurement.



Mercury measurement is specifically cross-sensitive to any molecular species, including SO_2 that absorbs in the UV.

Figure 4-23: SO2 Interferes With Mercury Measurements by AA

One method to remove the interferants is to pre-concentrate the mercury on a gold trap for a known period of time at a known flow rate. The gold trap is then heated, and the mercury is swept into the detection cell with an inert gas. A second method is to use a powerful magnet to slightly shift the wavelength of the mercury vapor lamp (Zeeman modulation). The broadband absorbers will attenuate the signal at both wavelengths, and the difference between the signals is attributed to the mercury concentration. A third method is to use two detection cells. The sample gas first passes through a cell, and the signal attenuation is measured. The sample gas then passes through a trap to remove the mercury and, finally, through a second cell to measure the attenuation caused by the interferants. Similar to the Zeeman-modulated method, the difference in signals is attributed to the mercury concentration.

4.3.1.1. CVAFS Method. Typically, the Cold Vapor Atomic Florescence Spectroscopy (CVAFS) method uses gold amalgamation to pre-concentrate the mercury. After the mercury is desorbed from the trap, it is swept into the detection cell by an argon carrier gas. The mercury atoms in the cell are excited to fluorescence by a pulsed mercury discharge lamp, which is measured by a photomultiplier tube. The fluorescence results in increased selectivity since only the mercury atoms will fluoresce. The fluorescence can be quenched through collision of excited mercury atoms with other components of the sample gas, particularly oxygen and nitrogen. In cases where the mercury concentration is high, nitrogen may be used as the carrier gas to suppress the fluorescence signal.

4.3.1.2. AES Method. The AES method is currently being developed by Envimetrics for mercury measurement. The method is based on the emission of light from mercury atoms induced by a high energy source such as plasma. The light is emitted at the characteristic 253.7-nm wavelength. The advantage of this method is that the electron energy can be optimized to produce more radiation from the mercury in the sample gas than any other constituent. The AES method also has the potential to be used as a multi-metal monitor.

4.3.1.3. Flue Gas Conditioning. Both CVAFS- and CVAAS-type mercury analyzers can only measure elemental mercury. Therefore, to measure the total mercury concentration in a sample gas stream, the oxidized forms must be reduced to elemental mercury in a conversion system. The most common method of reducing oxidized forms of mercury to elemental is using a liquid reducing agent such as SnCl2 (stannous chloride). This method is used extensively, but has proven to be problematic. The wet chemistry conversion systems are considered to be the limiting factor in reliability of Hg CEMs. The wet-chemistry systems use corrosive or caustic chemical solutions in large quantities. The spent reagents must be treated as hazardous waste which generates disposal concerns. In addition, all of the interactions between different flue gas constituents, the different mercury species, and the reducing reagents are not yet clearly understood.

Efforts to develop “dry” conversion units are beginning to produce results. These techniques center around using high-temperature catalysts or thermal reduction units to convert the oxidized mercury fraction to elemental mercury. These units also condition the sample gas by removing moisture and other interferants before the sample gas is sent to the analyzer. Although labeled as dry systems, most use chillers and gas–liquid separators to remove moisture from the sample gas stream.

There is some concern about the life and cost of catalysts used to reduce the oxidized forms of mercury to elemental mercury. Once proven, these units would greatly reduce the operational maintenance requirements.

4.3.1.4. Particulate Removal. Particulate-bound mercury captured on a filter can be reduced to Hg0, but because of particulate matter transport issues, it is impractical. Also, EPA Draft Performance Specification 12A only requires CEMs to measure “the total concentration (regardless of speciation) of vapor phase mercury.” Therefore, it is important to remove any particulate matter from the sample gas stream in a manner that ensures it does not interfere with the operation of the analyzer or impart a bias to the mercury data. Conventional filtration methods will not work because as the particulate matter forms a dust cake on the filter media, it has a greater chance to interact with the flue gas and the mercury. The total mercury concentration could be biased low if the particulate matter is reactive and captures mercury.

Although not important for measuring total mercury, the particulate matter on the filter could potentially bias the speciation of the measured mercury by oxidizing elemental mercury across the filter media. In an effort to greatly reduce or eliminate this problem, most CEM systems are either equipped with an inertial separation probe or a blowback filter of some type. In wet stack applications, downstream of a wet scrubber, water droplets in the stack make representative sample collection difficult. Mercury in the oxidized form could likely be associated with water droplets and not captured in isokinetic sampling.

4.3.1.5. Calibration. Regardless of the measurement technique or conversion system, all instruments must be calibrated. All of the instruments available are easily zeroed by passing a filtered mercury-free sample gas through the analyzer.

There are basically four ways to span a Hg CEM. The first way is manual injection of a known quantity of mercury. Since the vapor pressure of mercury is a well known function of temperature, only the volume injected and the temperature of the vapor need be known in order to determine the amount injected. This is considered a primary standard for calibration. The second way is the use of a calibrated permeation source which may be internal or external to the instrument. These permeation devices can also be used to spike a sample at the inlet to the sampling probe to demonstrate the integrity of the sampling system. The third way is the use of a calibration gas from a certified cylinder. The problem with cylinders is the high cost and low volume of gas in each cylinder. The last option (mainly for a CVAAS instrument using Zeeman modulation) involves using a small sealed cell with a known volume that contains a bead of elemental mercury. Again, the concentration in the cell is a function of the temperature of the cell. The cell is placed in the light path of the instrument and the concentration is known based on the temperature of the cell [2].

4.3.2. Tekran Series 3300

The TekranR Series 3300 speciating mercury continuous emissions monitor uses a CVAFS analyzer in conjunction with a dry conversion system and sampling probe to measure speciated mercury in a flue gas stream.

The sample gas is pulled through a stack-mounted high flow-rate inertial probe to minimize mercury measurement artifacts due to filtering. The sample is then diluted and transported through a heated line to a conditioning module, Figure 4-24. The diluted sample is split into two streams. In the first stream, a thermal conditioner unit reduces all of the mercury forms present in the sample to elemental mercury. Recombination is avoided by the quantitative removal of HCl and other gases by a thermal conditioner/scrubber system. The second pathway removes ionic (water soluble) mercury, leaving only the elemental mercury to pass through to the converter.

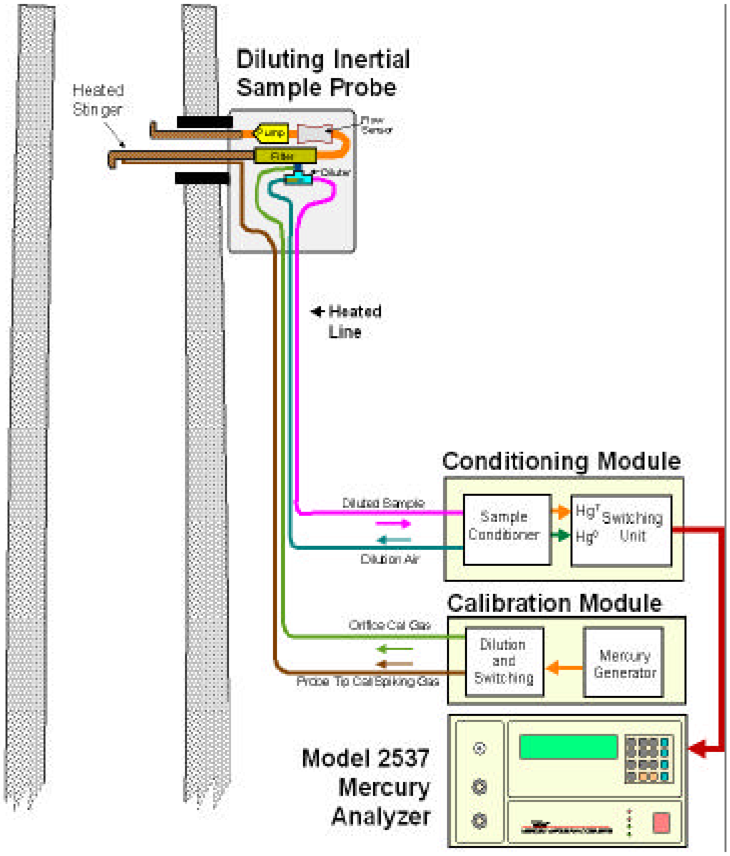


Figure 4-24: A Schematic of Tekran 3300 Hg CEM System

This stream is then subjected to additional conditioning to remove acid gases and excess humidity from the sample. Ionic mercury is determined by the difference.

This conversion unit has the advantage of not using chemical reagents or solid sorbents. The probe is capable of performing automated filter blowback, multipoint calibrations, and standard additions of elemental mercury into the sample matrix. Probe temperatures, flow rates and pressures are monitored and telemetered to the system controller via a datacom link.

The two conditioned streams are analyzed using a Tekran Model 2537A mercury vapor analyzer. This analyzer is in wide use all over the world and has demonstrated its accuracy, stability, and reliability under the most remote and rugged conditions. System components are presented in Figures 4-25 and 4-26.

Figure 4-25: Components of the Tekran 3300 System

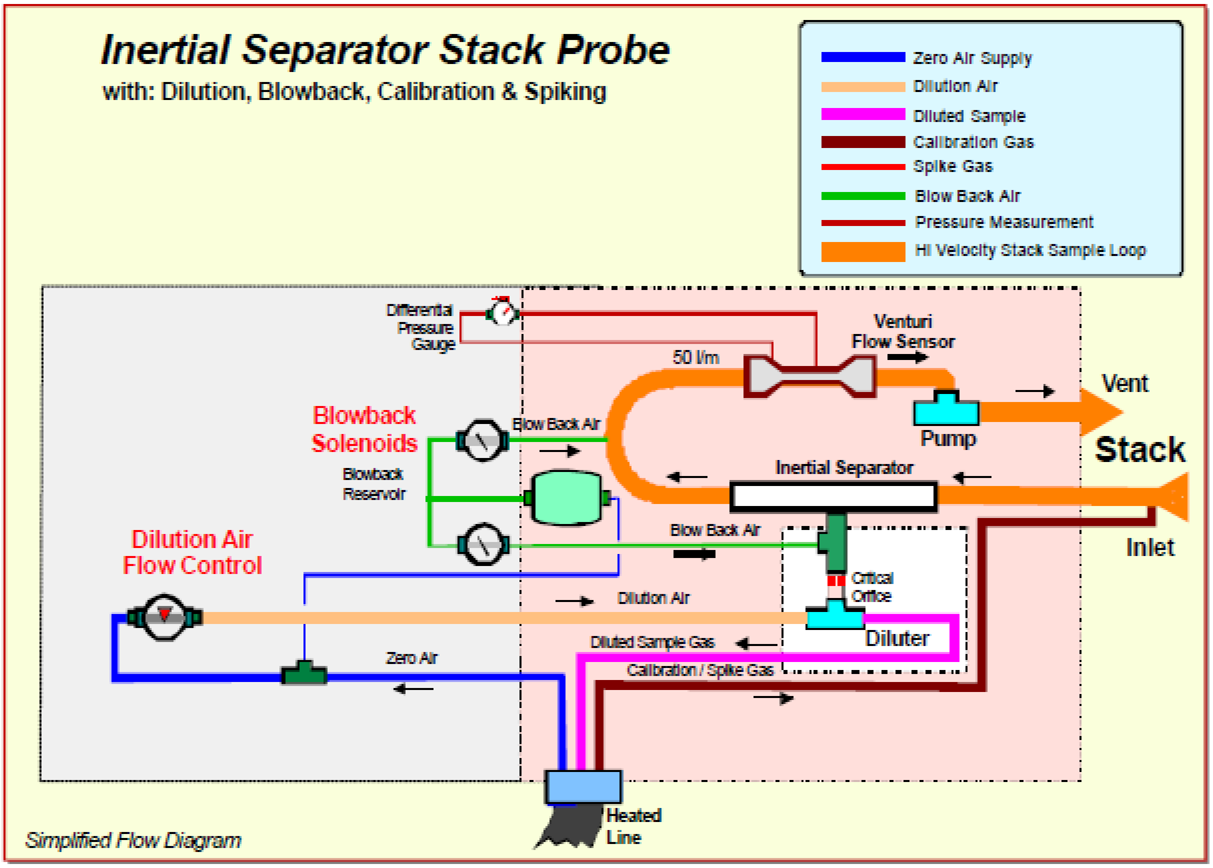


Figure 4-26: Inertial Separation Probe

The analyzer uses gold pre-concentration combined with atomic fluorescence detection. The advertised minimum detection limit for the analyzer is less than 0.05 µg/Nm3, or less than 1 ng/Nm3, for low Hg concentrations.

A source of compressed mercury-free argon is required for operation of the instrument. A calibration source allows both multipoint calibrations and standard additions to be automatically initiated. Both these operations are performed through the entire CEM path, including all probe filters.

The calibration unit generates concentrations of mercury by using a National Institute of Standards and Technology (NIST)-traceable temperature-controlled saturated mercury vapor source. Precision mass flow controllers are used to dilute the output of this source to the desired value. The unit is capable of continuously generating large flow rates of calibration gas at no ongoing cost – unlike expensive mercury calibration gas cylinders. The computer provides full control of each module within the system. Industry standard protocol is used to monitor and control each unit. All temperatures, flows, and pressures are displayed by the application program and may be set by authorized users. The system features remote operation and problem diagnosis, either via a modem and telephone line or through the Internet. Each instrument reading represents a true 2.5 minute -average Hg concentration.

4.3.3. Thermo Electron: Mercury Freedom SystemTM

Mercury Freedom SystemTM measures elemental, ionic, and total mercury in exhaust stacks from both coal-fired boilers and waste incinerators, using atomic fluorescence design that avoids use of gold trap (amalgamation). This design eliminates the need for an SO2 scrubber and provides continuous processing vs. batch collection by gold pre-concentration.

A glass-coated inertial filter and conversion at the stack prevent loss of ionic Hg. Dilution-based system reports Hg concentrations on a wet basis, which eliminates the need for flue gas moisture analyzers.

4.3.3.1. Primary System Components. The probe and converter are located at the stack. The sampling probe is designed to minimize measurement artifacts due to interactions with fly ash. It uses a high flow, sintered-metal inertial filter to provide a particulate-free, vapor-phase sample for analysis. Automated blowback helps to ensure trouble-free continuous operation, and all components exposed to sample gas are glass-coated to prevent reactions with mercury. Dilution and calibration take place within the probe. Calibration gas can be introduced either upstream or downstream of the inertial filter.

The probe controller, analyzer, calibrator, and zero gas generator are rackmounted and located in the CEM shelter. A high temperature module converts all vapor-phase species of mercury to elemental mercury for analysis. The proprietary conversion technology has been demonstrated to meet the U.S. EPA PS-12A criteria of <5% span value deviation from the certified gas value.

The microprocessor-driven probe control unit is connected by an umbilical to the stack probe and mercury converter. The controller automates probe calibration and dynamic spiking, and confirms auto dilution. In addition, it monitors probe temperature, measures flow rates and pressure in the sampling loop, and enables automated filter blowback.

A cold vapor atomic fluorescence analyzer provides continuous sample measurement, with no additional gases or pretreatment required, and virtually no interference from SO2. Detection limits down to 1 ng/Nm3 allow high sample dilution (100:1) reducing moisture, heat, and interfering pollutants.

A vapor generator allows standard calibration and dynamic spiking into the extraction probe. A wide calibration range of 0.1 to 300 μg/Nm3 allows direct calibration of the analyzer at post-dilution concentrations. The calibrator is ideally suited for daily zero/span checks and routine converter efficiency and linearity testing. The zero air supply delivers clean, dry dilution air to the probe, as well as air to the Hg calibrator for sensitive, accurate analyzer calibrations.

A photograph of the Thermo Mercury Freedom SystemTM located in the CEM shelter at the base of the stack at Armstrong is presented in Figure 4-27.

Figure 4-27: Thermo Electron Mercury Freedom SystemTM at Armstrong

4.3.4. GE-PSA

As requested by GE, description of the GE Hg measurement system, provided by GE, is presented per verbatim.

GE Energy and PS Analytical (PSA) have partnered to bring PSA's atomic fluorescence technology to the utility industry. GE Energy's Mercury CEM uses cold vapor atomic fluorescence spectrometry (CVAFS) to measure total vapor phase mercury stack emissions. This sensitivity allows plant operators to measure extremely low levels of mercury emissions, which maximizes mercury credits and improves the return on investment for installed mercury control equipment.

4.3.4.1. Mercury CEMS System Design Overview. Similar to conventional CEM, GE mercury CEM includes a probe, sample line, conditioning equipment, and analyzer. System design includes:

- 200°C heated inertial probe
- 200°C heated sample line
- Oxidized ($HgCl2$) to elemental ($Hg0$) mercury dry base conversion system
- Elemental mercury calibration gas generator
- Oxidized mercury calibration gas generator

The design changes from the conventional CEM are required to manage the extraction, transport and measurement of oxidized mercury. Vapor phase mercury in the coal-fired boiler flue gas stream is either in elemental or oxidized ($HgCl2$) form. Unlike elemental mercury, $HgCl2$ is prone to adhering to surfaces and is water-soluble. These traits make $HgCl2$ very attractive for mercury control technology solutions but provide measurement challenges. Managing mercuric chloride is critical to accurately measuring total vapor phase mercury. To address the challenges, several significant changes have been made to the standard CEM design, including changes in the probe and sample line.

4.3.4.2. Mercury Measurement Approaches. Mercury measurement can be made using either a dilution extraction (wet) or full strength extraction with moisture removal (dry) method. Either approach is acceptable, however, the wet method features a simplified, low maintenance design while achieving accurate and consistent results.

For most sites, using a wet-based (dilution) measurement system is the optimum approach since the measured concentration can be directly multiplied by the wet-based stack flow to calculate mass emissions. This eliminates the need for moisture measurement or F factors. A dry-based measurement system must be corrected for moisture content before it can be applied to the stack flow data.

4.3.4.3. Standard Mercury CEM Dilution-Based System Design. The GE standard design is a dilution-based system. This system consists of the following components:

- Inertial probe with dilution module
- Dilution air clean-up panel
- Heated, chemically inert, sample line
- Dry-based $HgCl2$ conversion module

- Analyzer using gold dual amalgamation traps with atomic fluorescence detection
- Cabinet-mounted analyzer and controller, with air conditioning unit
- Cabinet-mounted elemental mercury calibration gas generator
- Oxidized mercury calibration gas generator
- Carrier gas bottle rack, connection lines and pressure regulators

4.3.4.4. Inertial Probe. A standard dilution probe, when used in a Hg CEM application, tends to adsorb oxidized mercury. The oxidized mercury collects within the probe, then sporadically desorbs, causing spikes in measured mercury. To address this, an inertial probe is used. An inertial probe uses a race track design that pulls a high volume of flue gas axially through the probe, discharging it back into the stack. The high flow rate keeps particulate matter entrained along the probe race track. A portion of the race track housing contains a filter. The vacuum created by the dilution module eductor generates a relatively weak tangential flow. Due to the low tangential flow and the high axial flow rates, particulate matter is unlikely to move tangentially through the probe filter and into the sample path. A clean gaseous sample is extracted, while significantly reducing the risk of oxidized mercury adsorption onto dust collected in the filters. A photograph of the GE inertial probe is presented in Figure 4 -28.

The wetted parts of the probe and the dilution module are made of stainless steel, coated with an inert material. This coating is required for HgCl2 management, as HgCl2 may adsorb and desorb on non-coated stainless steel parts.

4.3.4.5. Sample Line. A heated, chemically inert sample line is used to transport the diluted sample from the probe to the converter module and onto the analyzer. The non-stick surface of the sample line prevents HgCl2 from adhering to the sample line walls. The sample line is heated to approximately 200°C, which further reduces the potential for HgCl2 adsorption during the sample transport process.

Figure 4-28: GE Inertial Separation Probe

4.3.4.6. Dry-Based HgCl2 Converter Module. Since the coal combustion process releases both elemental mercury (Hg0) and oxidized mercury (Hg +2) in the form of HgCl2 in the vapor phase, a means of reducing HgCl2 to Hg0 is required. There are two methods for reducing or converting HgCl2 to Hg0. The first approach is a wet chemistry approach. This method requires the mixing of reagents, typically at the cabinet, to generate the HgCl2 reduction solution. This approach can be adapted to changing site conditions and can provide valuable data. However, for continuous operation, it is not practical at a typical coal-fired utility.

The GE dry thermal catalytic converter consists of a pelletized proprietary material to achieve catalytic conversion. These pellets are contained in a quartz cylinder, which is locally heated to approximately 800°C. In this high-temperature environment, the catalyst causes the mercury in HgCl2 to reduce to elemental mercury (Hg0). Existing elemental mercury is unaffected. The converter cylinder is about eight inches in height with a diameter of about 0.25 inches. It is housed in a separate mounting from the analyzer, allowing the converter to be probe- or cabinet-mounted.

4.3.4.7. Atomic Fluorescence Analyzer Technology. Two commercially available technologies for measuring mercury are cold vapor atomic absorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectrometry (CVAFS). CVAAS instruments measure the amount of energy signal strength lost, presumably to Hg absorption. CVAFS measurement is based on Hg absorbing energy at a specific wavelength, which raises the atom to an excited state. The excited Hg atom then fluoresces, emitting light at a specific wavelength. CVAFS instruments measure the light emitted by excited Hg atoms. Due to CVAFS analyzers measuring the emission of energy rather than the absence, they are approximately 50 to 100 times more sensitive than CVAAS analyzers. This increased sensitivity is beneficial when:

- Measuring mercury concentrations that have been reduced via control mechanism to less than 1 μg/m3.
- Using a dilution extraction system, as the sample can now be diluted 50:1 or more with no degradation to sensitivity compared to a CVAAS analyzer.

The design of the CVAFS analyzer incorporates two gold amalgamation traps in series, Figure 4-29. These traps effectively clean the sample prior to introduction to the optical bench analyzer. In the event of fine particulate matter entering the Mercury CEMS (e.g., through loss of inertial probe eductor air), these traps provide a buffer between the extraction system and optical bench, minimizing the chance for optical bench contamination.

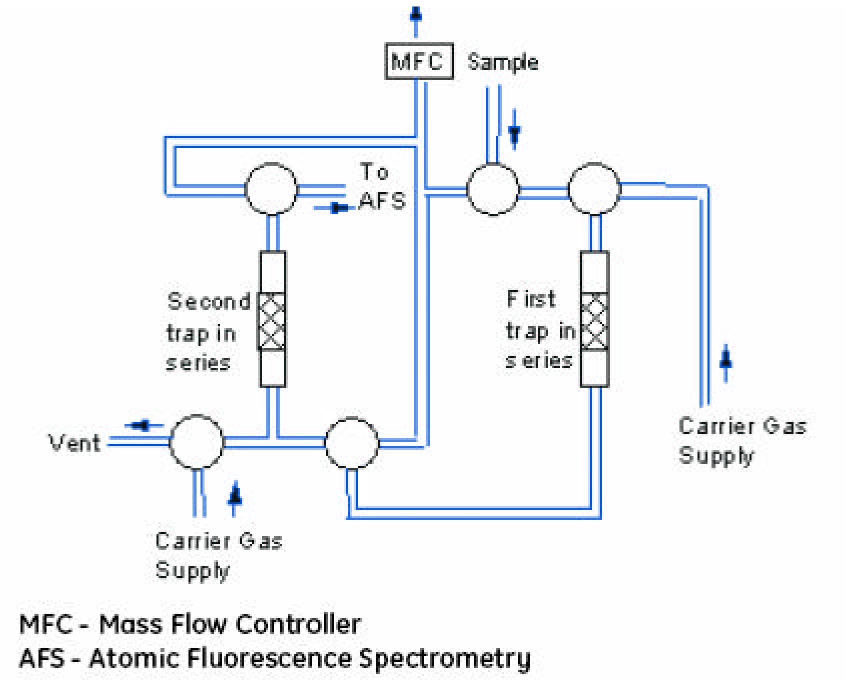


Figure 4-29: Gold Traps

4.3.4.8. Alternative Design for Very Low Emissions Concentrations. Depending on the type of coal burned and the design of the air pollution control train, it is possible for mercury emissions concentration to be well below 1 µg/m3. In this situation, the only viable solution is a full strength extractive system using a CVAFS analyzer. GE has field-tested a full-strength extractive Hg CEMs using no dilution with very favorable results, consistently measuring well below 0.5 µg/m3. The only changes between the standard dilution extraction design and the full strength extraction system tested were:

- Deletion of the dilution module and associated air clean-up panel
- Use of a shorter sample line length

CEMS data generated during these tests were compared to Ontario-Hydro runs and were within 10% of the Ontario-Hydro results.

4.3.4.9. Maintenance. GE's Mercury CEMS is designed for ease of maintenance and requires very little support beyond the EPA required checks.

Maintenance needs include:

- Daily checks of the air clean-up panel for dilution systems; similar to existing dilution system air panels
- Replacement of air clean-up panel filters as needed
- Quarterly probe filter checks

- Semi-annual replacement of the oxidized mercury catalyst
- Semi-annual replacement of the analyzer's first trap in the series
- Annual servicing of the analyzer's second trap in the sample gas flow stream
- Annual check of the analyzer optics bench
- Annual mass flow controller re-certification

A trained service technician should perform the annual checks.

4.3.4.10. DAHS Integration. Using the CEMS controller, information can be sent directly from the GE Mercury CEMS to the existing site DAHS. The DAHS will require configuring by the DAHS vendor to receive the Hg CEM data.

4.4. Semi-Continuous Mercury Monitors

4.4.1. Ohio Lumex: IRM-915

Field-transportable Ohio Lumex IRM-915 MiniCEM is designed for temporary stack installation and measurement of total or elemental mercury, Figure 4-30. It has been designed for testing and certification of permane ntly installed Hg CEMs. Set-up or take-down time is less than three hours.

Figure 4-30: Ohio Lumex IRM-915 MiniCEM

Real-time (one sample per minute) continuous mercury monitoring is based on the analytical approach of thermo catalytic conversion and Atomic Absorption for detection of mercury with Zeeman background correction. This approach requires no pre-concentration on gold eliminating the associated problems. The use of multi-path cell combined with a “dry” converter provides the highest sensitivity with no interferences from the combustion gas matrix. High converter temperature (700°C), short residence time and up to 1:100 dilution prevents Hg atoms from recombining with any “active” species generated due to high temperature decomposition of flue gas.

Heated sample extraction probe (Figure 4-31), heated filter with dilution/conversion assembly are used for “High” or “Low” particulate loading. Results are reported on “wet” basis as required by EPA regulations. Detection limit for flue gas is 0.2-1,000 ug/dsm3, total mercury on wet basis.

Figure 4-31: Ohio Lumex Probe/Filter/Converter Unit

Calibration. Mercury calibration gas, NIST traceable SRM’s with Hovacal generator.

Utilities. Power: 110V/60Hz, 20 amp. Compressed Air: 15-20 liters at 80 psig.

Weight. Analyzer: 90 lb Probe/Filter/Converter Unit: 150 lbs

Maintenance. Particulate cartridge filter and scrubber replaced as required (weekly).

4.4.2. Horiba

The field-transportable Horiba analyzer manufactured by Horiba Environmental and Process Instruments uses Cold Vapor Atomic Absorption Spectroscopy, and thermal catalytic conversion to measure total Hg emissions. During field testing at Armstrong, the instrument became contaminated (most likely by Selenium) and Horiba withdrew from the test. Photographs of the Horiba system and probe converter box are presented in Figure 4 -32.

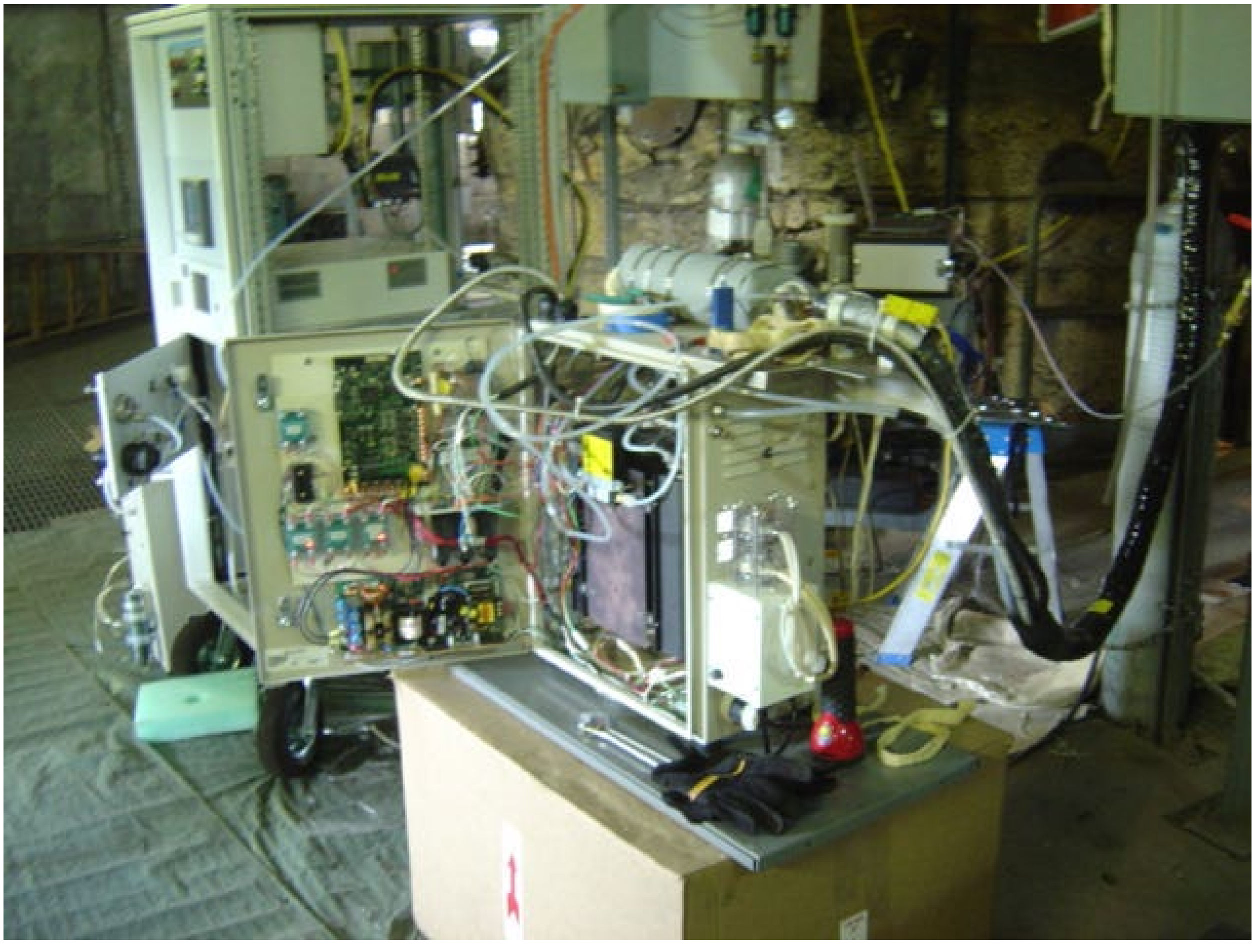


Figure 4-32: Horiba Portable Hg Analyzer

4.5. Other Mercury Monitors Used at Armstrong

4.5.1. Ohio Lumex RA 915+

The Ohio Lumex RA-915+ is a real-time continuous monitor for total and elemental mercury measurement (Figure 4-33). The instrument is based on differential Zeeman atomic absorption spectroscopy using high-frequency modulation of light polarization. A mercury lamp is placed in a permanent magnetic field which has the ability to slightly change the wavelength of the mercury light. This allows for background correction for such broadband absorbers as SO2, moisture, and particulate matter. The Lumex has a multi-pass cell which provides an effective path length of 10 meters. The instrument does not use gold amalgamation pre-concentration and this allows for a faster response time. In ambient air, a lower detection limit of 2ng/m3 can be achieved, according to the manufacturer.

Figure 4-33: Ohio Lumex RA-915+ Monitor

Ohio Lumex provides a cell for thermal reduction of oxidized mercury to elemental mercury. No catalyst is used in the thermal decomposition cell. Further testing needs to be completed with this system to ensure recombination of the oxidized mercury does not take place. The Lumex needs an external mercury supply, such as a permeation device or a gas cylinder, for calibration. The instrument does come with a small cell of fixed volume that contains saturated mercury vapor which can be used to check the calibration.

4.5.2. Ohio Lumex RA 915 CEM

Real-time continuous monitoring for total mercury is based on the analytical approach of thermo catalytic conversion and Atomic Absorption for detection of mercury with Zeeman background correction. This approach allows operation with no preconcentration on gold, eliminating the associated problems. The use of a multi-path cell combined with a dry converter provides high sensitivity with minimal interferences from the combustion gas matrix.

Mercury measurements take place in the heated cell zone of a converter coupled to a spectrometer. This prevents Hg atoms from recombining with any species generated due to high temperature decomposition of flue gas. Measurement results are reported on the "As is, hot, wet" basis. A heated particulate filter, heated transfer lines and heated head Teflon pump train extract gas samples before injected into the analyzer.

Technical Specifications:

- Detection limit: 5 mg/dsm3, total mercury
- Calibration: Single point, manual calibration, NIST traceable gas
- Set-up time: less than one hour
- Utilities: 110 V/60Hz, 1000W
- Weight: 50 lb
- Real-time measurements with 40 seconds between data points
- Air conditioned environment required for operation

Figure 4-34: Ohio Lumex RA 915 CEM Used at Armstrong

4.6. Sorbent Traps (40 CFR Part 75 Continuous Emission Monitoring, App. K)

Due to the challenges identified with Hg CEMs, a sorbent based mercury measurement method, EPA Method 324, has also been proposed for inclusion in the CFR titled "Determination of Vapor Phase Gas

Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling” (40 CFR Part 63, Appendix A: Method 324) [2]. This method would also be well suited for periodic compliance measurements at stationary emission sources emitting less than 29 pounds of mercury per year.

In addition to impinger-based sampling trains, gaseous mercury species, Hg2+ and Hg0, can be selectively captured on solid sampling medium through adsorption, amalgamation, diffusion, and ion exchange processes. Solid sorbents offer several advantages relative to liquid sorbents, including greater stability and easier handling. The mercury collected can be analyzed directly using sensitive techniques such as atomic fluorescence. These advantages provide the impetus for the development of solid sorption methods. However, the dry sorbent-based methods only provide a timeaveraged mercury concentration, and the sorbents must be sent to a lab for an analysis [2]. Based on these limitations, the dry sorbent methods cannot be used for on-line closed-loop mercury control.

Currently, two dry sorbent methods are available for mercury measurement: the flue gas mercury sorbent speciation (FMSS) method and the Quick SEMTM (QSEM) method. Both methods rely on capturing mercury on dry sorbents. The FAMS method is a speciation method, while the QSEM method measures the total mercury concentration in a flue gas stream.

4.6.1. FMSS Method

The FSTM method was developed by Frontier Geosciences based on earlier research with the mercury speciation adsorption method for measuring total gaseous mercury in a flue gas stream. The FMSS method pulls a semi-isokinetic sample from a flue gas duct through a mini-particulate filter and a heated solid sorbent sample train. The filter and the sorbent train are analyzed to determine Hg(p) , Hg2+, and Hg0 , Figure 4-35.

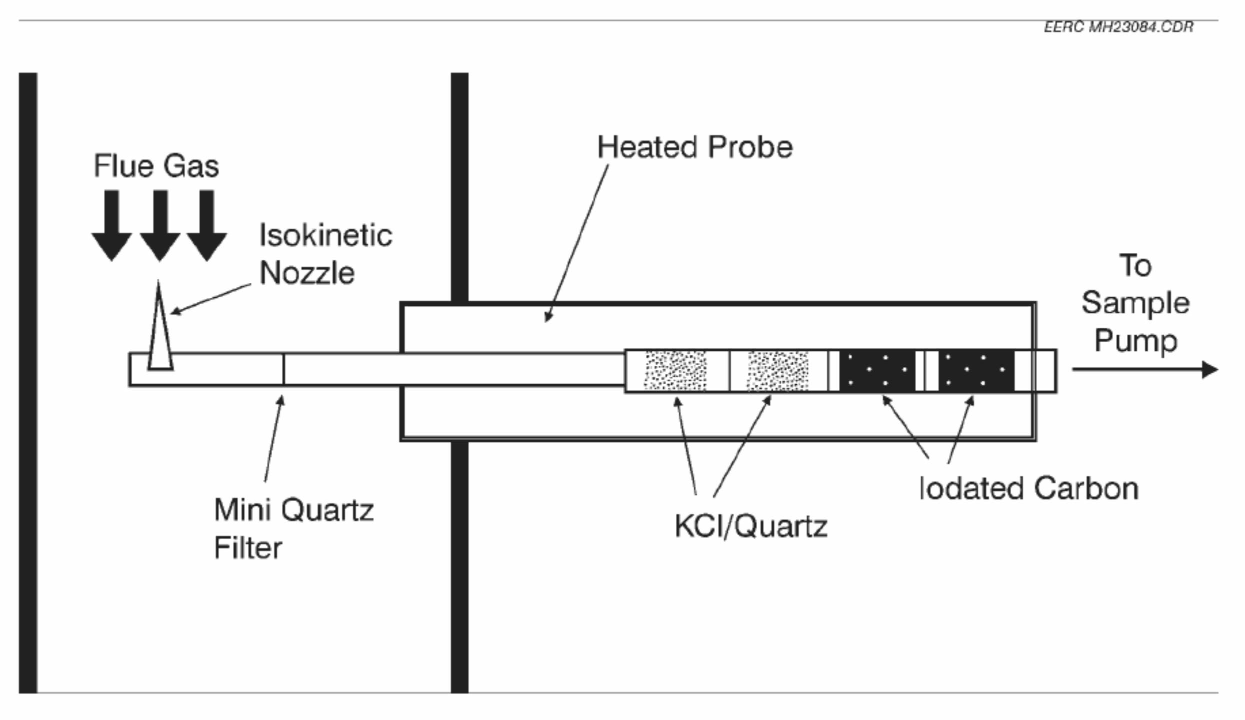


Figure 4-35: A Schematic of the FMSS Sampling Train

The diameter of the inlet nozzle is sized to provide isokinetic flow based on the nominal duct velocity. The mini-particulate filter consisting of a small quartz fiber filter disk is inserted into a quartz tube on a pure nickel support screen to collect fly ash for Hg(p) determination [2]. The FMSS method sorbent train consists of dual dry sorbent traps for the gas-phase Hg species.

The first trap contains dry KCl-coated quartz chips and is used to capture the Hg2+. The second trap containing tri-iodine-impregnated activated carbon traps is used to capture the Hg0 in the flue gas stream. After sample collection, the entire sample train trap is sent to a laboratory for analysis. Analysis of the sorbent traps is conducted by CVAFS, following strong acid digestion, BrCl oxidation, aqueous SnCl2 reduction, and dual gold amalgamation (EPA Method 1631B, modified). The analysis of the Hg(p) on the fly ash is done by thermal desorption at 800°C, passing through a heated MnO converter, gold pre-concentration, and CVAFS detection.

The FSTM method was validated by the EERC according to a modified EPA Method 301 [2]. The mean relative percent difference (RPD) was ±22% for Hg0, ±8% for Hg2+, ±10% for total Hg, and ±6.5% for Hg(p). The FMSS exhibited good agreement with Ontario Hydro methods, and accuracy was better than ±20% for all species for the range of conditions in the validation study, including ruggedness tests. The mean accuracy of the duplicates and the triplicates for the FMSS method was better than 97% for Hg2+, total Hg, and Hg0.

4.6.2. QSEM Method

The QSEMTM method was developed by EPRI, ADA Environmental Solutions, and Frontier Geosciences to measure total vapor-phase mercury mass concentration in a flue gas stream. A schematic of the sampling train is illustrated in Figure 4-36. Where QSEMTM is used to collect data to demonstrate regulatory compliance, it must be performed with paired sorbent traps. This method is being proposed as EPA Method 324 [2].

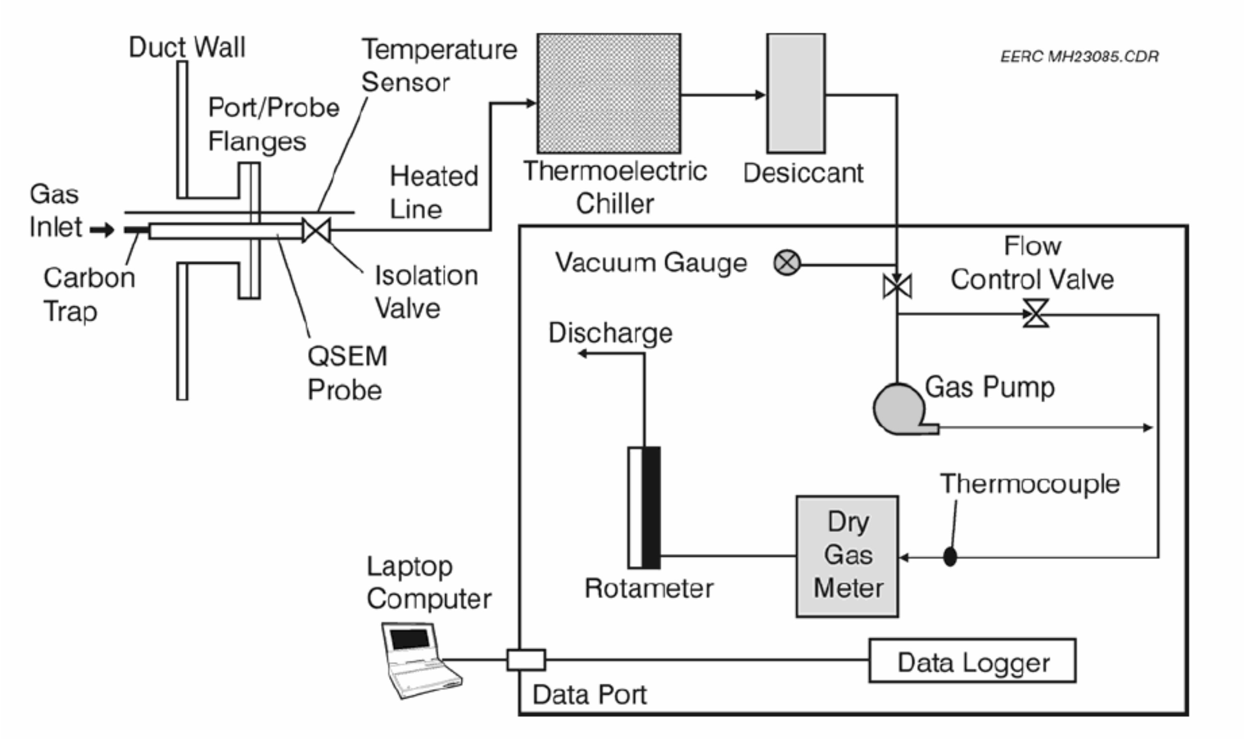


Figure 4-36: A Schematic of the Quick SEM™ Sampling Train

The method is designed for use in low-dust applications with mercury concentrations ranging from 0.03 to100 µg/dNm3. Known volume of flue gas is extracted with a nominal rate of 0.2 to 0.6 liters per minute from a duct through a single or paired iodine-impregnated carbon traps. Sample recovery consists of an acid leaching of the exposed traps and the leachate analyzed by CVAFS detection. Laboratory equipment is required for analysis by AF. Analysis of the leachate can also be performed using CVAAS detection. The AA analysis can be performed by existing recognized procedures, such as that contained in ASTM Method D6784-02 or EPA Method 29.

Components of the QSEMTM sampling train include:

- Sorbent Trap. Use sorbent traps with separate main and backup sections in series for collection of Hg. Selection of the sorbent trap shall be based on:
  - Achievement of the performance criteria for this method.
  - Availability of data that demonstrates the method can pass the EPA Method 301 criteria and that the results are comparable with those from EPA Method 29, EPA Method 101A

or ASTM Method 6784-02 for the measurement of vapor-phase Hg in a similar flue gas matrix [2].

The QSEMTM method requires the analysis of Hg in both main and backup portions of the sorbent within each trap. The sorbent trap should be obtained from a reliable manufacturing source that has clean handling procedures in place for ultra lowlevel Hg analysis. This will help assure the low Hg environment required for manufacturing sorbent traps with low blank levels of Hg.

Sorbent trap sampling requirements or needed characteristics are shown in Table 4-2. The sorbent trap is supported on a probe and inserted directly into the flue gas stream, as shown in Figure 4-36. The sampled sorbent trap is the entire Hg sample.

Table 4-2 Sorbent Trap and Sampling Requirements

Parameter	Small Sorbent Trap	Large Sorbent Trap
Loading Range [µg]	■ Min = 0.025 µg/trap ■ Max = 150 µg/trap	■ Min = 0.10 µg/trap ■ Max = 1,800 µg/trap
Required Sampling Duration	■ Min = 30 minutes ■ Max = 24 hours	■ Minimum = 24 hours ■ Maximum = 10 days
Required Sampling Temperature	■ 200 to 375°F	■ 200 to 425°F
Required Sampling Rate	■ 0.2 to 0.6 l/min, ■ Start at 0.4 l/min ■ Must be constant proportion of stack flow rate within ± 25% if greater than 12 hours. ■ Constant rate within ± 25% if less than 12 hours.	■ 0.2 to 0.6 l/min ■ Start at 0.4 l/min ■ Must be constant proportion of stack flow rate within ± 25%

- Sampling (QSEM) Probe. The probe assembly must have a leak-free attachment to the sorbent trap. For duct temperatures from 200 to 375°F, no heating is required. For duct temperatures less than 200°F, the sorbent tube must be heated to at least 200°F or higher to avoid liquid condensation in the sorbent trap by using a heated probe. For duct temperatures greater than 375°F a large sorbent trap must be used, and no heating is required. A thermocouple is used to monitor stack temperature.
- Heated Umbilical Vacuum Line. A 250°F heated umbilical line is used to convey the sampled gas that has passed through the sorbent trap and probe assembly to the moisture knockout (thermoelectric chiller and desiccant).
- Moisture Knockout. Impingers and desiccant can be combined to dry the sample gas prior to entering the dry gas meter. Alternative sample drying methods are acceptable as long as they do not affect sample volume measurement.
- Vacuum (Gas) Pump. A leak-tight vacuum gas pump capable of delivering a controlled extraction flow rate between 0.1 to 0.8 liters per minute.
- Dry Gas Meter. A dry gas meter that is calibrated according to the procedures in 40 CFR Part 60, Appendix A Method 5, must be used to measure the total sample volume collected. The dry gas meter must be sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling and equipped with a temperature sensor capable of measuring typical meter temperatures accurately to within 3°C (5.4°F).

4.6.3. Ohio Lumex and Apex Instruments

Ohio Lumex and Apex Instruments have teamed up to provide a sorbent trap system. The XC-6000EPC MercSampler, provided by Apex Instruments, consists of the following: probe, paired sorbent traps, automated data acquisition and handling system, moisture removal components, sample pump, dry gas meter and heated umbilical line, Figure 4-37. Sorbent traps, and sorbent analysis instrumentation were provided by Ohio Lumex.

Figure 4-37: The XC-6000EPC MercSampler

4.6.3.1. Apex Instruments Sampling System. The monitoring system samples stack gas at a rate proportional to the stack gas volumetric flow rate. Sampling is a batch process. Mercury mass emissions per hour during the sampling period are calculated by using stack gas flow rate measured by a certified flow monitor and correcting it to standard conditions (pressure and temperature). Each system requires the use of paired sorbent traps. For each pair of sorbent traps analyzed, the average of the two Hg concentrations are used for reporting purposes under Â§75.84.

Each sorbent trap contains a main section, backup section and third section to allow spiking with a calibration gas of known Hg concentration. A certified flow monitoring system and correction for stack gas moisture content are required.

The automated data acquisition and handling system ensures the sampling rate is proportional to the stack gas volumetric flow rate. After each sample collection period, the mass of Hg adsorbed in each sorbent trap is determined according to the applicable procedures in appendix K to part 75.

The sorbent media used to absorb Hg are configured in a trap using three distinct and identical sections, which could be analyzed separately.

- Section 1 - Primary capture of gaseous Mercury
- Section 2 - Determination of breakthrough
- Section 3 - Spiked with known amount of gaseous Hg prior to sampling for determining recovery efficiency

The sorbent media can be any collection material capable of capturing and recovering all gaseous forms of Hg for subsequent analysis. Examples include carbon or a chemically treated filter. Selection of the sorbent media is based on the material's ability to achieve the performance criteria contained in Section 8 of Appendix K. In addition, selection is based on the sorbent vapor-phase Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. Paired sorbent traps are supported on a probe(s) and inserted directly into the flue gas stream.

Each sorbent trap is mounted for gas samples to enter the trap directly. This mount can be within the probe or at the entrance. Each probe and/or sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent traps. The probes use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located.

A moisture removal device or system, suitable for continuous duty (e.g. Peltier cooler), is included to remove water vapor from the gas stream prior to entering the dry gas meter.

A known mass of gaseous Hg is spiked onto Section 3 of each sorbent trap prior to sampling. A practical system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Mercury salt solutions (e.g., Hg(NO3)2).

Any analytical system capable of quantitatively recovering and quantifying total gaseous Hg from sorbent media is acceptable provided that the analysis can meet the performance criteria in Section 8 of this procedure. Candidate analytical techniques include ultraviolet atomic fluorescence (UVAF); ultraviolet atomic absorption (UVAA), with and without gold trapping; and in situ X-ray fluorescence (XRF) analysis.

4.6.3.2. Ohio Lumex Sorbent Traps. Sorbent traps, provided by Ohio Lumex for the Armstrong test, are presented in Figure 4-38.

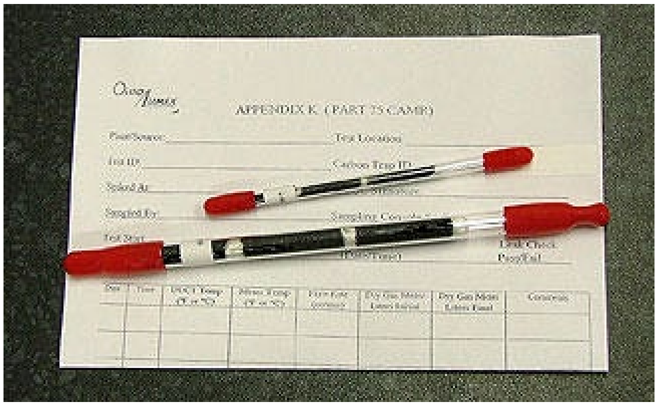


Figure 4-38: Sorbent Traps by Ohio Lumex

Ohio Lumex sorbent trap specifications and characteristics:

- Spiked/not spiked 3-section sorbent traps are available in sizes 6 mm and 10 mm OD; 4-section traps are available for Hg specialization
- Iodinated, acid washed coconut shell charcoal. 150 mg and 1g loading on small/large trap section.
- Low mercury background levels: less then 2 ng per section
- Easy to remove and easy to set for “leak check” cap plugs
- Extra thick glass for trap rigidity
- Customized spiking level for the 3rd section: 50 to 200,000 ng
- Long term storage stability: 1year
- Sampling duration: up to 2 weeks
- High-capacity mercury loading: up to 200,000 ng per section
- In-house analysis with short turnaround time

4.6.3.3. Trap Analysis Procedure. RA-915+ analyzer with RP-M324 attachment, Figure 4-39, is designed for field on-site or laboratory testing of sorbent trap tubes for Sorbent Trap Monitoring of Hg emissions from coal fired power plants. U.S. EPA validated thermal decomposition is referenced in appendices K part 75 of the Clean Air Mercury Rule. The AA technology is used for no sample preparation analysis. Analysis time is less than two minutes per sample. No liquid chemicals or gas are required, and no chemical waste is generated.

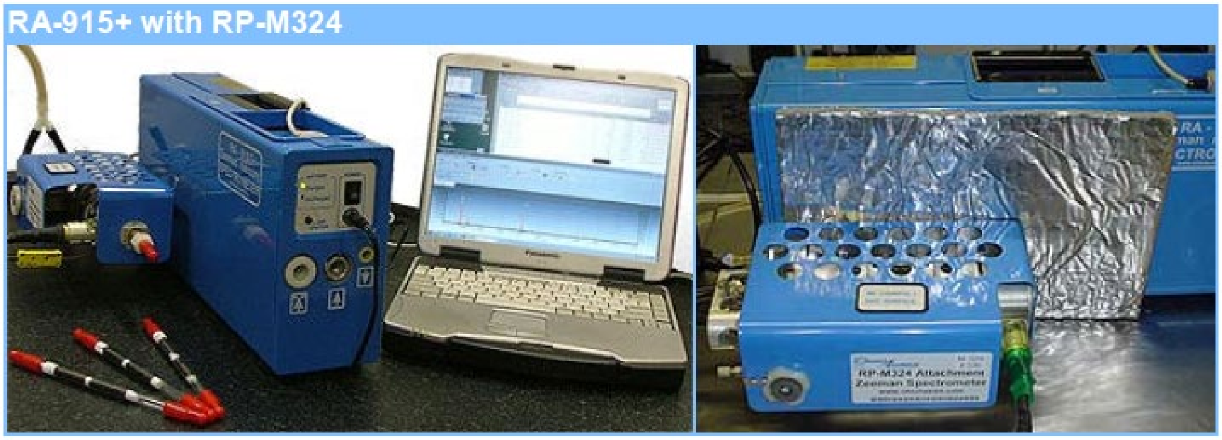


Figure 4-39: RA-915+ Analyzer with RP-M324 Attachment

A sorbent trap tube is cut and sorbent is transferred onto a quartz ladle. The ladle is inserted into the analyzer thermo catalytic conversion chamber heated to 800°C wherein mercury is converted from a bound state to the atomic state by thermal decomposition in a two-section furnace.

This approach requires no pre-concentration on gold, eliminating the associated problems. The use of multi-path cell combined with "dry" converter provides highest sensitivity with no interferences from the sample matrix. Mercury measurements take place in the heated cell zone of converter directly coupled to spectrometer. High temperature (800°C) and short residence time prevents Hg atoms from recombining with any "active" species generated due to high temperature decomposition of sample matrix. An external pump is used to draw ambient air and purify it for combustion. No cylinders of oxidizer or compressed gases are required.

4.6.4. Frontier Geoscience

Frontier Geosciences, Inc. (FGS) utilizes a specially designed dry sorbent trap to collect mercury emissions from flue gas streams and provide Hg concentration data that complies with EPA Clean Air Mercury Rule 40 CFR Part 75 Appendix K. FGS developed the FSTM traps required by Appendix K and was a primary contributor to the methods that preceded it.

The trap collects all available vapor phase mercury, elemental and oxidized forms, when inserted into a combustion flue gas stream and a measured amount of gas is pulled through it. The traps are then analyzed using EPA Method 1631 Revision E, using CVAFS. Mercury concentrations are determined on a mass basis (mg/m3) and then combined with flue gas flow data (m3/min) to calculate the continuous mass emission rate of total vapor phase mercury.

This technique requires minimal training for plant staff, can be used for shortterm or continuous sampling, utilizes routine field quality control, and maintains a fast turn-around-time for results.

4.6.4.1. Speciation of Mercury In Emissions. The FGS Flue-gas Adsorbent Mercury Speciation (FAMS) Method utilizes a specially designed multiple-stage dry sorbent trap to collect three mercury species from flue gas streams, Figure 4-40. The technique selectively and sequentially captures particulate mercury (Hgp), gaseous oxidized mercury (Hg2+), and gaseous elemental mercury (Hg0) on separate sections of the traps and delivers three samples of different mercur y species from a single test.

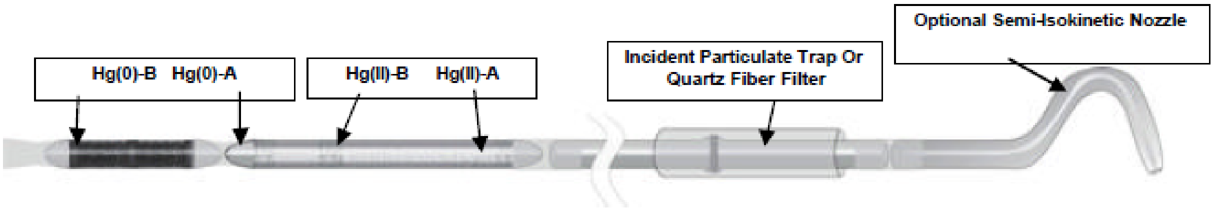


Figure 4-40: Schematic of Flue Gas Adsorbent Mercury Speciation (FAMS) Trap

The temperature of the trap is maintained at 95°C ± 5° during sampling to prevent water condensation. The mercury (Hg0) sorbed onto the chemically impregnated carbon, and the mercury (Hgp) on the glass wool plug are leached out in the laboratory using hot-refluxing HNO3/H2SO4 and then oxidized with BrCl. The mercury (Hg2+) sorbed onto the KCl is dissolved in BrCl. Aliquots of all three digests are then analyzed using EPA Method 1631 Revision E, using CVAFS.

The Frontier Geoscience test setup, sampling equipment, and probes are described in Section 3.3 of this report.

4.6.5. Clean Air – CONSOL

The MET-Team used a portable, automated sorbent trap sampling system to perform the short-term sorbent trap tests in accordance with 40 CFR 75, Appendix K procedures. Figure 4-41 shows a photograph of the system in use during this program.

Figure 4-42 illustrates the system schematic for the automated sampling system. The complete system consists of two independent gas sampling trains (designated as A and B). Sorbent traps of both (paired) sampling trains are contained within a single sampling probe. Each sampling train includes an Autosampler (a.k.a. MET Monitor), a moisture removal system (chiller) and a heated sample line.

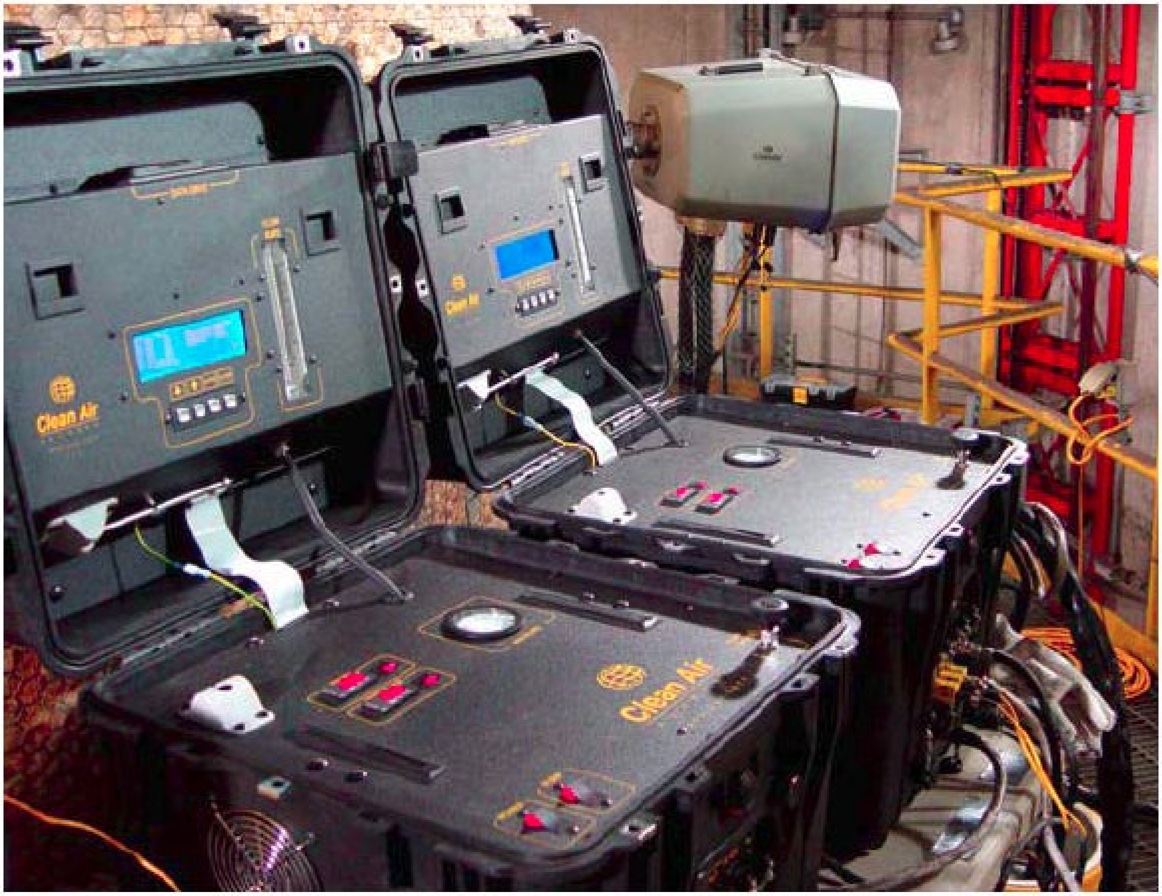


Figure 4-41: Portable Sampling System in Use at Armstrong Unit 2 Stack

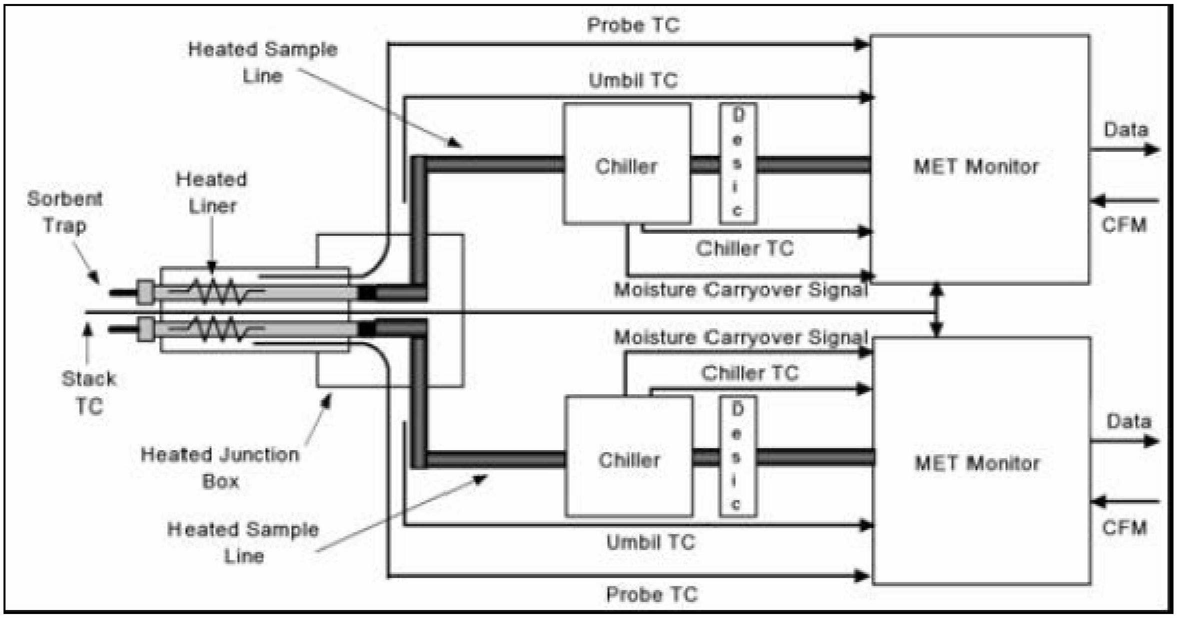


Figure 4-42: Automated Sorbent Trap Sampling System

Each Autosampler contains a dry gas meter equipped with a quaditure optical encoder that acts as a sample gas volume totalizer and is used for sample flow rate control. The components are housed in a NEMA-4 type enclosure that allows for remote as well as direct access to all operating modes, data and parameters. Data is continuously acquired and stored by the Autosampler and include:

- Stack Temperature
- Sample Vacuum Pressure
- Probe Temperature
- Barometric Pressure
- Heated Umbilical Temperature
- Sample Volume
- Temperature of Chiller
- Sample Flow Rate
- Sample Temperature
- Stack Flow Rate Surrogate (Disabled)
- Local Temperature
- Power Supply Voltage

The Autosampler supports logging intervals of 10 or 60 minutes (10-minute logging was used for this program). All data are stored locally on a removable memory medium, allowing for lifetime storage of data. Data can be monitored and downloaded remotely using a serial connection (RS485). Only the local storage option was activated during this program.

The moisture removal system used for this program consisted of an ice-chilled stainless steel coil condenser. A desiccant container downstream of the chiller constituted the final stage of the moisture removal system. The standard commercial system for this product replaces the ice-chilled condenser with a thermoelectric gas conditioner.

The sample probe accommodates two (paired) sorbent traps. All gas-exposed components of the probe were provided with a Silcosteel®-CR coating. During field testing at Armstrong, the MET-Team operated the samplers at a constant nominal flow rate of 0.5 l/min during all but one test run (Sampler A was operated at a nominal rate of 1.5 l/min for the afternoon run on July 13th).

The sorbent traps were manufactured by SKC, Inc. (Eighty Four, PA), and consisted of glass tubes (10mm OD x 7.8mm ID x 160mm long) packed with three onegram sections of iodinated carbon, Figure 4-43. The third section of each tube was also pre-spiked with a known amount of elemental mercury using bulk gas-phase spiking.

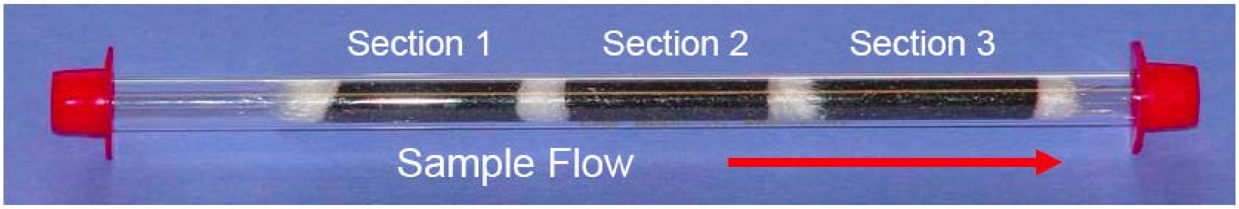


Figure 4-43: Appendix K Sorbent Trap

The sorbent traps were analyzed via acid digestion with bromochloride oxidation of each carbon section and subsequent analysis of the diluted aliquots by cold vapor atomic fluorescence spectroscopy (CVAFS) with double amalgamation technology. The instrumentation included a Tekran Instruments Series 2600 Mercury Analysis System. The analyses were performed by Consol Energy, Inc. (Library, PA). All calculations followed 40 CFR 75, Appendix K specifications.

An alternative system was used to collect a series of samples overnight (July 14- 15, 2006), as well as another set of short-term samples on July 14, 2006. This system was identical to that described above, with the exception that it used a critical orifice instead of a dry gas meter to measure the sample gas flow rate and total volume. The orifice was sized to sample gas at a constant rate of 0.4 l/min.

4.7. Instrumental Reference Method

A major concern for both certifying a Hg CMM based on PS 12A and ongoing QA/QC requirement under 40 CFR, Part 75 is the requirement that all RATAs are to be conducted using the Ontario Hydro method [3]. Obtaining nine valid paired sample trains is a challenge and will be very expensive for utilities.

To address this issue, EPA is developing specifications for an instrument-based reference method. A draft procedure is already available and Instrumental Reference Method (IRM) will be approved by EPA as a Reference Method in Spring/Summer 2007 time frame.

One of the main issues currently being heavily debated is the dynamic spiking requirement, i.e., the ability to dynamically spike both elemental (Hg0) and oxidized mercury (Hg2+) to the tip of the sampling probe. Dynamic spiking requires the addition of a small amount of spike gas into the sample gas matrix. This is not required in the new regulations for the Hg CMMs [3].

To comply with this IRM requirement, all of the major CMM manufacturers have developed some type of mercury generation and delivery system. In order for the results from these systems to be accepted, they will need to be National Institute of Standards and Technology (NIST)-traceable. EPA has asked NIST to help provide traceability for gas standards. EPA and NIST are currently working on certification of Hg0 gas cylinders and mercury gas generators, such as those provided by the PS Analytical and Tekran systems, for delivering Hg0. NIST also plans to look at the longterm stability of the gas cylinders and mercury generators.

A new equation for the mercury vapor pressure curves is also being proposed by NIST. Currently NIST, PS Analytical, and Tekran all use slightly different equations for Hg vapor pressure.

The first field test of the IRM was conducted at Armstrong. IRM test activities, procedures, and are presented in the Appendix of this report. THE APPENDIX IS WRITTEN BY EPA AND ITS CONTRACTOR ARCADIS.

5. TEST RESULTS

Field testing at Armstrong was performed at Units 1 and 2. Since Unit 2 was not available during the first two days of the field test (Saturday July 8th and Sunday July 9th 2006), Tests 1 and 2 were performed at Unit 1. Mercury concentration in the Unit 1 stack was measured by using two paired OHM trains and two single EU trains. The probes from all sampling trains were positioned as closely to each other in the stack as possible without causing interference. In addition to the OHM and EU sampling, Hg measurements were also conducted by using the Ohio Lumex/Apex Appendix K sorbent trap sampling train. Since all Hg CMMs were installed on the Unit 2 stack, a comparison between the Reference Method and CMM measurements could not be performed for Tests 1 and 2.

After Unit 2 came on line on Sunday (July 9, 2006) afternoon, the testing effort shifted to Unit 2, and Tests 3 to 18 were performed on Unit 2. After the initial problem with Unit 2 unavailability, field testing continued uninterrupted for an additional eight days. The last day of testing was Monday (July 17, 2006) when mercury stratification tests were performed using a sampling train composed of the U.S. and European components. Stratification tests, test equipment, procedures, and results are described in Section 6 of this report. Test dates, start and end times for each test, and unit load are summarized in Table 5-1. As the data from Table 5-1 show, the Unit 2 tests were performed over a range of unit loads from 75 to 176 MW.

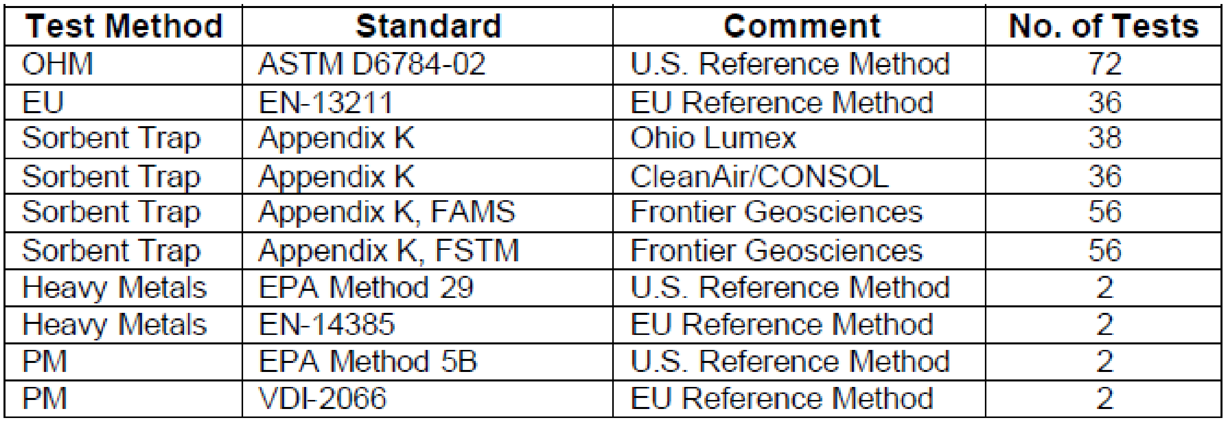
A direct comparison between the Reference Methods, Hg CMMs, and Sorbent Traps was performed at Armstrong Unit 2 during Tests 3 to 18. The results are presented in the following subsections. The total number of OHM, EU, and sorbent trap tests is summarized in Table 5-2.

Table 5-1 Test Dates, Start and End Times

TEST DATES AND TIMES

Unit	Date	Day	Pg	Test Number	Start Time	End Time	OHM Sampling Train
			MW				
1	7/8/2006	Saturday		1	14:00	15:30	A B
1	7/9/2006	Sunday	68	2	10:55	12:25	A B
2	7/10/2006	Monday	75	3	9:33	11:15	A B
2	7/10/2006		168	4	14:00	15:38	A B
2	7/11/2006	Tuesday	121	5	9:00	10:35	A B
2	7/11/2006		167	6	14:00	15:30	A B
2	7/12/2006	Wednesday	170	7	9:05	10:45	A B
2	7/12/2006		166	8	14:00	15:37	A B
2	7/13/2006	Thursday	170	9	9:13	10:47	A B
2	7/13/2006		170	10	13:55	15:30	A B
2	7/14/2006	Friday	175	11	9:17	11:02	A B
2	7/14/2006		175	12	14:08	15:45	A B
2	7/15/2006	Saturday	174	13	9:30	11:05	A B
2	7/15/2006		175	14	14:00	15:35	A B
2	7/16/2006	Sunday	176	15	9:40	11:20	A B
2	7/16/2006		176	16	13:10	14:48	A B
2	7/17/2006	Monday	174	17	9:15	10:52	A B
2	7/17/2006		174	18	14:08	15:46	A B

Table 5-2 Tests Performed at Armstrong



Test Method	Standard	Comment	No. of Tests
OHM	ASTM D6784-02	U.S. Reference Method	72
EU	EN-13211	EU Reference Method	36
Sorbent Trap	Appendix K	Ohio Lumex	38
Sorbent Trap	Appendix K	CleanAir/CONSOL	36
Sorbent Trap	Appendix K, FAMS	Frontier Geosciences	56
Sorbent Trap	Appendix K, FSTM	Frontier Geosciences	56
Heavy Metals	EPA Method 29	U.S. Reference Method	2
Heavy Metals	EN-14385	EU Reference Method	2
PM	EPA Method 5B	U.S. Reference Method	2
PM	VDI-2066	EU Reference Method	2

5.1. Coal and Ash Data

The coal and ash samples were collected three times per test day and analyzed for Hg, Cl, LOI, higher heating value (HHV), sulfur and other constituents. The coal data on the as-received (AR) basis is presented in Table 5-3, while the ash composition data is given in Table 5-4. Variation in the coal and ash composition during the test, presented in Figures 5-1 to 5-3, shows that coal properties have changed after Test 10 (July 13, 2006). During the first part of the test, coal from the local mines, delivered by trucks, was fired. This local coal resulted in high mercury emissions; in excess of 20 mg/dsm3. A low-mercury coal was ordered from a mine in Virginia and delivered to the Armstrong station by rail. This coal resulted in mercury emissions in the 7-10 mg/dsm3 range.

The Virginia coal also had a lower ash content, higher HHV (Figure 5-1), much lower Hg content (less than 50%), and lower Cl- content (Figure 5-2) compared to the local coals. The Cl-/Hg ratio for the Virginia coal, Figure 5-3, was more than 50 percent higher compared to the local coals.

The lower coal mercury content and higher Cl-/Hg ratio of the Virginia coal resulted in significantly lower Hg emissions (7-10 mg/dsm3) compared to the local coals (> 20 mg/dsm3), Figure 5-4. This change in coal properties allowed test data to be collected over a range of mercury concentrations from 7 - 23 mg/dsm3.

The effect of the Cl-/Hg ratio on mercury emissions, presented in Figure 5-5, shows that for the low values of that ratio, Hg emissions were affected significantly by an increase in the Cl-/Hg ratio. However, for values of the Cl-/Hg ratio higher than 5,500, this parameter had no effect on Hg emissions.

A correlation, with a correlation coefficient R2 = 0.8, between the total mercury concentration in flue gas, Hg T, and mercury content in coal is presented in Figure 5-6. The results show that the flue gas HgT concentration increases linearly with the coal mercury content. The Hg emission limit for Armstrong is also presented. The results show that the Hg emissions compliance at Armstrong cannot be achieved by coal switching alone. Additional mercury emissions control measures will be needed at Armstrong.

Table 5-3 Armstrong Coal Data on As-Received Basis

Armstrong Station						As Received Basis										
		Date	Test	ADL	Moisture	Ash	Vol. Mat	Sulfur	HHV	Carbon	Hydrogen	Nitrogen	Oxygen	Chloride	Mercury	Fluoride
Sample ID	Sample		No.		%	%	%	%	BTU/lb	%	%	%	%	ppm	ppm	ppm
4133	Composite Coal	03-Jul-06		5.52	7.23	13.84	28.73	2.10	**11,826**	65.98	5.19	1.28	11.61	1,367	**0.36**	62.45
4134	Composite Coal	04-Jul-06		5.65	7.42	8.93	32.62	1.97	**12,568**	70.96	5.54	1.39	11.20	1,213	**0.18**	46.31
4135	Composite Coal	05-Jul-06		5.67	7.44	8.09	33.23	1.96	**12,752**	71.38	5.67	1.38	11.52	1,150	**0.15**	25.52
4136	Composite Coal	06-Jul-06		6.38	8.05	7.45	33.91	1.97	**12,716**	73.02	5.62	1.40	10.55	1,075	**0.14**	27.01
4137	Composite Coal	07-Jul-06		5.33	7.20	10.48	32.13	1.98	**12,345**	69.57	5.47	1.39	11.11	1,152	**0.17**	36.23
4138	Composite Coal	08-Jul-06	**1**	5.42	7.26	13.71	27.73	2.00	**11,842**	67.17	5.12	1.25	10.75	1,271	**0.28**	38.86
4139	Composite Coal	10-Jul-06	**3**	5.93	7.81	14.05	28.53	2.05	**11,653**	65.46	5.14	1.27	12.02	1,216	**0.31**	55.55
4140	Composite Coal	10-Jul-06	**4**	6.03	7.99	13.50	27.57	2.00	**11,689**	65.90	5.15	1.25	12.20	1,242	**0.33**	57.96
4141	Composite Coal	11-Jul-06	**5**	5.64	7.68	12.90	28.25	2.15	**11,838**	63.98	5.13	1.22	14.62	1,237	**0.33**	55.94
4142	Composite Coal	11-Jul-06	**5**	5.41	7.59	13.58	28.00	2.15	**11,721**	66.96	5.06	1.26	10.99	1,211	**0.34**	54.89
4143	Composite Coal	11-Jul-06	**6**	5.96	8.01	13.33	28.41	2.21	**11,670**	65.89	5.17	1.26	12.14	1,208	**0.34**	68.16
4144	Composite Coal	12-Jul-06	**7**	5.80	7.83	15.67	28.12	2.13	**11,355**	64.09	5.04	1.21	11.86	1,192	**0.32**	64.69
4145	Composite Coal	12-Jul-06	**7**	5.71	7.85	14.78	28.11	1.99	**11,524**	65.43	5.10	1.26	11.43	1,276	**0.32**	61.77
4146	Composite Coal	12-Jul-06	**8**	6.05	8.26	13.87	28.15	2.18	**11,593**	65.96	5.14	1.25	11.59	1,289	**0.35**	63.46
4147	Composite Coal	13-Jul-06	**9**	5.02	6.71	15.22	27.86	1.94	**11,639**	65.52	5.00	1.22	11.10	1,228	**0.34**	64.45
4148	Composite Coal	13-Jul-06	**9**	5.50	7.21	14.01	27.55	1.95	**11,755**	68.70	5.16	1.25	8.92	1,306	**0.35**	58.75
4149	Composite Coal	13-Jul-06	**10**	6.16	7.92	13.18	28.03	2.16	**11,776**	67.17	5.22	1.22	11.05	1,315	**0.38**	55.83
4150	Composite Coal	14-Jul-06	**11**	4.56	6.22	8.27	34.61	2.13	**12,893**	74.22	5.61	1.39	8.38	1,051	**0.18**	40.88
4151	Composite Coal	14-Jul-06	**12**	4.53	6.14	7.90	35.47	2.26	**12,968**	74.23	5.58	1.41	8.61	956	**0.14**	24.42
4152	Composite Coal	15-Jul-06	**13**	4.71	6.29	8.06	35.44	2.32	**12,974**	73.60	5.65	1.51	8.86	883	**0.16**	22.96
4153	Composite Coal	15-Jul-06	**13**	4.41	6.07	7.71	35.47	2.23	**13,005**	74.25	5.67	1.41	8.75	889	**0.13**	43.24
4154	Composite Coal	15-Jul-06	**14**	4.55	6.09	7.64	35.55	2.22	**13,011**	74.10	5.61	1.36	9.08	919	**0.14**	28.11
4155	Composite Coal	16-Jul-06	**15**	4.65	6.21	7.55	35.49	2.19	**13,007**	74.20	5.64	1.39	9.03	903	**0.13**	23.65
4156	Composite Coal	16-Jul-06	**15**	4.44	6.10	7.58	35.47	2.24	**13,022**	74.33	5.65	1.44	8.76	918	**0.12**	24.57
4157	Composite Coal	16-Jul-06	**16**	5.16	6.80	7.43	35.21	2.24	**12,899**	74.26	5.69	1.38	8.99	925	**0.14**	27.18
4158	Composite Coal	17-Jul-06	**17**	5.13	6.72	7.61	35.27	2.22	**12,941**	74.03	5.68	1.39	9.06	932	**0.14**	63.24
4159	Composite Coal	17-Jul-06	**17**	4.84	6.38	7.53	35.43	2.34	**13,009**	74.25	5.66	1.37	8.86	899	**0.13**	32.18
4160	Composite Coal	17-Jul-06	**18**	4.87	6.45	7.48	35.37	2.26	**12,991**	71.79	5.65	1.37	11.46	929	**0.12**	51.37

Table 5-4 Armstrong Ash Composition Data

						Flyash				
	Armstrong Power Station	Date	Time	Test Number		Sulfur	Chloride	Mercury	Fluoride	LOI
Sample ID	Sample Name				Sample	%	ppm	ppm	ppm	%
4161	Flyash 7.10.06 12:00	10-Jul-06	12:00	3	Flyash	0.21	252	0.92	67	6.13
4162	Flyash 7.10.06 3:10	10-Jul-06	15:10	4	Flyash	0.18	247	0.55	34	7.70
4163	Flyash 7.11.06 11:30	11-Jul-06	11:30	5	Flyash	0.27	325	0.73	71	12.37
4164	Flyash 7.11.06 4:40	11-Jul-06	16:40	6	Flyash	0.21	264	1.38	68	8.52
4165	Flyash 7.12.06 8:00	12-Jul-06	8:00	7	Flyash	0.14	261	0.85	50	4.78
4166	Flyash 7.12.06 12:00	12-Jul-06	12:00	8	Flyash	0.16	308	0.64	31	5.48
4167	Flyash 7.13.06 8:00	13-Jul-06	8:00	9	Flyash	0.18	236	0.83	29	6.49
4168	Flyash 7.13.06	13-Jul-06		10	Flyash	0.14	276	0.58	40	4.94
4169	Flyash 7.14.06 9:00	14-Jul-06	9:00	11	Flyash	0.28	254	0.53	53	11.70
4170	Flyash 7.14.06 1:00	14-Jul-06	13:00	12	Flyash	0.27	232	0.38	41	12.57
4171	Flyash 7.15.06 9:00	15-Jul-06	9:00	13	Flyash	0.32	258	0.61	44	13.59
4172	Flyash 7.15.06 1:00	15-Jul-06	13:00	14	Flyash	0.35	230	0.33	41	11.37
4173	Flyash 7.16.06 8:00	16-Jul-06	8:00	15	Flyash	0.31	267	1.01	61	19.75
4174	Flyash 7.16.06 1:30	16-Jul-06	13:30	16	Flyash	0.36	185	0.36	46	14.19
4175	Flyash 7.17.06 9:00	17-Jul-06	9:00	17	Flyash	0.35	258	0.30	28	9.90

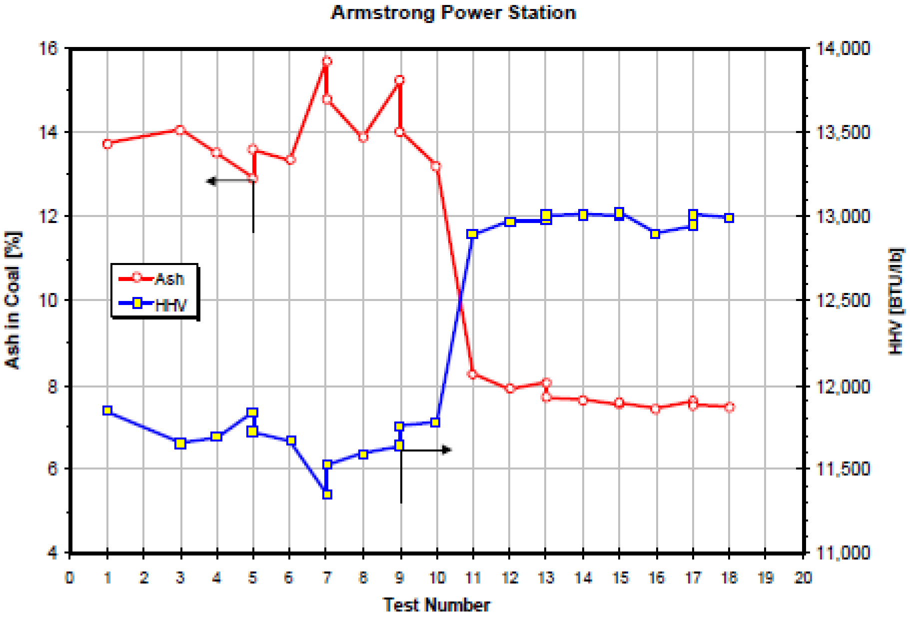


Figure 5-1: Ash Content and HHV of As-Received Coal

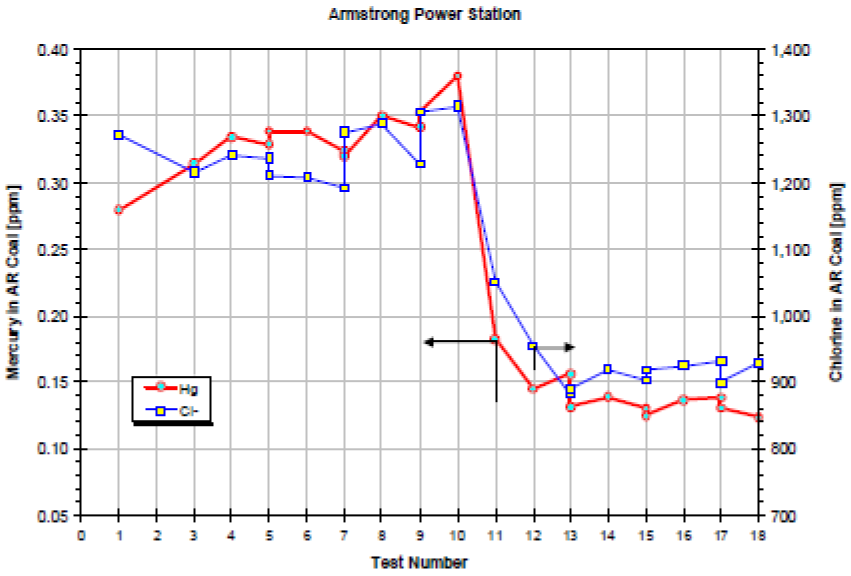


Figure 5-2: Mercury and Chlorine in As-Received Coal

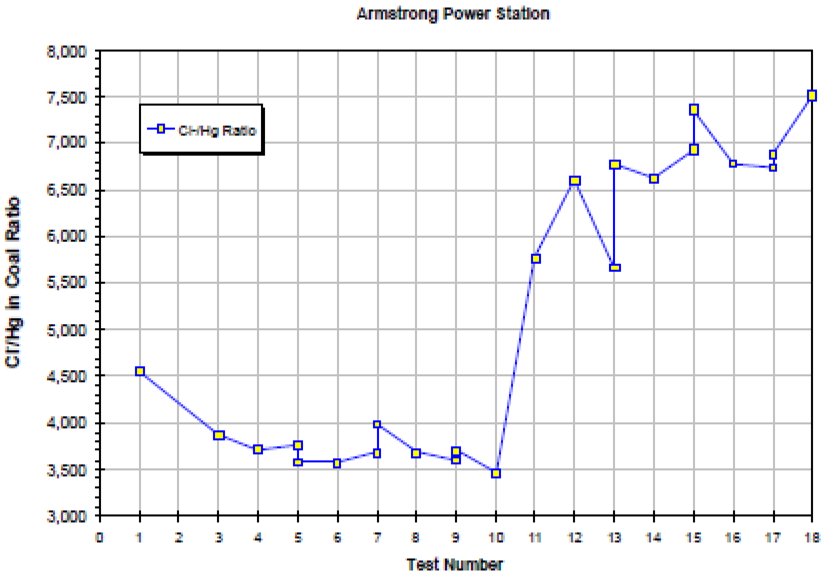


Figure 5-3: Coal Cl-/Hg Ratio

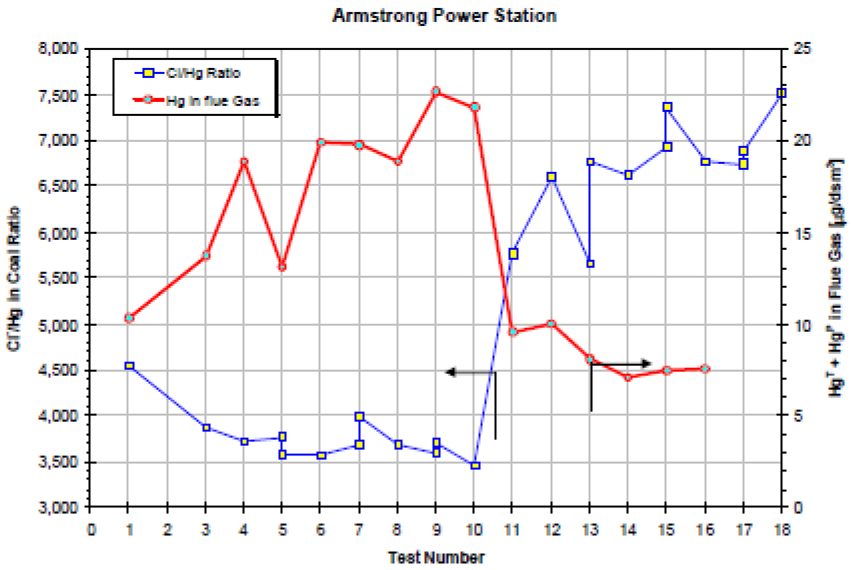


Figure 5-4: Coal Cl-/Hg Ratio and Mercury in Flue Gas

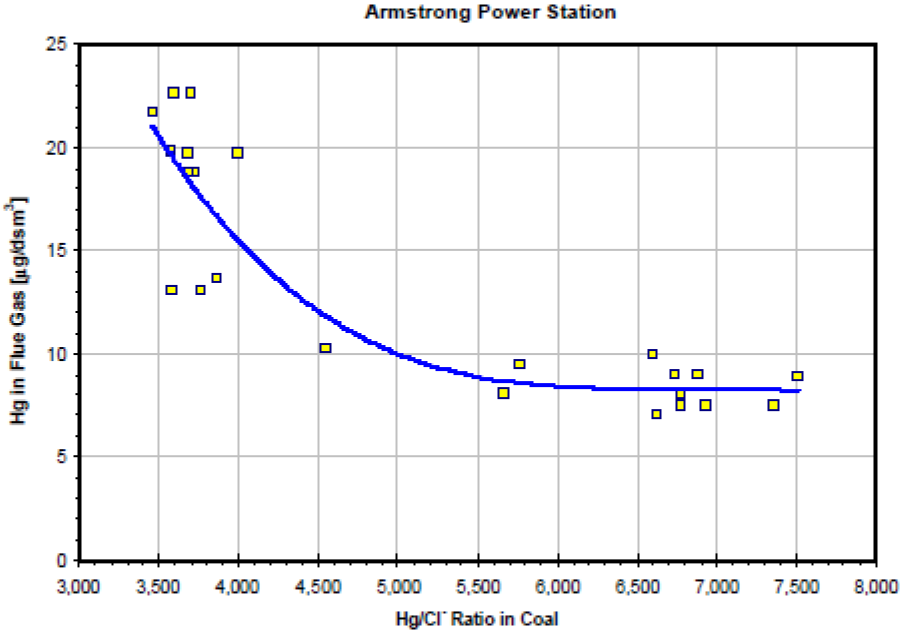


Figure 5-5: Gas-Phase Hg as a Function of Coal Cl-/Hg Ratio

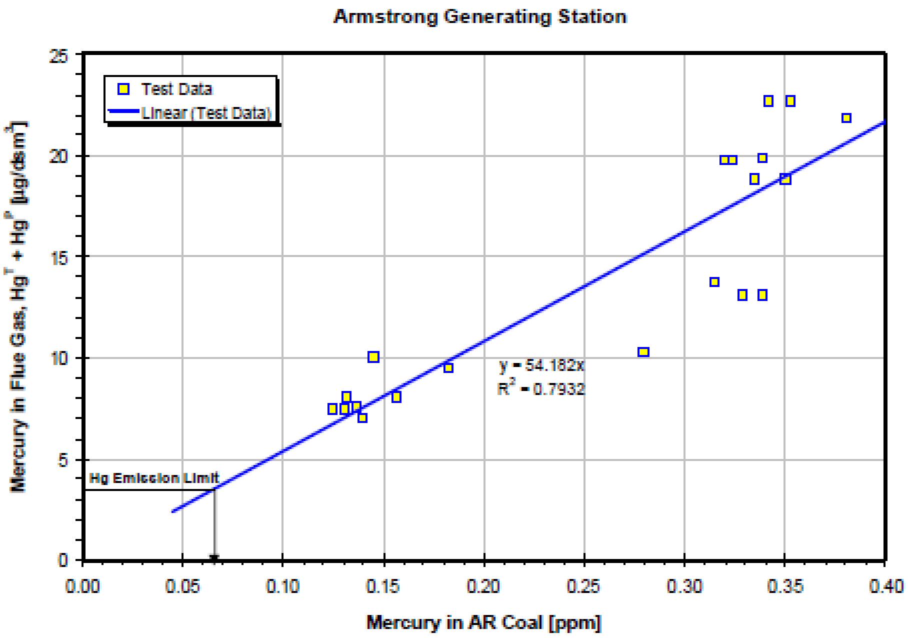


Figure 5-6: Mercury in Flue Gas as a Function of Coal Mercury Content

5.2. Units of Measure

After receiving raw data from the test teams participating in the Armstrong field test and CMM data from the Hg CEM vendors, it was realized that different units of measure are used by different teams and instruments. To ensure an accurate and fair comparison of the results, a significant effort was devoted to obtain reliable information on actual units of measure used by the test teams and Hg CEM manufacturers. The results are summarized in Table 5-4. The standard conditions (STP), as stipulated in EPA regulations, are:

Standard Temperature = 20°C (68°F)

Standard Pressure = 22.921 “Hg (760 mmHg, or 101,300 N/m2).

The standard units of measure for mercury, as required by EPA regulations are mg/dsm3 or mg/wsm3. The standard cubic meter, sm3, is unfortunately often confused with a normal cubic meter, Nm3. The normal cubic meter is defined as a mass of gas at 0°C (32°F) and standard pressure. The difference between the standard and normal cubic meters is 6.8 percent. Therefore, if mercury concentration is reported in Nm3, it has to be multiplied by a correction factor of 0.93176 to get mercury concentration in sm3.

As Table 5-5 shows, a variety of “standard” conditions were used by the test teams in CMM manufacturers. All raw data obtained at Armstrong were corrected to the EPA STP conditions using correction factors from Table 5-5.

Table 5-5 Units of Measure, Standard Conditions, and Correction Factors

			Standard Pressure			Standard Temperature			Unit of Measure	Comment	Molar Volume	Difference	Correction
Vendor	Measurement	Basis	inches Hg	mm Hg	N/m^2	Deg. F	Deg. C	Deg. K			m^3/kmol	%	Factor
Ohio Lumex/Apex	Sorbent Traps	Dry	29.921	760	101,300	68	20.00	293.15	µg/dsm^3	EPA-STP, Standard	24.060	0.0	1.000000
CleanAir/CONSOL	Sorbent Traps	Dry	29.921	760	101,300	68	20.00	293.15	µg/dsm^3	EPA-STP, Standard	24.060	0.0000	1.000000
Frontier Geoscience	Sorbent Traps	Dry	29.921	760	101,300	70	21.11	294.26	µg/ds'm^3	Not a standard STP	24.151	0.3790	1.003790
WKU	OHM	Dry	29.921	760	101,300	68	20.00	293.15	µg/dsm^3	EPA-STP, Standard	24.060	0.0000	1.000000
CESI	OHM	Dry	29.921	760	101,300	32	0.00	273.15	µg/dNm^3	EU-STP	22.418	-6.8224	0.931776
Ohio Lumex	CMM	Wet	29.921	760	101,300	32	0.00	273.15	µg/wNm^3	EU-STP	22.418	-6.8224	0.931776
Tekran	CMM	Wet	29.921	760	101,300	32	0.00	273.15	µg/wNm^3	EU-STP, Used at Armstrong	22.418	-6.8224	0.931776
			29.921	760	101,300	68	20.00	293.15	µg/wsm^3	EPA-STP	24.060	0.0000	1.000000
Thermo Electron	CMM	Wet	29.921	760	101,300	68	20.00	293.15	µg/wsm^3	EPA-STP	24.060	0.0000	1.000000
GE-PSA	CMM	Wet	29.921	760	101,300	68	20.00	293.15	µg/wsm^3	EPA-STP	24.060	0.0000	1.000000
Horiba	CMM												

5.3. OHM Results

The OHM test results from Armstrong are summarized in Tables 5-6 and 5-7. The total gas-phase (Hg+2 and Hg0) and particulate-bound (HgP) mercury concentrations, measured by two paired OHM trains, are presented in Table 5-6 on a dry basis. As described previous ly, Tests 1 and 2 were performed on Unit 1, Tests 3 – 10 were performed on Unit 2 with high-Hg coal from the local mines, and Tests 11 – 18 were conducted on Unit 2 with the low-Hg Virginia coal. The relative difference (RD) between paired trains is also presented. For Port 1, the average value of RD is 6.2 percent, while the Port 3 average value of RD is 4.2 percent. The RD value exceeded 10 percent for only one test: Test 6 and Port 3.

Mercury concentrations, obtained on a dry basis, were corrected to a wet basis using the expression: wet = dry x (1- moisture). The OHM results, expressed on a wet basis, are presented in Table 5-7. The average RD value for Port 1 is 5.7 percent; for Port 3 it is 4 percent. With the results expressed on a wet basis, the RD values were somewhat lower compared to the dry basis results. The RD value exceeded 10 percent for Test 6 and Port 3.

The flue gas moisture content, measured during the test and summarized in Table 5-8, was used to perform the dry to wet conversion. The average value of the flue gas moisture content for all tests was approximately 8.2 percent. The excess O2 levels, measured by a calibrated O2 analyzer at the OHM flow control box are also presented. The average O2 level, measured on a dry basis at the OHM flow control box, was 7.6 percent.

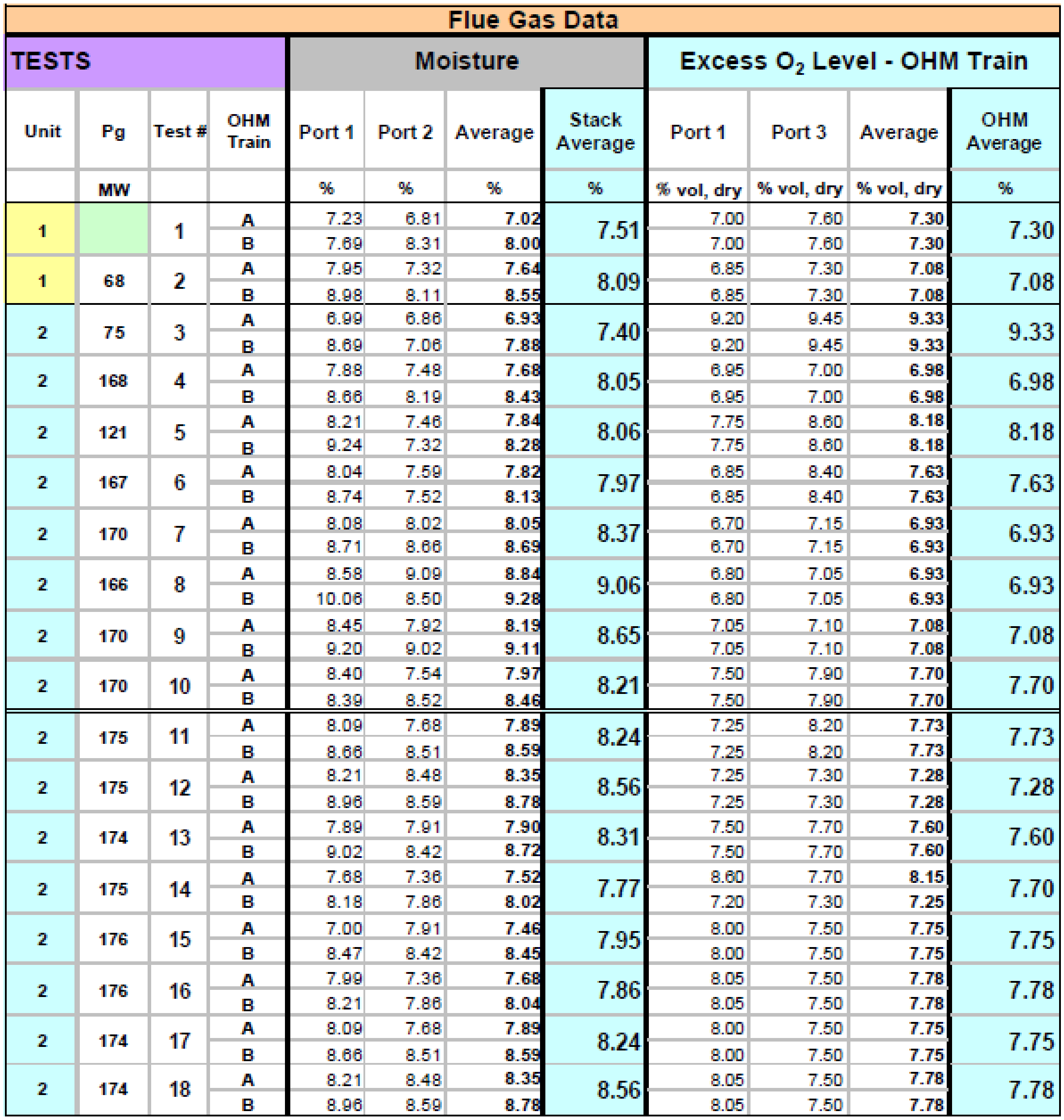
Table 5-6 OHM Results Expressed on a Dry Basis

TESTS				OHM, Dry-Gas Phase Only						OHM, Dry-Particulates				OHM, Dry-Total			
Unit	Pg	Test #	OHM Train	Port 1	RD Port 1	Port 3	RD Port 3	Average	Stack Average	Port 1	Port 3	Average	Stack Average	Port 1	Port 3	Average	Stack Average
	MW			µg/dsm³	%	µg/dsm³	%	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³
1		1	A	10.04		10.75		10.40	10.27	0.03	0.03	0.03	0.03	10.07	10.78	10.43	10.30
			B	10.86	3.9	9.41	6.6	8.06		0.03	0.03	0.03		10.89	9.44	10.17	
1	68	2	A	11.40		11.44		11.42	12.20	0.03	0.04	0.04	0.04	11.43	11.48	11.46	12.24
			B	12.67	5.3	13.29	7.5	10.41		0.03	0.04	0.04		12.70	13.33	13.02	
2	75	3	A	12.46		15.02		13.74	13.67	0.03	0.04	0.04	0.04	12.49	15.06	13.78	13.71
			B	13.98	5.7	13.22	6.4	10.98		0.03	0.04	0.04		14.01	13.26	13.64	
2	168	4	A	18.22		17.39		17.81	18.81	0.03	0.03	0.03	0.03	18.25	17.42	17.84	18.84
			B	20.22	5.2	19.40	5.5	14.94		0.03	0.03	0.03		20.25	19.43	19.84	
2	121	5	A	12.26		13.02		12.64	13.08	0.03	0.03	0.03	0.03	12.29	13.05	12.67	13.11
			B	14.76	9.3	12.29	2.9	12.10		0.03	0.03	0.03		14.79	12.32	13.56	
2	167	6	A	20.32		20.78		20.55	19.85	0.05	0.03	0.04	0.04	20.37	20.81	20.59	19.89
			B	21.86	3.7	16.44	11.7	13.98		0.05	0.03	0.04		21.91	16.47	19.19	
2	170	7	A	18.36		19.26		18.81	19.70	0.05	0.06	0.06	0.06	18.41	19.32	18.87	19.75
			B	21.76	8.5	19.40	0.4	16.54		0.05	0.06	0.06		21.81	19.46	20.64	
2	166	8	A	18.18		18.52		18.35	18.79	0.05	0.06	0.06	0.06	18.23	18.58	18.41	18.85
			B	20.58	6.2	17.88	1.8	14.88		0.05	0.06	0.06		20.63	17.94	19.29	
2	170	9	A	20.01		22.81		21.41	22.61	0.05	0.04	0.05	0.05	20.06	22.85	21.46	22.65
			B	23.53	8.1	24.08	2.7	18.56		0.05	0.04	0.05		23.58	24.12	23.85	
2	170	10	A	22.90		21.04		21.97	21.77	0.03	0.04	0.04	0.04	22.93	21.08	22.01	21.80
			B	19.91	7.0	23.22	4.9	16.70		0.03	0.04	0.04		19.94	23.26	21.60	
2	175	11	A	9.50		8.76		9.13	9.52	0.03	0.03	0.03	0.03	9.53	8.79	9.16	9.55
			B	10.08	3.0	9.72	5.2	7.59		0.03	0.03	0.03		10.11	9.75	9.93	
2	175	12	A	9.45		9.66		9.56	9.97	0.04	0.03	0.04	0.04	9.49	9.69	9.59	10.00
			B	10.91	7.2	9.85	1.0	9.31		0.04	0.03	0.04		10.95	9.88	10.42	
2	174	13	A	7.44		7.79		7.62	8.05	0.03	0.04	0.04	0.04	7.47	7.83	7.65	8.08
			B	8.54	6.9	8.42	3.9	7.95		0.03	0.04	0.04		8.57	8.46	8.52	
2	175	14	A	6.58		6.75		6.67	7.03	0.03	0.06	0.05	0.05	6.61	6.81	6.71	7.08
			B	7.22	4.6	7.58	5.8	6.48		0.03	0.06	0.05		7.25	7.64	7.45	
2	176	15	A	6.73		7.32		7.03	7.42	0.04	0.05	0.05	0.05	6.77	7.37	7.07	7.47
			B	8.09	9.2	7.54	1.5	8.27		0.04	0.05	0.05		8.13	7.59	7.86	
2	176	16	A	6.67		7.36		7.02	7.49	0.04	0.05	0.05	0.05	6.71	7.41	7.06	7.53
			B	7.91	8.5	8.00	4.2	8.14		0.04	0.05	0.05		7.95	8.05	8.00	
2	174	17	A	8.09		9.71		8.90	8.99	0.04	0.05	0.05	0.05	8.13	9.76	8.95	9.03
			B	7.40	4.5	10.75	5.1	7.53		0.04	0.05	0.05		7.44	10.80	9.12	
2	174	18	A	9.07		8.28		8.68	8.91	0.03	0.05	0.04	0.04	9.10	8.33	8.72	8.95
			B	9.81	3.9	8.46	1.1	7.40		0.03	0.05	0.04		9.84	8.51	9.18	

Table 5-7 OHM Results Expressed on a Wet Basis

TESTS				OHM, Wet-Gas Phase Only				OHM, Wet-Particulates				OHM, Wet-Total					
Unit	Pg	Test #	OHM Train	Port 1	Port 3	Average	Stack Average	Port 1	Port 3	Average	Stack Average	Port 1	RD Port 1	Port 3	RD Port 3	Average	Stack Average
	MW			µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	%	µg/wsm³	%	µg/wsm³	µg/wsm³
1		1	A	9.31	10.02	**9.67**	9.50	0.028	0.028	**0.028**	0.028	9.34		10.05		**9.69**	9.52
			B	10.02	8.63	**9.33**		0.028	0.028	**0.028**		10.05	**3.7**	8.66	**7.4**	**7.46**	
1	68	2	A	10.49	10.60	**10.55**	11.21	0.028	0.037	**0.032**	0.032	10.52		10.64		**10.58**	11.24
			B	11.53	12.21	**11.87**		0.027	0.037	**0.032**		11.56	**4.7**	12.25	**7.0**	**9.50**	
2	75	3	A	11.59	13.99	**12.79**	12.66	0.028	0.037	**0.033**	0.032	11.62		14.03		**12.82**	12.69
			B	12.77	12.29	**12.53**		0.027	0.037	**0.032**		12.79	**4.8**	12.32	**6.5**	**9.98**	
2	168	4	A	16.78	16.09	**16.44**	17.29	0.028	0.028	**0.028**	0.028	16.81		16.12		**16.46**	17.32
			B	18.47	17.81	**18.14**		0.027	0.028	**0.027**		18.50	**4.8**	17.84	**5.1**	**13.70**	
2	121	5	A	11.25	12.05	**11.65**	12.02	0.028	0.028	**0.028**	0.028	11.28		12.08		**11.68**	12.05
			B	13.40	11.39	**12.39**		0.027	0.028	**0.028**		13.42	**8.7**	11.42	**2.8**	**11.17**	
2	167	6	A	18.69	19.20	**18.94**	18.26	0.046	0.028	**0.037**	0.037	18.73		19.23		**18.98**	18.30
			B	19.95	15.20	**17.58**		0.046	0.028	**0.037**		20.00	**3.3**	15.23	**11.6**	**12.83**	
2	170	7	A	16.88	17.72	**17.30**	18.04	0.046	0.055	**0.051**	0.050	16.92		17.77		**17.35**	18.09
			B	19.86	17.72	**18.79**		0.046	0.055	**0.050**		19.91	**8.1**	17.77	**0.0**	**15.27**	
2	166	8	A	16.62	16.84	**16.73**	17.08	0.046	0.055	**0.050**	0.050	16.67		16.89		**16.78**	17.13
			B	18.51	16.36	**17.43**		0.045	0.055	**0.050**		18.55	**5.4**	16.42	**1.4**	**13.44**	
2	170	9	A	18.32	21.00	**19.66**	20.65	0.046	0.037	**0.041**	0.041	18.36		21.04		**19.70**	20.69
			B	21.37	21.91	**21.64**		0.045	0.036	**0.041**		21.41	**7.7**	21.94	**2.1**	**17.00**	
2	170	10	A	20.98	19.45	**20.21**	19.98	0.027	0.037	**0.032**	0.032	21.00		19.49		**20.25**	20.01
			B	18.24	21.24	**19.74**		0.027	0.037	**0.032**		18.27	**7.0**	21.28	**4.4**	**15.50**	
2	175	11	A	8.73	8.09	**8.41**	8.73	0.028	0.028	**0.028**	0.028	8.76		8.11		**8.44**	8.76
			B	9.21	8.89	**9.05**		0.027	0.027	**0.027**		9.23	**2.6**	8.92	**4.7**	**6.93**	
2	175	12	A	8.67	8.84	**8.76**	9.11	0.037	0.027	**0.032**	0.032	8.71		8.87		**8.79**	9.14
			B	9.93	9.00	**9.47**		0.036	0.027	**0.032**		9.97	**6.7**	9.03	**0.9**	**8.58**	
2	174	13	A	6.85	7.17	**7.01**	7.38	0.028	0.037	**0.032**	0.032	6.88		7.21		**7.05**	7.41
			B	7.77	7.71	**7.74**		0.027	0.037	**0.032**		7.80	**6.2**	7.75	**3.6**	**7.26**	
2	175	14	A	6.07	6.25	**6.16**	6.49	0.028	0.056	**0.042**	0.042	6.10		6.31		**6.21**	6.53
			B	6.63	6.98	**6.81**		0.028	0.055	**0.041**		6.66	**4.3**	7.04	**5.5**	**6.01**	
2	176	15	A	6.26	6.74	**6.50**	6.83	0.037	0.046	**0.042**	0.041	6.30		6.79		**6.54**	6.87
			B	7.40	6.91	**7.15**		0.037	0.046	**0.041**		7.44	**8.3**	6.95	**1.2**	**7.58**	
2	176	16	A	6.14	6.82	**6.48**	6.90	0.037	0.046	**0.042**	0.041	6.17		6.86		**6.52**	6.94
			B	7.26	7.37	**7.32**		0.037	0.046	**0.041**		7.30	**8.3**	7.42	**3.9**	**7.68**	
2	174	17	A	7.44	8.96	**8.20**	8.25	0.037	0.046	**0.041**	0.041	7.47		9.01		**8.24**	8.29
			B	6.76	9.84	**8.30**		0.037	0.046	**0.041**		6.80	**4.7**	9.88	**4.6**	**7.14**	
2	174	18	A	8.33	7.58	**7.95**	8.14	0.028	0.046	**0.037**	0.037	8.35		7.62		**7.99**	8.18
			B	8.93	7.73	**8.33**		0.027	0.046	**0.037**		8.96	**3.5**	7.78	**1.0**	**6.74**	

Table 5-8 Measured Flue Gas Moisture and Excess O2 Levels

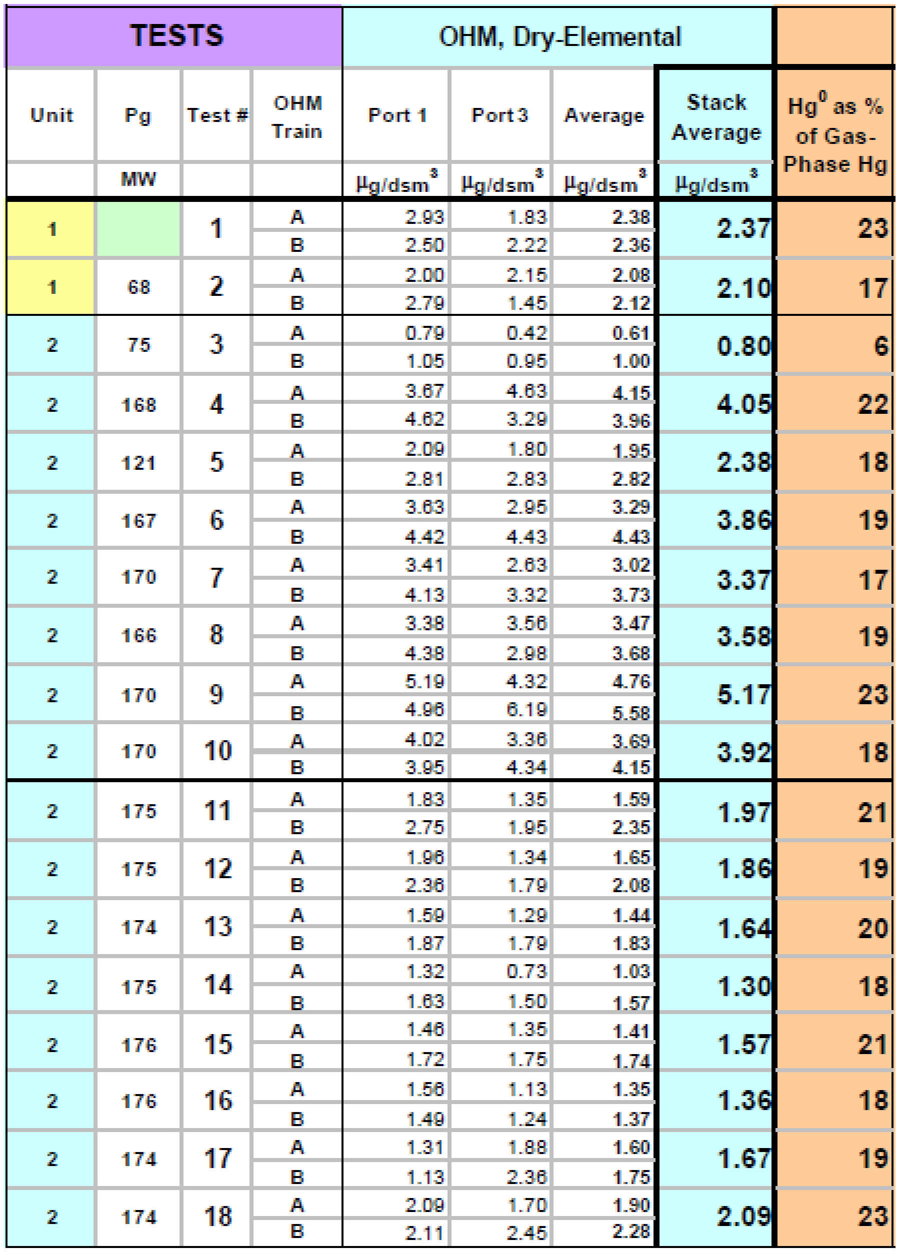


Flue Gas Data											
TESTS				Moisture				Excess O_2 Level - OHM Train			
Unit	Pg	Test #	OHM Train	Port 1	Port 2	Average	Stack Average	Port 1	Port 3	Average	OHM Average
	MW			%	%	%	%	% vol, dry	% vol, dry	% vol, dry	%
1		1	A	7.23	6.81	7.02	7.51	7.00	7.60	7.30	7.30
			B	7.69	8.31	8.00		7.00	7.60	7.30	
1	68	2	A	7.95	7.32	7.64	8.09	6.85	7.30	7.08	7.08
			B	8.98	8.11	8.55		6.85	7.30	7.08	
2	75	3	A	6.99	6.86	6.93	7.40	9.20	9.45	9.33	9.33
			B	8.69	7.06	7.88		9.20	9.45	9.33	
2	168	4	A	7.88	7.48	7.68	8.05	6.95	7.00	6.98	6.98
			B	8.66	8.19	8.43		6.95	7.00	6.98	
2	121	5	A	8.21	7.46	7.84	8.06	7.75	8.60	8.18	8.18
			B	9.24	7.32	8.28		7.75	8.60	8.18	
2	167	6	A	8.04	7.59	7.82	7.97	6.85	8.40	7.63	7.63
			B	8.74	7.52	8.13		6.85	8.40	7.63	
2	170	7	A	8.08	8.02	8.05	8.37	6.70	7.15	6.93	6.93
			B	8.71	8.66	8.69		6.70	7.15	6.93	
2	166	8	A	8.58	9.09	8.84	9.06	6.80	7.05	6.93	6.93
			B	10.06	8.50	9.28		6.80	7.05	6.93	
2	170	9	A	8.45	7.92	8.19	8.65	7.05	7.10	7.08	7.08
			B	9.20	9.02	9.11		7.05	7.10	7.08	
2	170	10	A	8.40	7.54	7.97	8.21	7.50	7.90	7.70	7.70
			B	8.39	8.52	8.46		7.50	7.90	7.70	
2	175	11	A	8.09	7.68	7.89	8.24	7.25	8.20	7.73	7.73
			B	8.66	8.51	8.59		7.25	8.20	7.73	
2	175	12	A	8.21	8.48	8.35	8.56	7.25	7.30	7.28	7.28
			B	8.96	8.59	8.78		7.25	7.30	7.28	
2	174	13	A	7.89	7.91	7.90	8.31	7.50	7.70	7.60	7.60
			B	9.02	8.42	8.72		7.50	7.70	7.60	
2	175	14	A	7.68	7.36	7.52	7.77	8.60	7.70	8.15	7.70
			B	8.18	7.86	8.02		7.20	7.30	7.25	
2	176	15	A	7.00	7.91	7.46	7.95	8.00	7.50	7.75	7.75
			B	8.47	8.42	8.45		8.00	7.50	7.75	
2	176	16	A	7.99	7.36	7.68	7.86	8.05	7.50	7.78	7.78
			B	8.21	7.86	8.04		8.05	7.50	7.78	
2	174	17	A	8.09	7.68	7.89	8.24	8.00	7.50	7.75	7.75
			B	8.66	8.51	8.59		8.00	7.50	7.75	
2	174	18	A	8.21	8.48	8.35	8.56	8.05	7.50	7.78	7.78
			B	8.96	8.59	8.78		8.05	7.50	7.78	

5.3.1. Elemental Mercury

Since OHM is a speciation method, elemental mercury (Hg0) concentration was measured in addition to the oxidized (Hg+2) and particulate-bound (HgP) mercury. Measured Hg0 concentrations are summarized in Table 5-9. The results show that, at Armstrong, elemental mercury represents approximately 20 percent of the total gasphase mercury.

Table 5-9 Elemental Mercury Concentration at Armstrong



TESTS				OHM, Dry-Elemental				
Unit	Pg	Test #	OHM Train	Port 1	Port 3	Average	Stack Average	Hg^0 as % of Gas-Phase Hg
	MW			µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	
1		1	A	2.93	1.83	2.38	2.37	23
			B	2.50	2.22	2.36		
1	68	2	A	2.00	2.15	2.08	2.10	17
			B	2.79	1.45	2.12		
2	75	3	A	0.79	0.42	0.61	0.80	6
			B	1.05	0.95	1.00		
2	168	4	A	3.67	4.63	4.15	4.05	22
			B	4.62	3.29	3.96		
2	121	5	A	2.09	1.80	1.95	2.38	18
			B	2.81	2.83	2.82		
2	167	6	A	3.63	2.95	3.29	3.86	19
			B	4.42	4.43	4.43		
2	170	7	A	3.41	2.63	3.02	3.37	17
			B	4.13	3.32	3.73		
2	166	8	A	3.38	3.56	3.47	3.58	19
			B	4.38	2.98	3.68		
2	170	9	A	5.19	4.32	4.76	5.17	23
			B	4.96	6.19	5.58		
2	170	10	A	4.02	3.36	3.69	3.92	18
			B	3.95	4.34	4.15		
2	175	11	A	1.83	1.35	1.59	1.97	21
			B	2.75	1.95	2.35		
2	175	12	A	1.96	1.34	1.65	1.86	19
			B	2.36	1.79	2.08		
2	174	13	A	1.59	1.29	1.44	1.64	20
			B	1.87	1.79	1.83		
2	175	14	A	1.32	0.73	1.03	1.30	18
			B	1.63	1.50	1.57		
2	176	15	A	1.46	1.35	1.41	1.57	21
			B	1.72	1.75	1.74		
2	176	16	A	1.56	1.13	1.35	1.36	18
			B	1.49	1.24	1.37		
2	174	17	A	1.31	1.88	1.60	1.67	19
			B	1.13	2.36	1.75		
2	174	18	A	2.09	1.70	1.90	2.09	23
			B	2.11	2.45	2.28		

5.3.2. Particulate-Bound Mercury

As presented in Tables 5-6 and 5-7, at Armstrong, the particulate-bound mercury (HgP) is very low (0.03 to 0.05 mg/dsm3) and represents a very small fraction of the total mercury (approximately 0.1 – 0.2 percent). This is expected since Armstrong Generating Station is equipped with two ESPs and the average opacity (representing particulate loading in the flue gas stream) is very lo w, of the order of 3 percent or less. Therefore, at Armstrong, the particulate-bound mercury can be neglected in the analysis.

The OHM results are also presented in graphical form in Figures 5-7 to 5-11. The stack-average total (HgT) mercury concentration measured in 18 tests at Armstrong, and expressed on a wet basis, is presented in Figure 5-7. The stackaverage value was determined as an average of four individual measurements obtained from two paired OHM sampling trains. The change in mercury emissions due to the coal change after Test 10 is easily discernable.

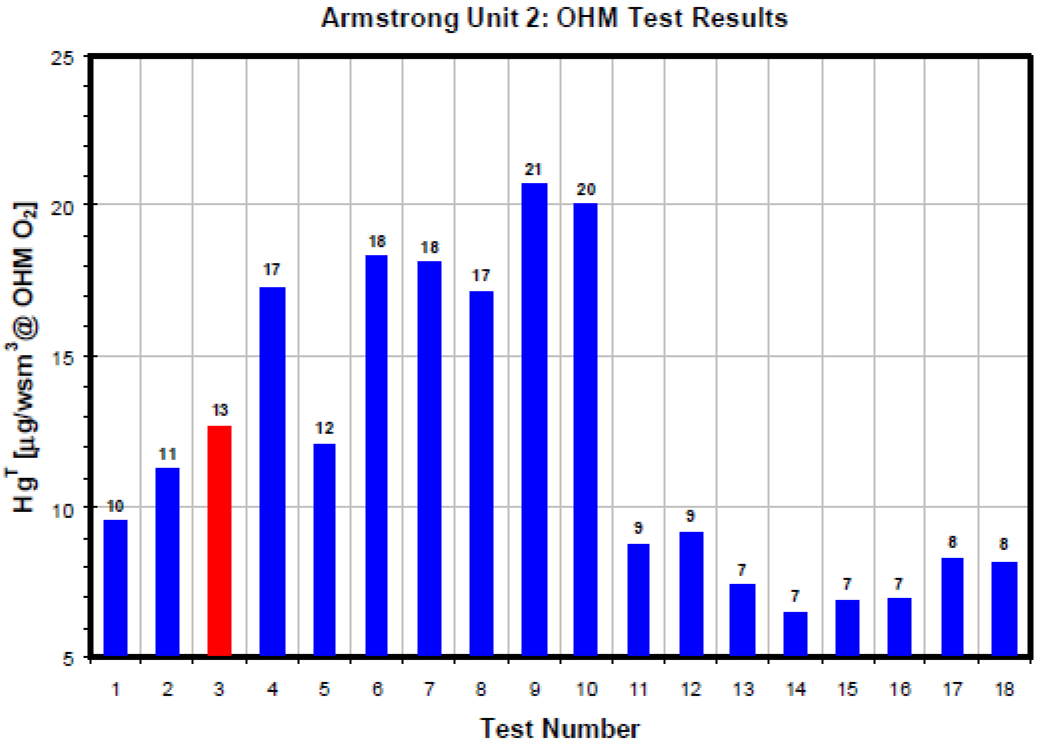


Figure 5 -7: Stack-Average HgT Concentration Measured by Two Paired OHM Sampling Trains

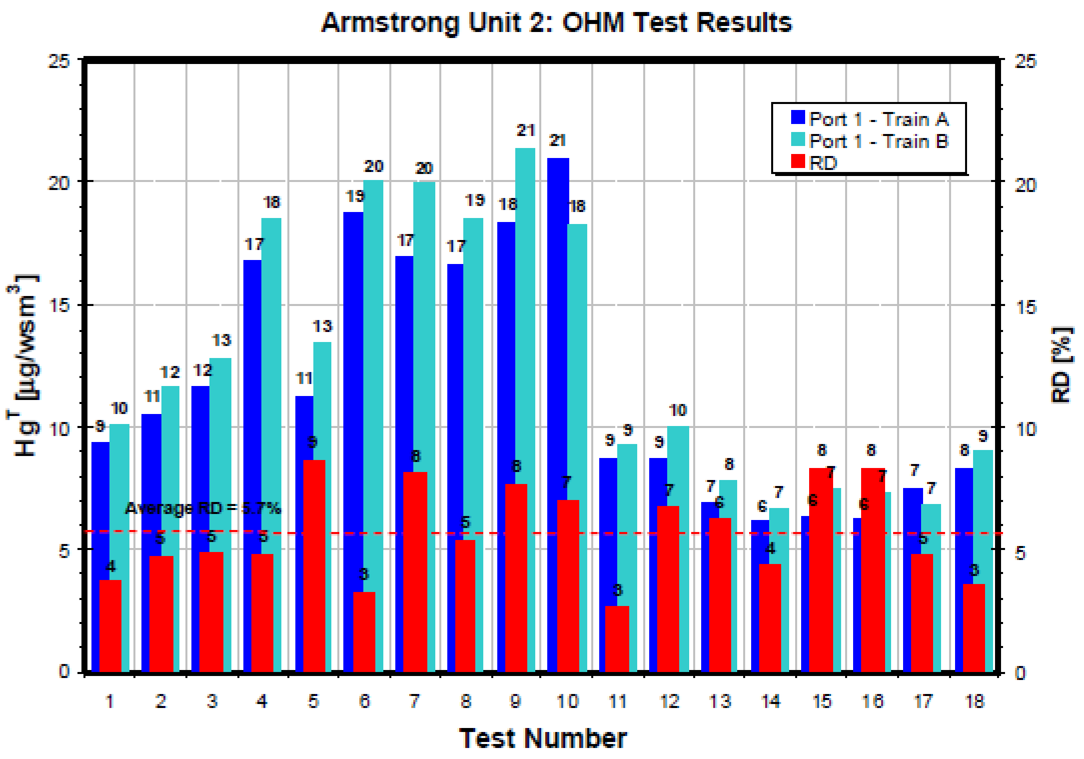


Figure 5-8: HgT and RD: Paired OHM Sampling Trains A and B at Port 1

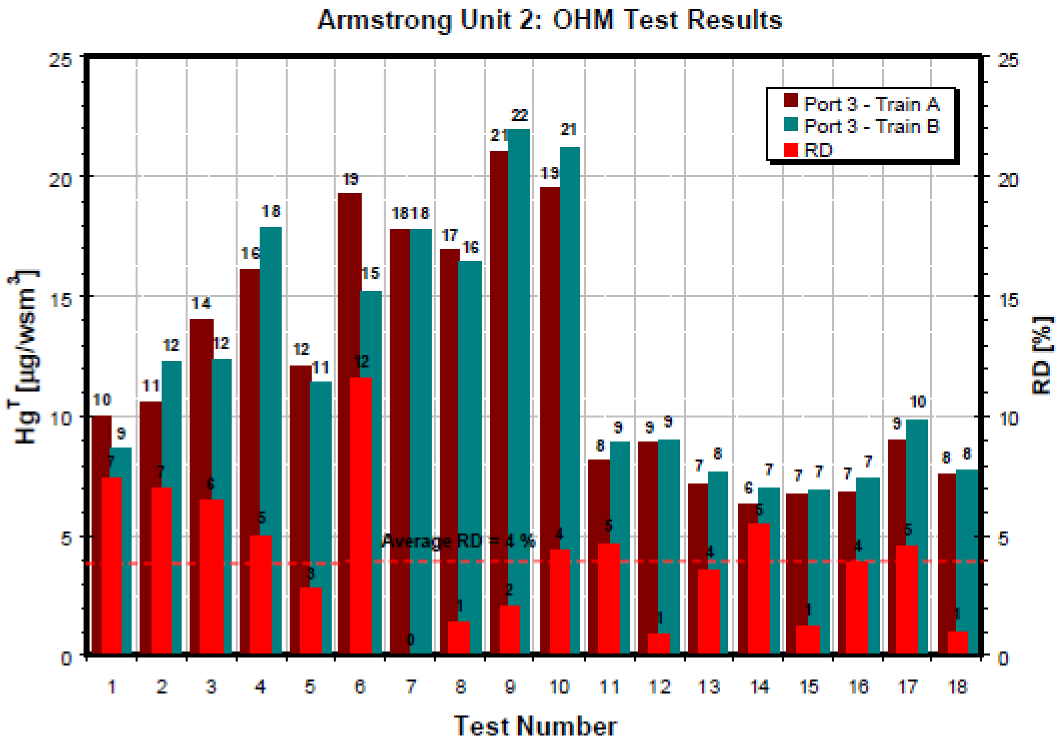


Figure 5-9: HgT and RD: Paired OHM Sampling Trains A and B at Port 3

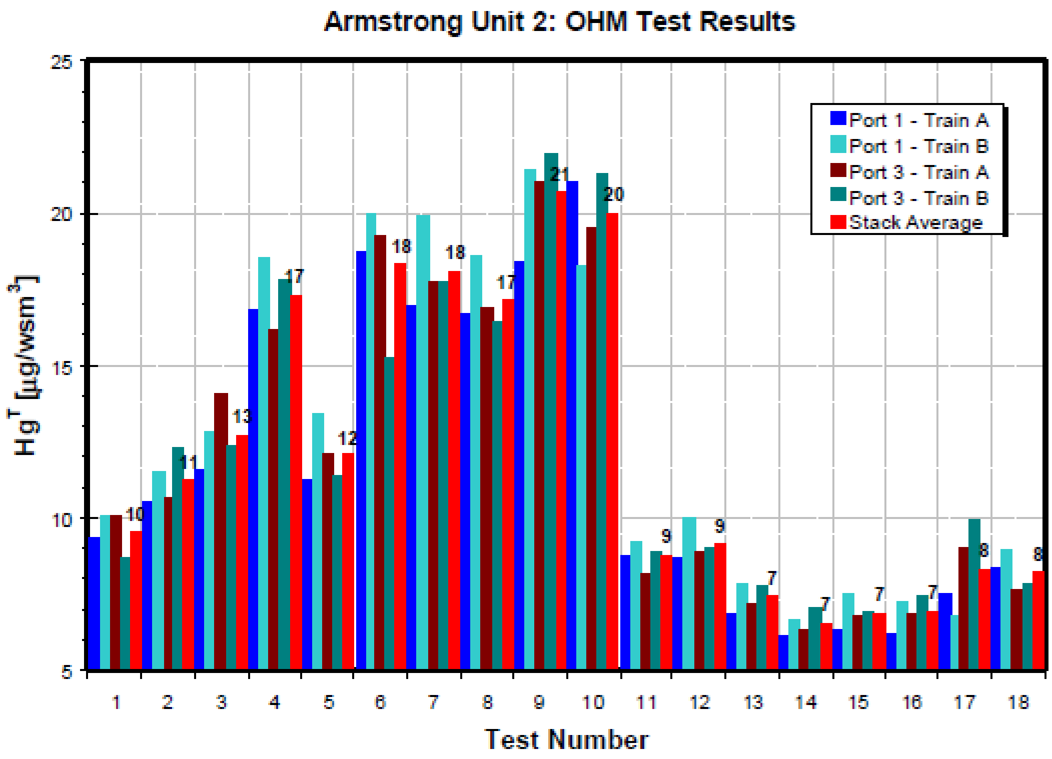


Figure 5-10: HgT Values Measured by Two Paired OHM Trains at Ports 1 and 3

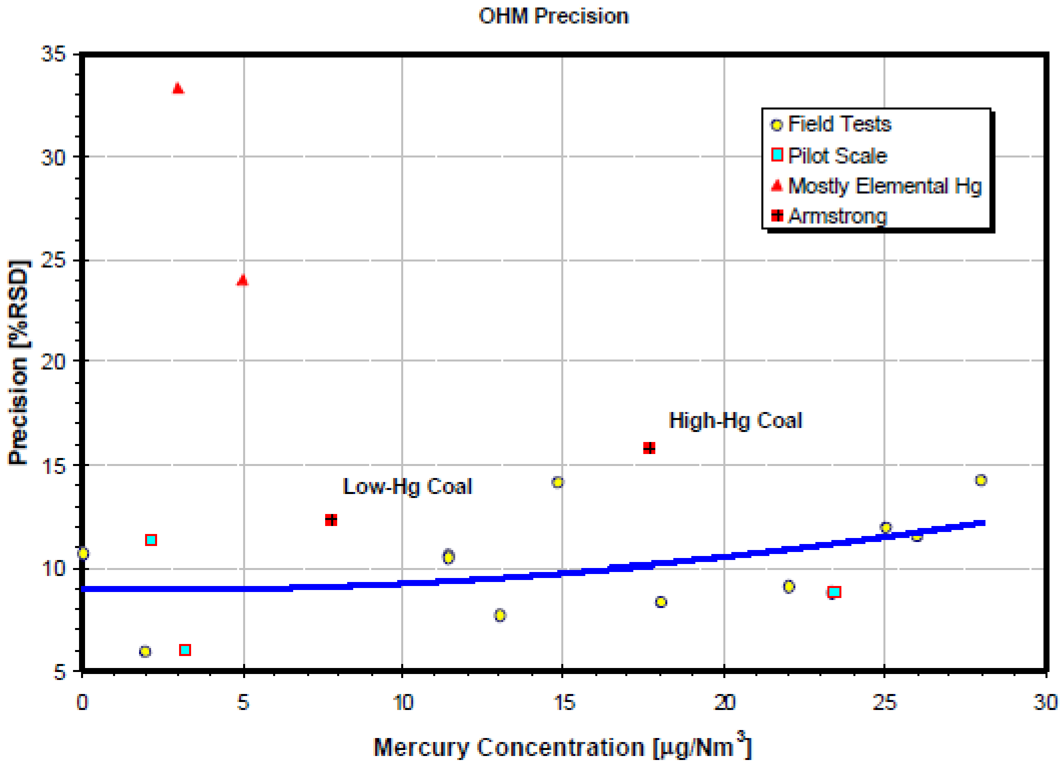


Figure 5-11: Precision of the OHM Tests

Although sootblowing was put on hold during the test, near the end of Test 3 the unit operator initiated sootblowing which affected mercury measurements. To indicate this, results for Test 3 are shown in the color red in Figure 5-7.

The total mercury concentration values, HgT, measured by the paired OHM sampling trains A and B at Port 1, are presented in Figure 5-8. The RD values are also shown. The average value of the train-to-train relative difference (RD) for Port 1 is 5.7 percent.

The relative difference RD is calculated as:

$$RD = |CA - CB|/(CA + CB) \times 100\% \quad \text{Eqn. 5-1}$$

Quantities CA and CB are mercury concentrations measured by the A and B sampling trains, respectively.

Figure 5-9 presents the total mercury concentration values, Hg T, measured by the paired OHM sampling trains A and B at Port 3. The RD values are also shown. The average value of the train-to-train relative difference (RD) for Port 3 is 4 percent.

The HgT values measured by paired trains at Armstrong are presented in Figure 5-10, along with the stack-average value of HgT. The results show that despite the changes in mercury concentration caused by changes in fuel quality and unit load, the mercury concentration values, measured simultaneously by four individual sampling trains located in two ports, were very close to each other. The average train-to-train standard deviation for four OHM trains and all test points is 0.9 mg/wsm3 (7.7 percent). The standard deviation for the high-Hg coal is 1.2 mg/wsm3 (7.5 percent), for the low-Hg coal it is 0.6 mg/wsm3 (7.9 percent).

When calculating test statistics, test data were divided in two sets: the high-Hg and low-Hg coal sets. The Unit 1 and Test 3 test data were omitted from the analysis. The results are summarized in Table 5-10. The average HgT concentration for the high- Hg coal data set is 17.7 mg/wsm3, standard deviation (S) is 2.9 mg/wsm3, Relative Standard Error (RSE) is 16.5 percent, and the 95 percent confidence interval is ± 1.1 mg/wsm3. For the low-Hg coal data set, the average HgT concentration is 7.8 mg/wsm3, S is 1 mg/wsm3, RSE is 14.1 percent, and the 95 percent confidence interval is ± 0.4 mg/wsm3.

Table 5-10 Test Statistics: OHM

Data Set	Average Hg^T	Standard Deviation	Relative Standard Error, RSE	95% Confidence Interval
	µg/wsm^3	µg/wsm^3	%	µg/wsm^3
High-Hg coal	17.7	2.9	16.5	± 1.1
Low-Hg coal	7.8	1.1	14.1	± 0.4

The RSE values obtained at Armstrong are compared to the results from other OHM tests in Figure 5-11. The results show that for the low-Hg coal, the RSE value for Armstrong was very close to the OHM tests performed at other units. For the high-Hg test, the RSE value for Armstrong was higher. This higher RSE value is due to the large variability in mercury content in coals that were delivered from a number of local mines.

5.4. Mercury Monitors

Three continuous Hg CMMs, manufactured by Tekran, Thermo Electron, and GE-PSA, and two semi-continuous mercury monitors, manufactured by Ohio Lumex and Horiba were installed and tested at Armstrong. The CMMs were located in the CEM shelters at the base of the stack and flue gas samples were delivered to the mercury analyzers by using 400 to 450 feet long heated umbilical cords. The portable semi-continuous mercury monitors were located at the CEM platform and used very short umbilical cords.

Due to the system contamination (most likely caused by Selenium), Horiba withdrew from the test after two days of testing. The Hg monitor installation, location, and operating principles are described in Sections 3.3, 3.4, and 4.3 of this report. For the reader's convenience, measurement principles and the other main features of Hg CEMs tested at Armstrong are summarized in Table 5-11.

As described in Section 3 (Technical Approach), two tests were performed each day under constant unit load operating conditions, see Figure 3-1. The first constant load period was in the morning, while the second one was in the afternoon. Duration of the test period corresponded to the duration of the OHM test (typically 2 hours).

Table 5-11 Measurement Principles and Features of Hg CEMs

Manufacturer	Monitor Location	Sample Extraction Probe	Sample Treatment	Measurement Principle
Tekran	Ground	■ Inertial, dilution probe. ■ 450 ft heated umbilical line	Thermal conversion at the ground	CVAF with gold preconcentration
Thermo Electron	Ground	■ Inertial probe ■ 450 ft umbilical line	Thermal conversion at the probe	CVAF without gold preconcentration
GE-PSA	Ground	■ Inertial, dilution probe ■ 400 ft heated umbilical line	Dry thermal converter at the ground	CVAF with two gold traps
Ohio Lumex	CEM Platform	■ Probe with heated filter and sample dilution/ thermal conversion. ■ Short heated umbilical line	Thermal conversion performed at the probe	AA with Zeeman background correction, no gold preconcentration
Horiba	CEM Platform	■ Thermal catalytic conversion at the probe. ■ Short heated umbilical line	Thermal catalytic conversion	CVAAS, no gold traps

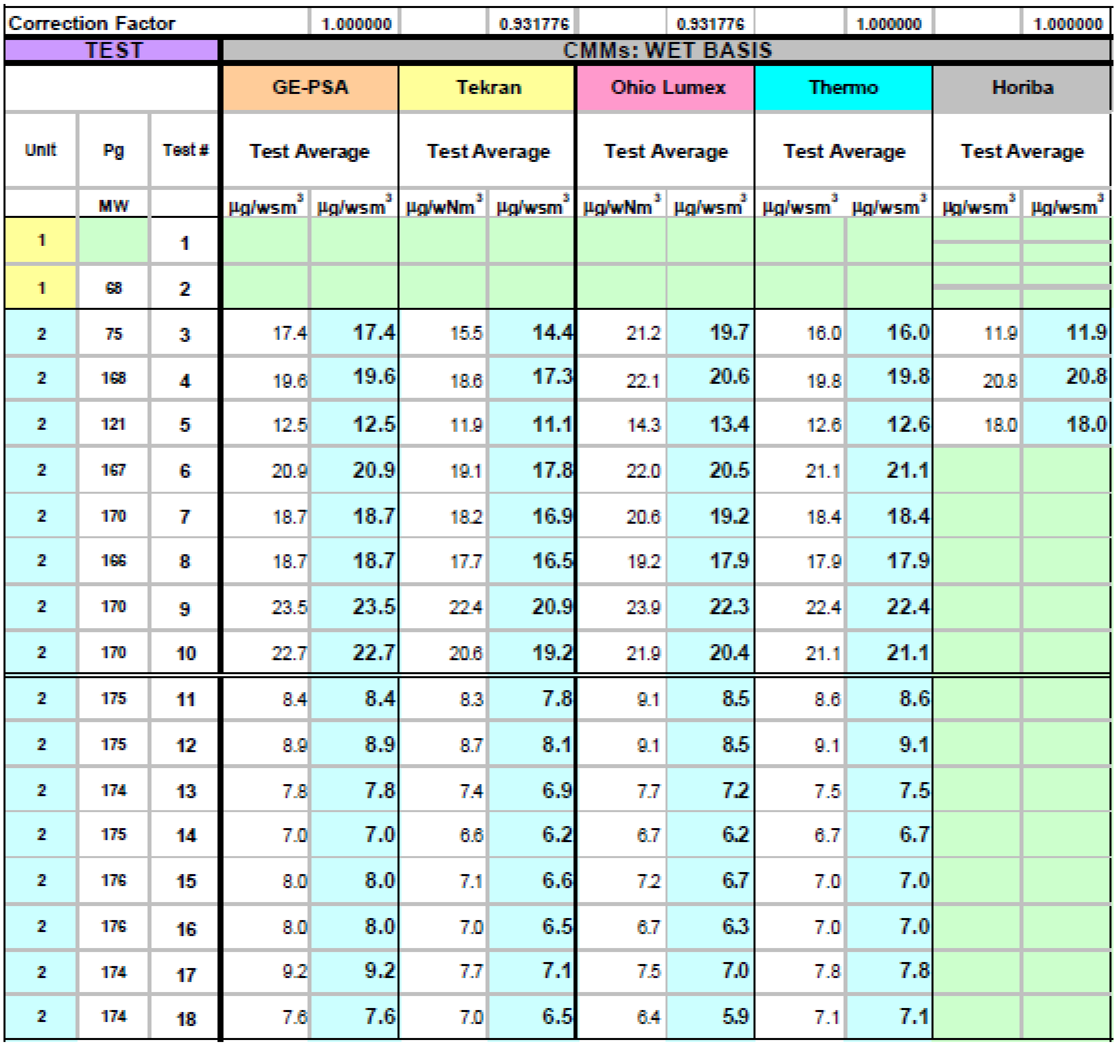
The CMM, sorbent trap and plant operating data, and other information was collected at the end of each day and analyzed. The total gas-phase (Hg+2 + Hg0) mercury concentrations, measured by the continuous and semi-continuous mercury analyzers, corrected to the standard EPA STP conditions, and expressed on a wet basis, are summarized in Table 5-12. The instantaneous, 1- or 2.5-minute average Hg values, provided by the Hg CEMs, were averaged over the duration of each test (approximately 2 hours).

A comparison of the mercury emissions, measured by the five Hg monitors during eight days of testing, is presented in Figures 5-12 to 5-20. The OHM results are presented for comparison.

The results presented in Figure 5-12 show that mercury concentrations measured by different Hg monitors compared well and exhibited the same trends. On this first day of CMM testing, a few data lapses occurred for all continuous Hg monitors.

It has to be noted that a semi-continuous Hg monitor by Ohio Lumex was operated only during the time OHM sampling was performed. The semi-continuous Hg monitor, manufactured by Horiba, was operated in a continuous mode. Vertical blue limes in Figure 5-12 denote the start and end of each test, while the thick horizontal lines represent OHM results (average value for all four OHM trains).

Table 5-12 Average Gas-Phase Hg Concentration Measured by Hg Monitors



Correction Factor				1.000000		0.931776		0.931776		1.000000		1.000000
TEST			CMMs: WET BASIS									
			GE-PSA		Tekran		Ohio Lumex		Thermo		Horiba	
Unit	Pg	Test #	Test Average		Test Average		Test Average		Test Average		Test Average	
	MW		µg/wsm³	µg/wsm³	µg/wNm³	µg/wsm³	µg/wNm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³
1		1										
1	68	2										
2	75	3	17.4	17.4	15.5	14.4	21.2	19.7	16.0	16.0	11.9	11.9
2	168	4	19.6	19.6	18.6	17.3	22.1	20.6	19.8	19.8	20.8	20.8
2	121	5	12.5	12.5	11.9	11.1	14.3	13.4	12.6	12.6	18.0	18.0
2	167	6	20.9	20.9	19.1	17.8	22.0	20.5	21.1	21.1		
2	170	7	18.7	18.7	18.2	16.9	20.6	19.2	18.4	18.4		
2	166	8	18.7	18.7	17.7	16.5	19.2	17.9	17.9	17.9		
2	170	9	23.5	23.5	22.4	20.9	23.9	22.3	22.4	22.4		
2	170	10	22.7	22.7	20.6	19.2	21.9	20.4	21.1	21.1		
2	175	11	8.4	8.4	8.3	7.8	9.1	8.5	8.6	8.6		
2	175	12	8.9	8.9	8.7	8.1	9.1	8.5	9.1	9.1		
2	174	13	7.8	7.8	7.4	6.9	7.7	7.2	7.5	7.5		
2	175	14	7.0	7.0	6.6	6.2	6.7	6.2	6.7	6.7		
2	176	15	8.0	8.0	7.1	6.6	7.2	6.7	7.0	7.0		
2	176	16	8.0	8.0	7.0	6.5	6.7	6.3	7.0	7.0		
2	174	17	9.2	9.2	7.7	7.1	7.5	7.0	7.8	7.8		
2	174	18	7.6	7.6	7.0	6.5	6.4	5.9	7.1	7.1		

The sudden drop in gas–phase mercury concentration that has occurred around 10:35 a.m. on July 10, 2006, was caused by a sootblowing event. Although sootblowing was supposed to be on hold during the test, the unit operator initiated a sootblowing sequence that affected mercury readings. As soon as sootblowing was initiated, the gas-phase mercury concentration measured by all mercury monitors suddenly dropped (see Figure 5-12). This sudden drop is believed to be caused by mercury adsorption/absorption on solid particles that were dislodged from the tube surface by sootblowing and entered the flue gas stream.

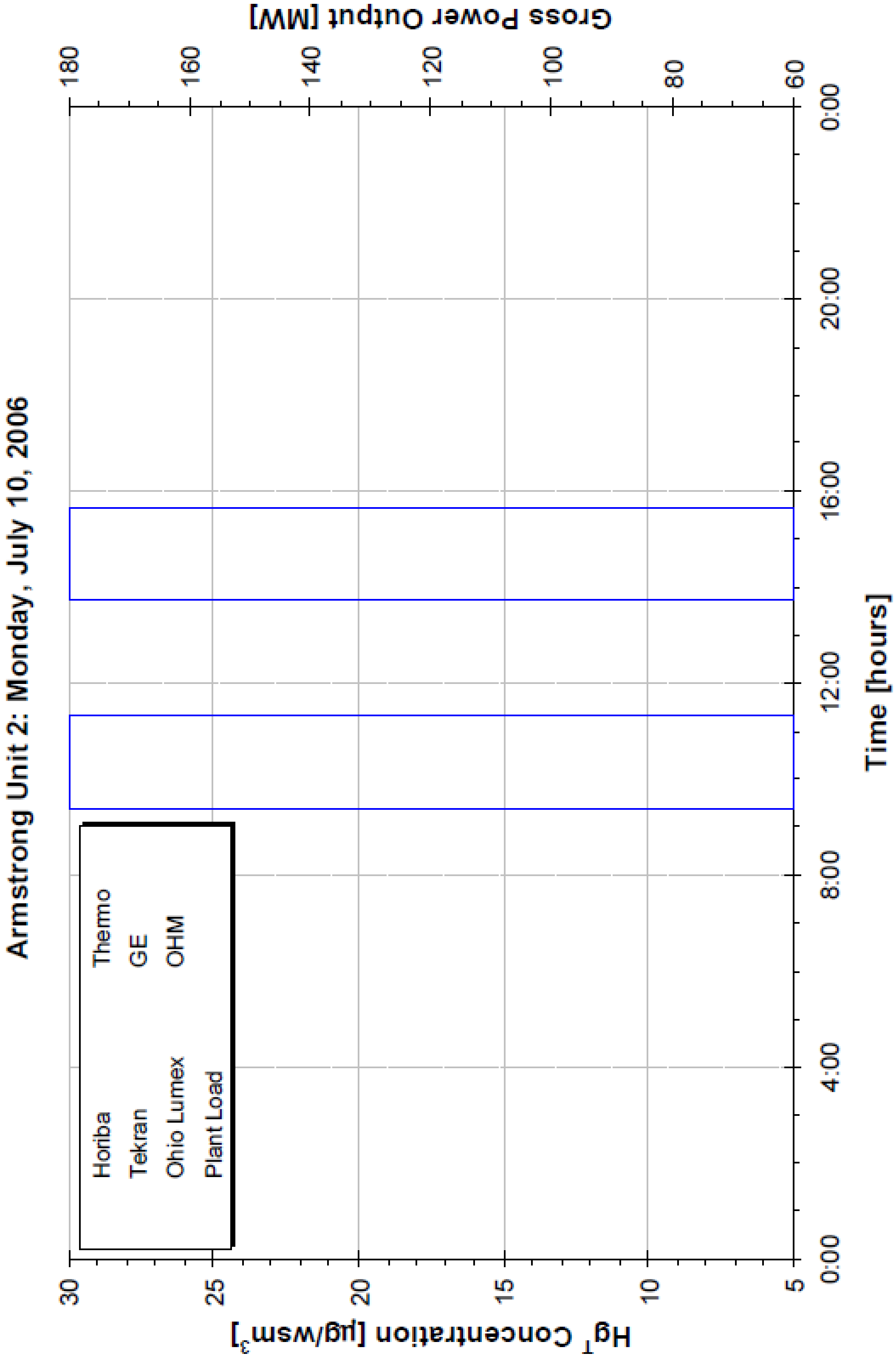


Figure 5-12: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 10th 2006, Tests 3 and 4

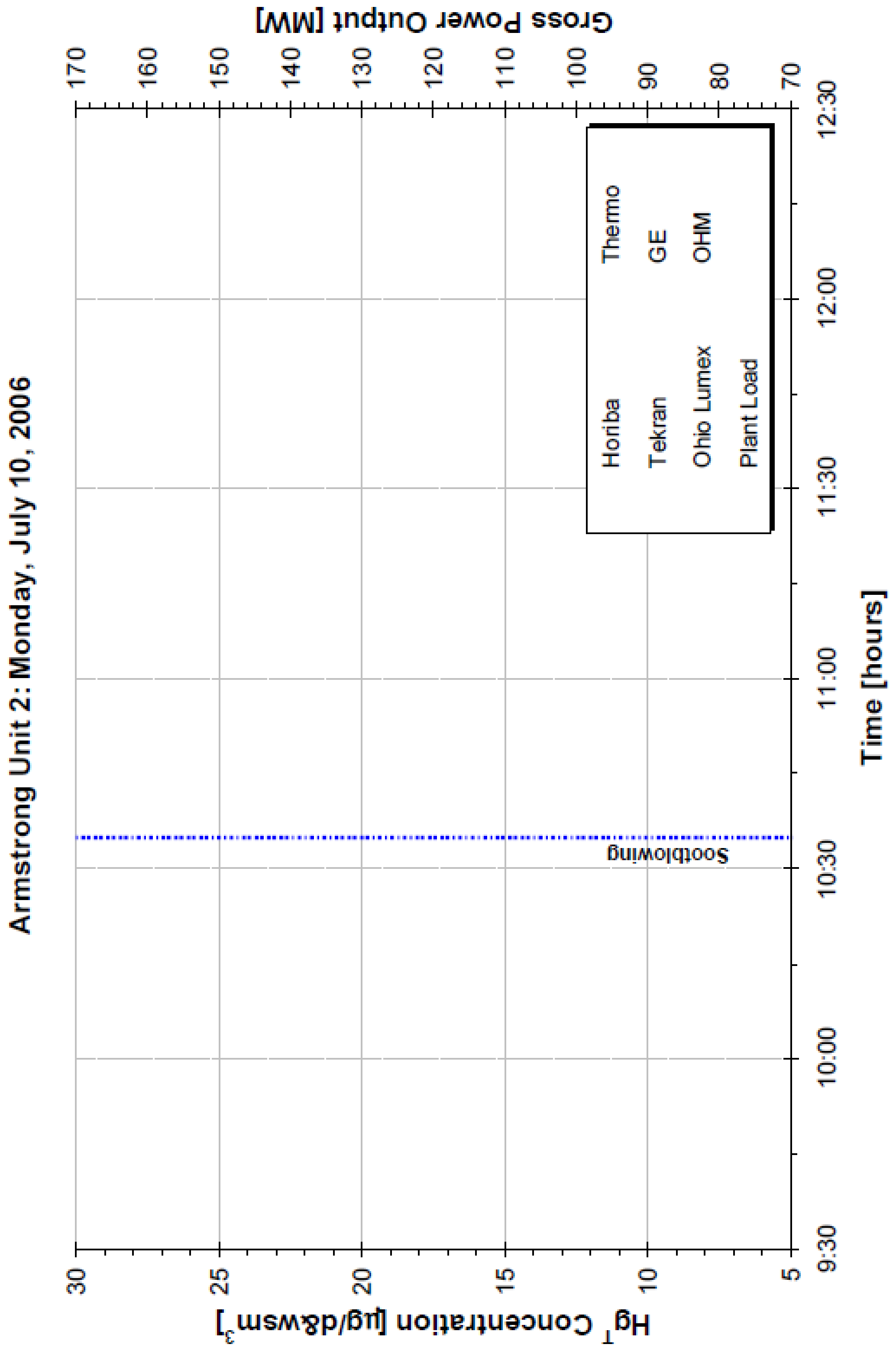


Figure 5-13: Response to the Sootblowing Event, Test 3

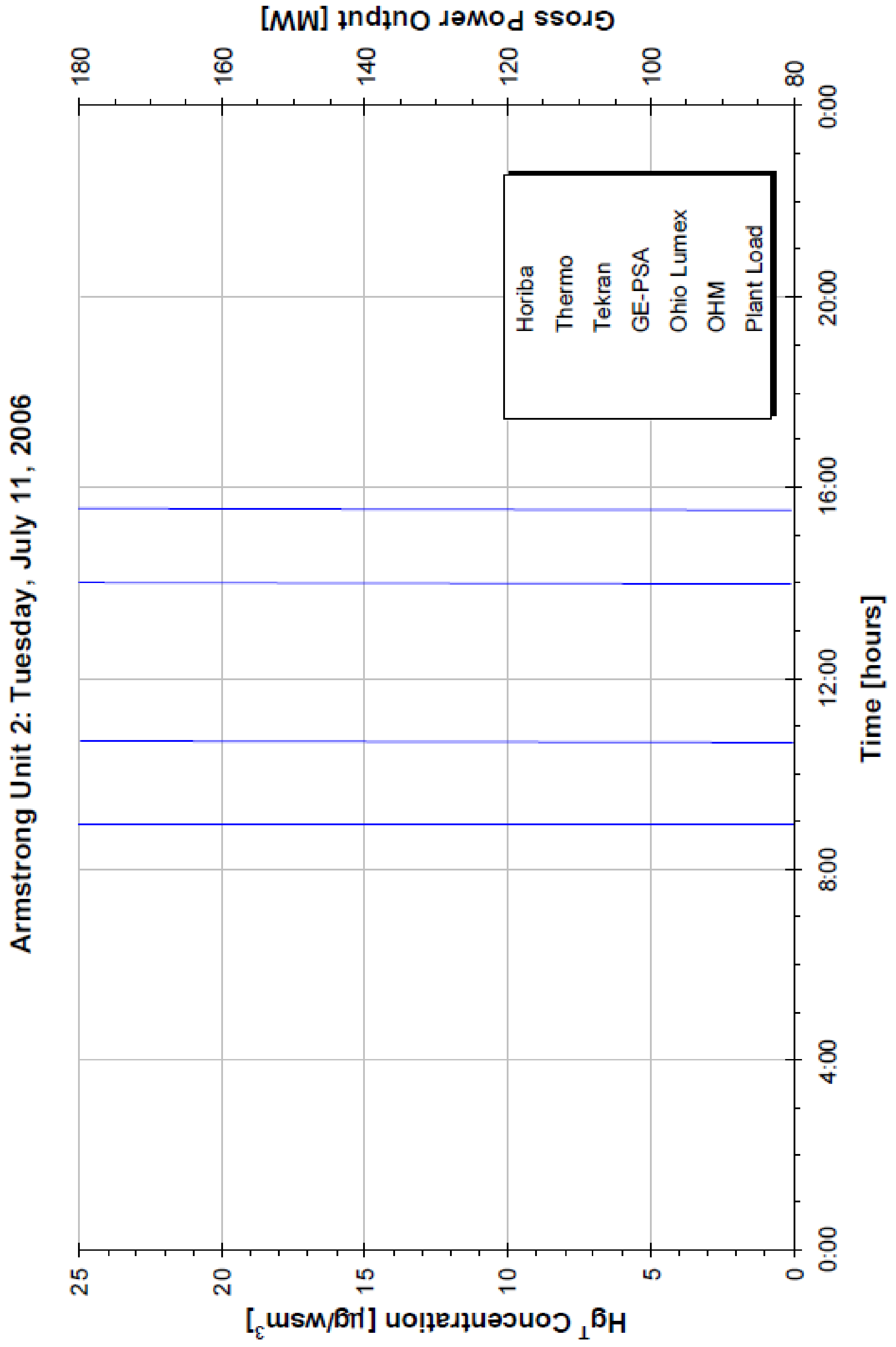


Figure 5-14: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 11, 2006, Tests 5 and 6

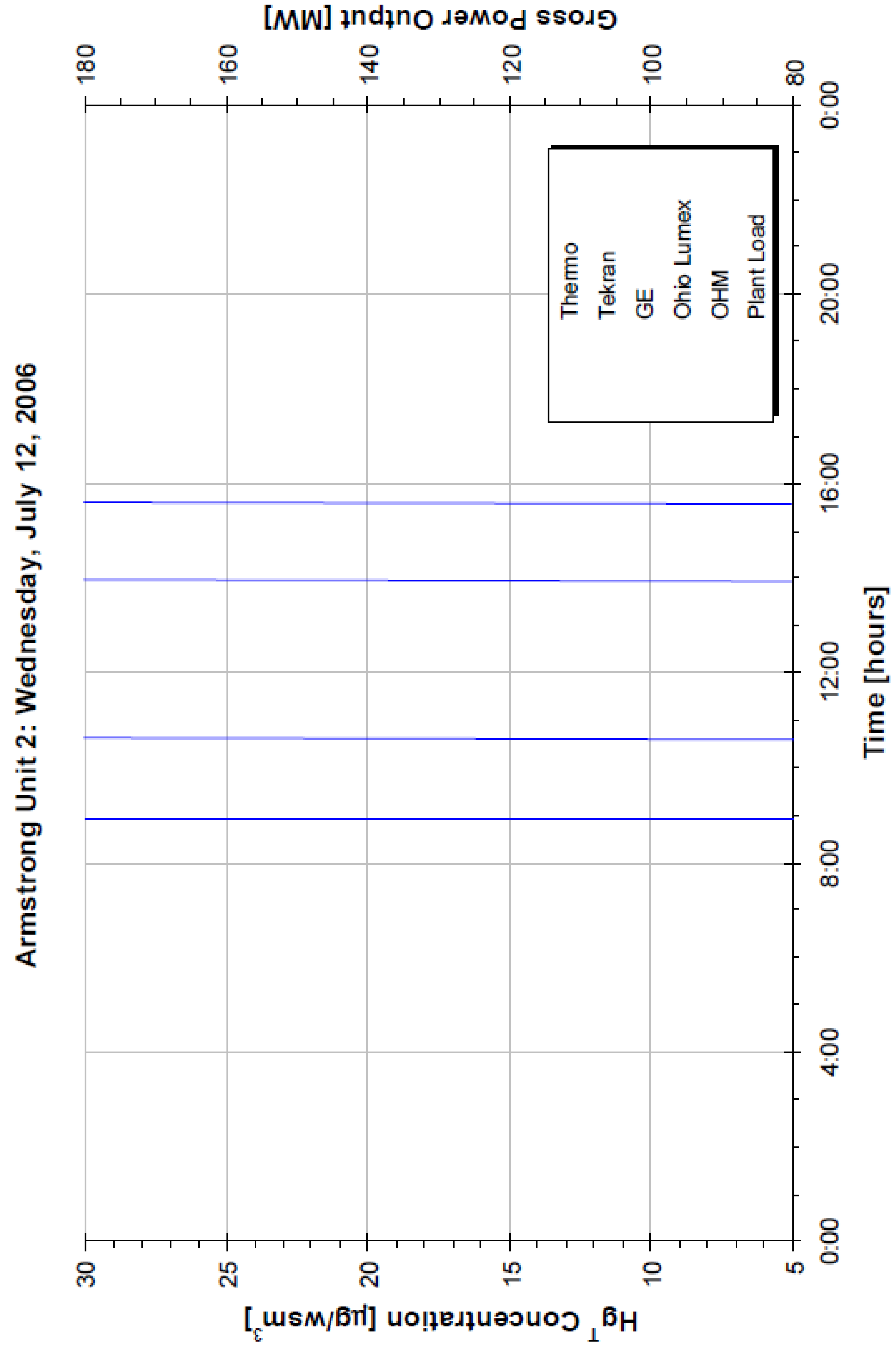


Figure 5-15: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 12, 2006, Tests 7 and 8

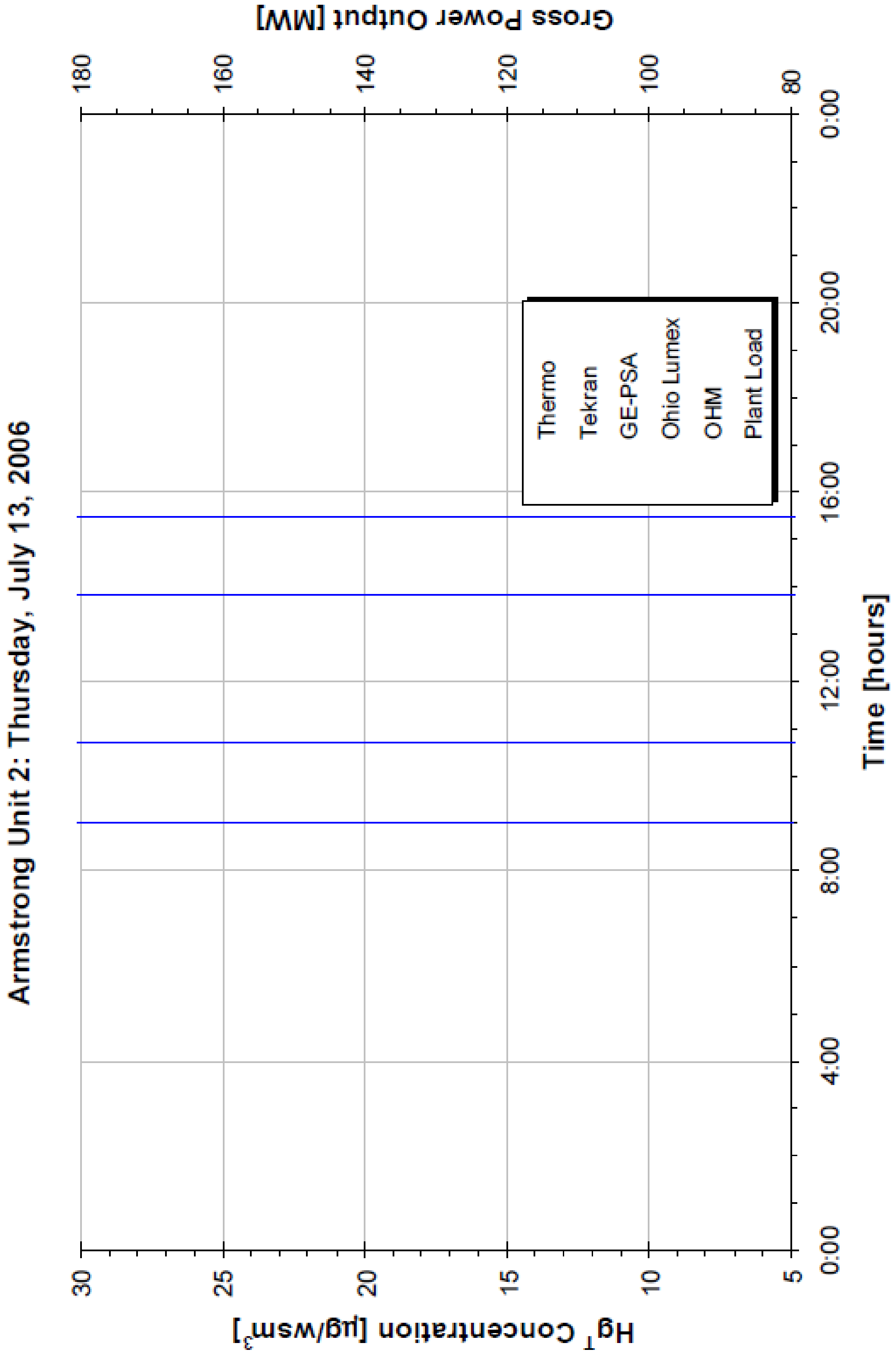


Figure 5-16: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 13, 2006, Tests 9 and 10

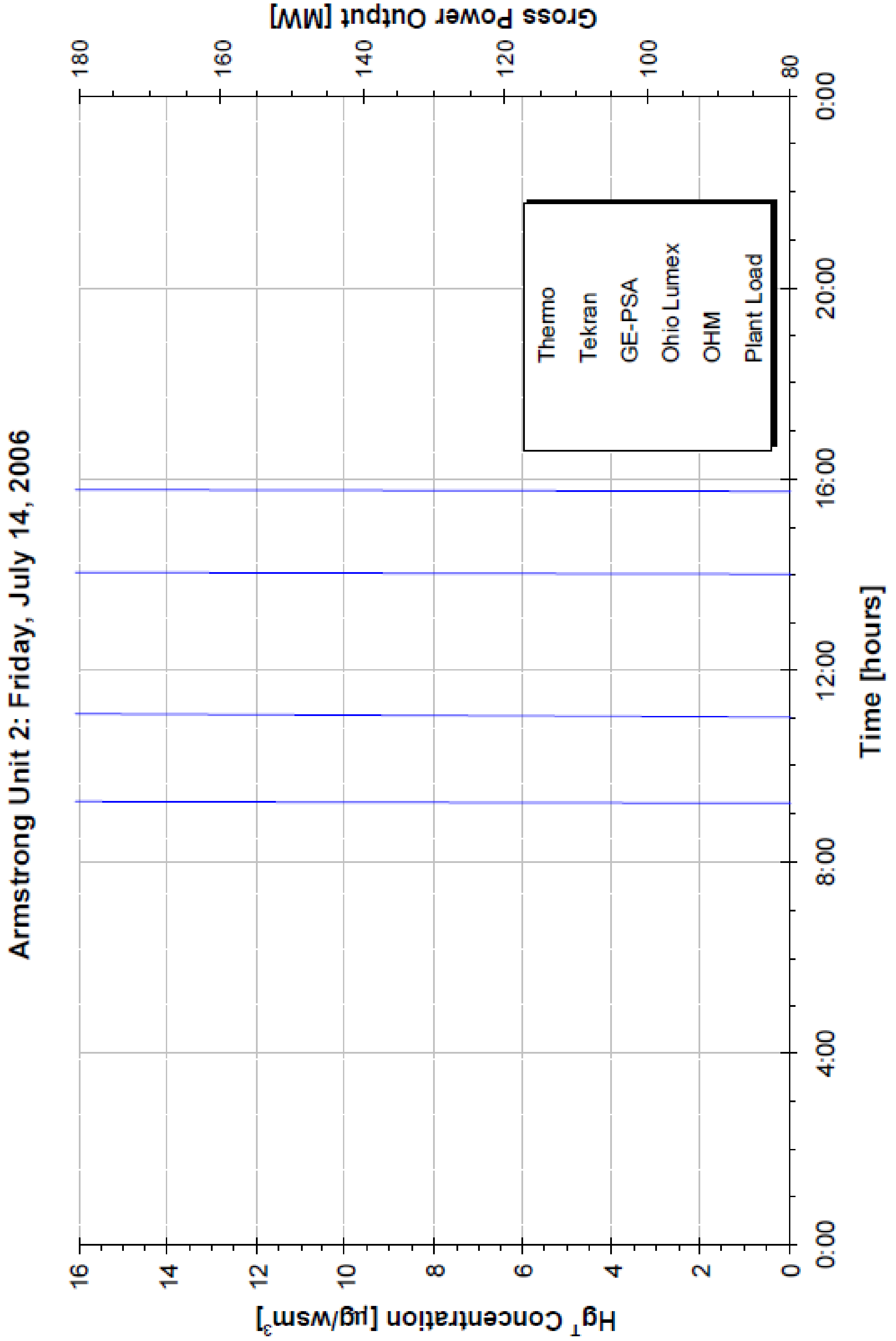


Figure 5-17: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 14, 2006, Tests 11 and 12

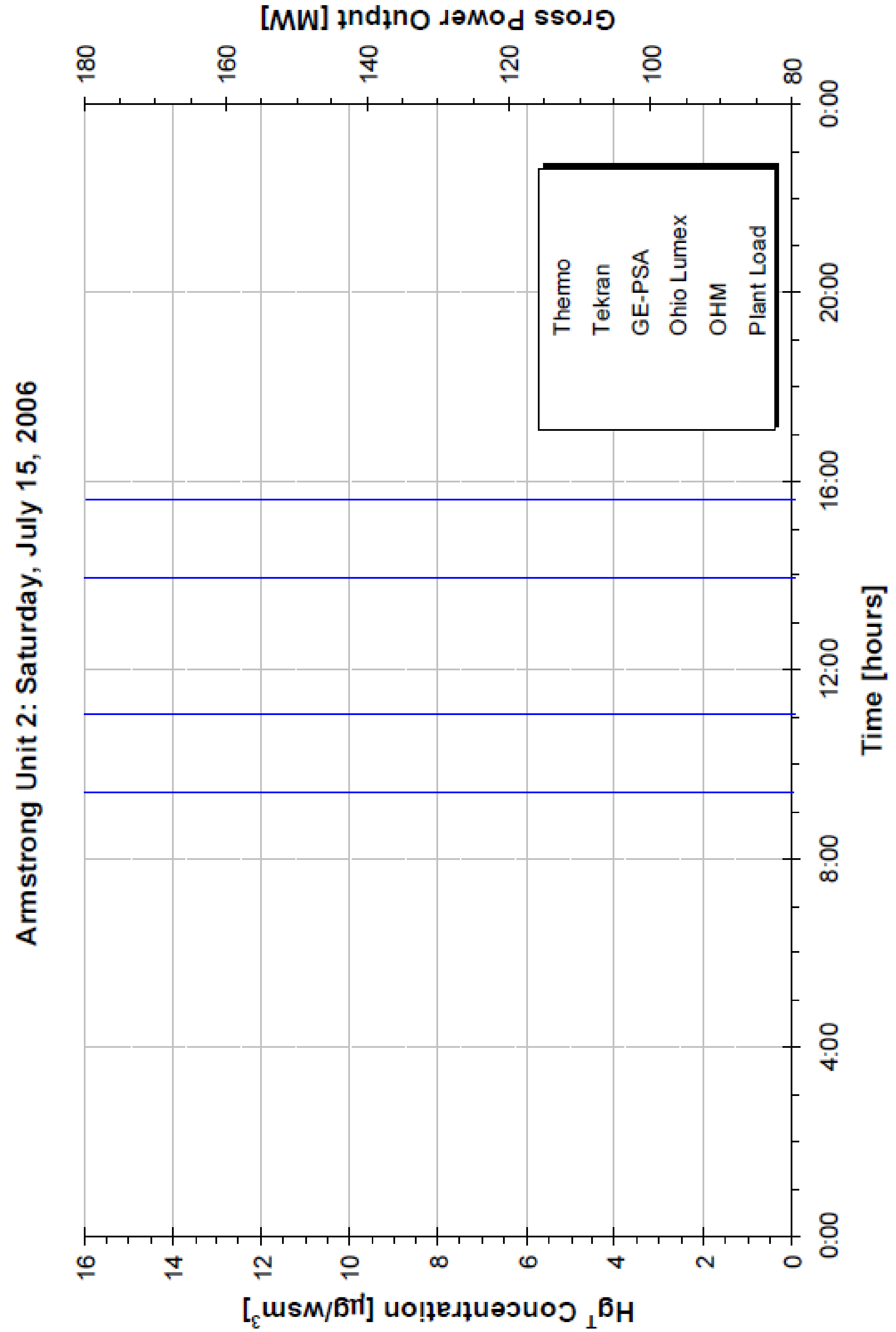


Figure 5-18: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 15, 2006, Tests 13 and 14

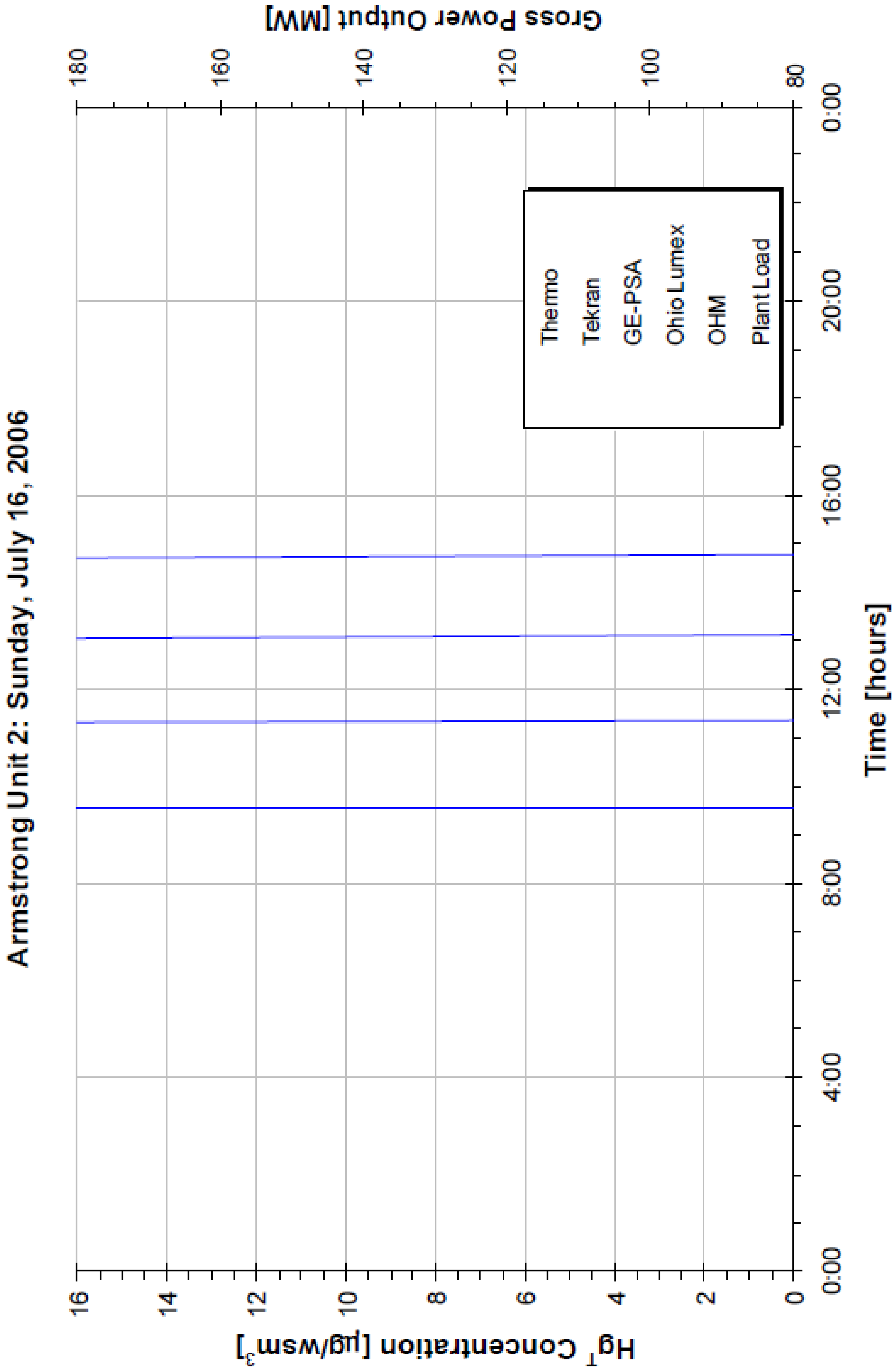


Figure 5-19: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 16, 2006, Tests 15 and 16

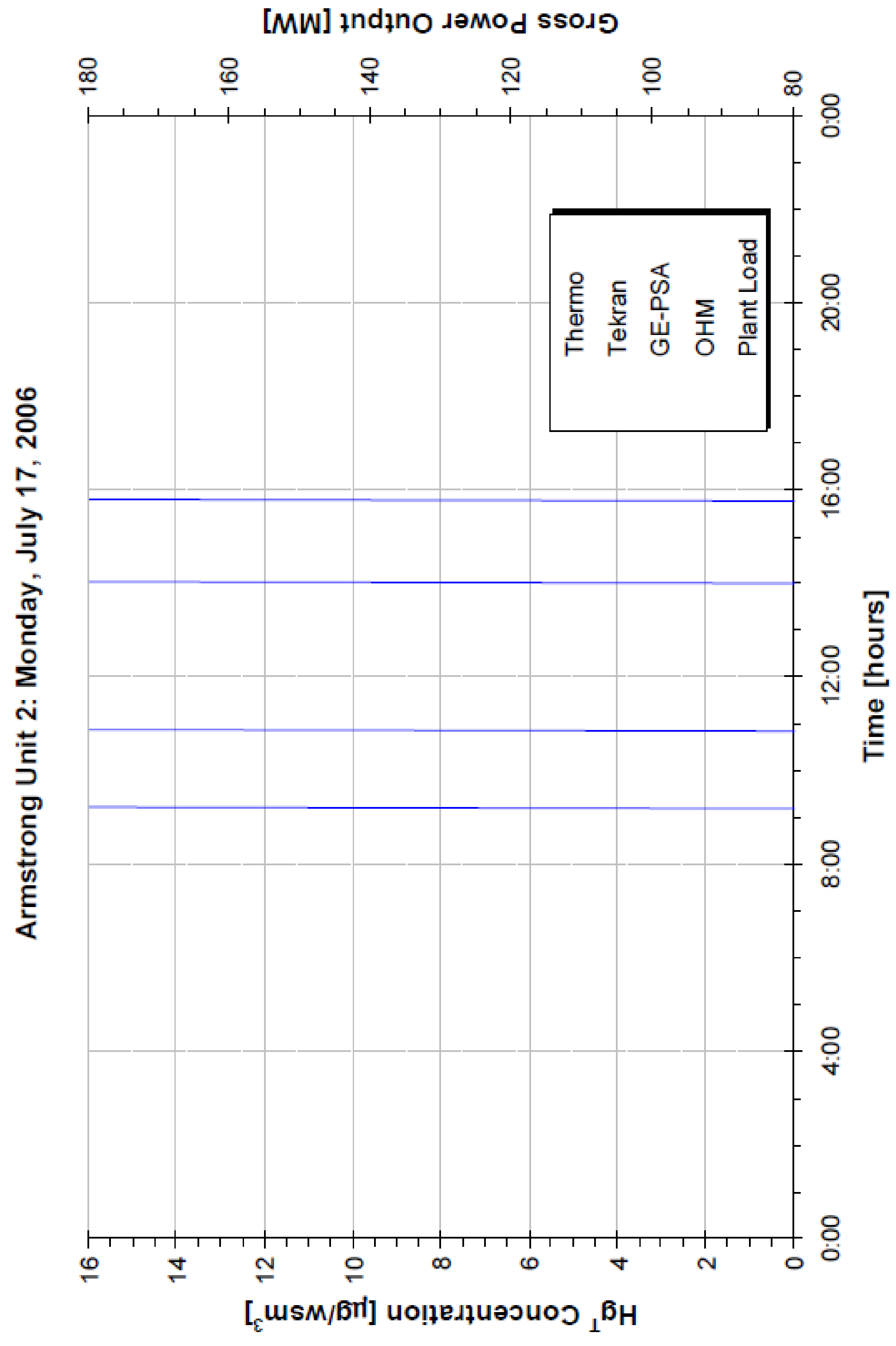


Figure 5-20: Comparison of Gas-Phase Mercury Concentration Measured by Mercury CEMs and OHM: July 17, 2006, Tests 17 and 18

The Hg monitors' response to the sootblowing event is presented in Figure 5-13 on an expanded time scale. It is interesting to note that Tekran and Horiba responded almost immediately. Thermo Electron and GE-PSA responded five minutes after the sootblowing event, while Ohio Lumex responded 10 minutes after the event. However, the drop in gas-phase mercury concentration, measured by all monitors, was almost the same.

Based on this experience it is recommended that for obtaining good quality repeatable mercury measurements that are required for RATAs, it is extremely important that sootblowers are not used during the RATA test.

A comparison of the gas-phase mercury concentration measurements obtained by mercury CEMs and OHM for other test days is presented in Figures 5-14 to 5-20.

The results presented in Figures 5-12 to 5-20 show an excellent agreement in the total gas-phase mercury concentration measured by all Hg monitors, despite differences in their location, measurement principle, or length of the umbilical line. It seems that agreement has improved as the low-Hg coal from Virginia, having a more uniform composition, was fired compared to the local high-Hg coals with varying coal composition. Also, an excellent agreement was achieved between mercury monitors and OHM.

5.5. Comparison of Mercury Monitors and OHM

5.5.1. Tekran Hg Monitor vs. OHM. A comparison of the gas-phase mercury concentration measured by the Tekran 3300 Hg monitor and Reference Method (OHM) is presented in Figure 5 -21.

The average mercury concentrations for individual test points are indicated by yellow squares. Test 3, which was affected by a sootblowing event, is indicated by a solid red square and stands out from the rest of the data. The correlation coefficient R2 of 0.9777 indicates an excellent agreement between the gas-phase mercury concentration measured by Tekran Hg CMM and OHM. The slope of the correlation line represents bias between the two measurements. The value of y of 0.9692 indicates that the total gas-phase mercury concentration measured by the Tekran CMM at Armstrong is, on average, 3.1 percent lower compared to the OHM results.

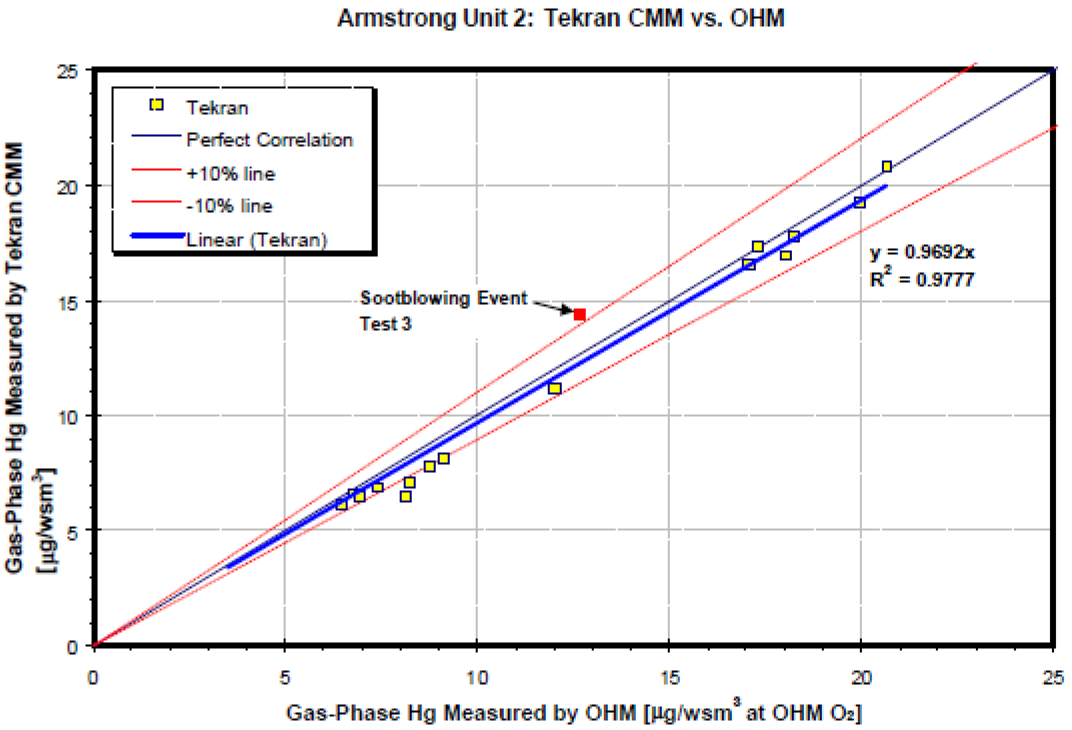


Figure 5 -21: Comparison of Gas-Phase Hg Concentration Measured by Tekran CMM and OHM: All Test Points

Figure 5-22 is similar to Figure 5-21, except that the data point corresponding to Test 3 was removed from the analysis. Removing the Test 3 data point improved the correlation coefficient R2 from 0.9777 to 0.9883 but lowered the slope of the correlation line from 0.9692 to 0.9592. The smaller slope indicates a larger difference between the Tekran Hg monitor and OHM. At Armstrong, the gas-phase mercury concentration measured by the Tekran CMM is, therefore, on average, 4.1 percent lower compared to the OHM results.

Test statistics, such as the average value, standard deviation (S), RSE, 95 percent Confidence Interval (CI), 95 percent Relative Confidence Interval (RCI) calculated for the high-Hg coal, low-Hg coal, and for all test points, are summarized in Table 5-13. As the data show, precision of the OHM is better compared to the Tekran CMM precision.

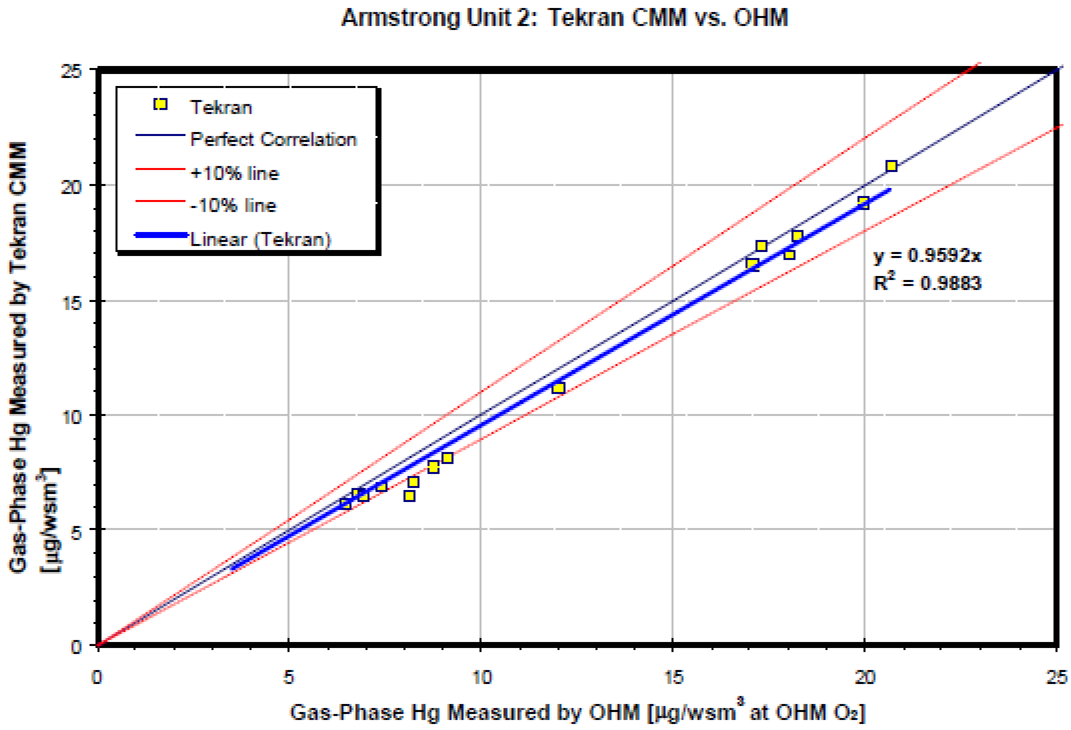


Figure 5 -22: Comparison of Gas-Phase Hg Concentration Measured by Tekran CMM and OHM: Test 3 Data Point Removed

Table 5-13 Tekran vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Tekran	OHM	Tekran	OHM	Tekran	OHM
Average Hg^T	µg/wsm³	17.1	17.7	7.0	7.8	11.9	12.4
Std. Dev.	µg/wsm³	± 3.0	± 2.9	± 0.7	± 1.1	± 5.5	± 5.5
RSE	%	± 17.8	± 16.5	± 9.5	± 14.1	± 46.1	± 44.2
No. of Tests	NA	7	28	8	32	15	60
95% CI	µg/wsm³	± 2.8	± 1.1	± 0.6	± 0.4	± 3.0	± 1.4
95% RCI	%	± 16.4	± 6.4	± 7.9	± 5.0	± 25.5	± 11.4
Bias Error	%	-3.1		-10.4		-4.2	

The bias error between the Tekran and OHM results is calculated as:

$B = (Hg^Tavg,Tekran/Hg^Tavg,OHM – 1) \times 100\%$ Eqn. 5-2

The average value of B for all test points, except Test 3, calculated from Equation 5-2, is -4.2 percent. This is very close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is -3.1 percent. For the low-Hg coal, B is -10.4 percent.

It has to be noted that high values of standard deviation, RSE, CI, and RCI calculated from all test points, except Test 3, are caused by the large variation in fuel quality that occurred during the test and not by the random or bias measurement errors. These values are presented here for the sake of completeness.

5.5.2. Thermo Electron Hg Monitor vs. OHM

Figure 5-23 shows a comparison between the gas-phase mercury concentration measured by the Thermo Electron Mercury Freedom Hg monitor and the OHM. The Test 3 data point, affected by sootblowing, was removed from the analysis.

The correlation coefficient R2 of 0.9813 indicates excellent correlation between the gas-phase mercury concentration measured by the Thermo Electron CMM and the OHM. The slope of the correlation line y of 1.0629 indicates that the gas-phase mercury concentration measured by the Thermo Electron CMM at Armstrong is, on average, 6.3 percent higher compared to the OHM results.

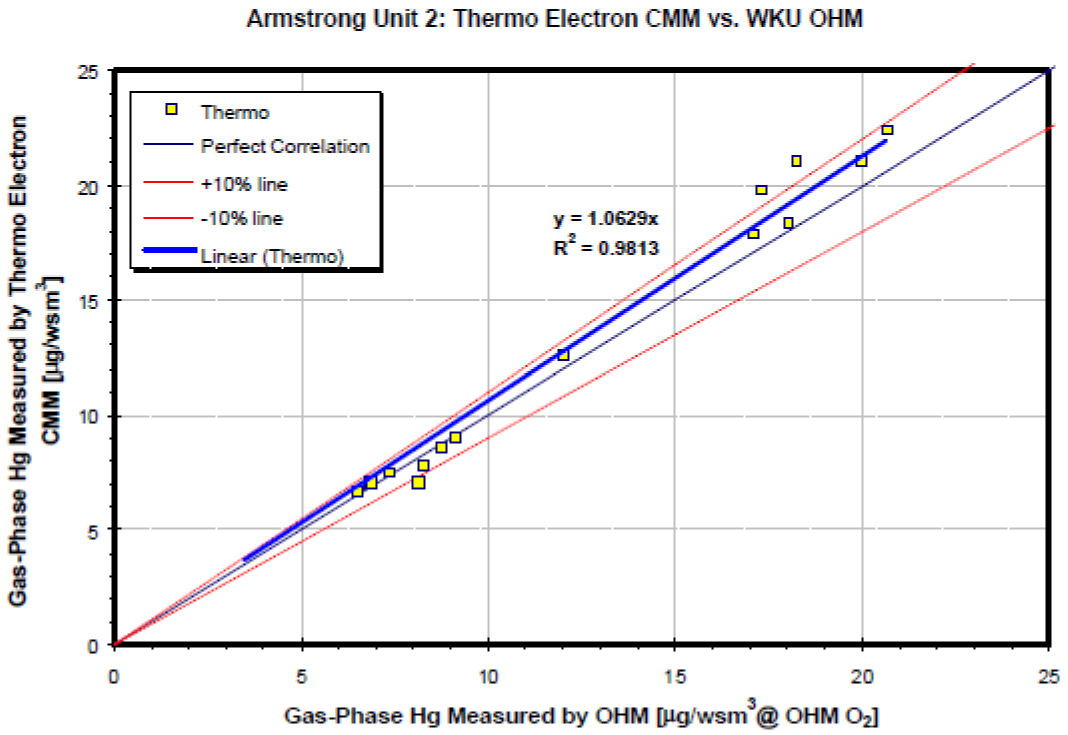


Figure 5 -23: Comparison of Gas-Phase Hg Concentration Measured by Thermo Electron CMM and OHM: Test 3 Data Point Removed

Test statistics are summarized in Table 5-14. As the data show, the OHM precision is better compared to the Thermo Electron CMM precision.

Table 5-14 Thermo Electron vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Thermo	OHM	Thermo	OHM	Thermo	OHM
Average Hg^T	$\mu g/wsm^3$	19.0	17.7	7.6	7.8	13.1	12.4
Std. Dev.	$\mu g/wsm^3$	± 3.2	± 2.9	± 0.8	± 1.1	± 6.1	± 5.5
RSE	%	± 17.0	± 16.5	± 11.2	± 14.1	± 46.8	± 44.2
No. of Tests	NA	7	28	8	32	15	60
95% CI	$\mu g/wsm^3$	± 3.0	± 1.1	± 0.7	± 0.4	± 3.4	± 1.4
95% RCI	%	± 15.8	± 6.4	± 9.3	± 5.0	± 25.9	± 11.4
Bias Error	%	7.8		-2.3		6.2	

The average value of B for all test points except Test 3, calculated from Equation 5-2, is 6.2 percent. This is very close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 7.8 percent. For the low-Hg coal, B is -2.3 percent.

5.5.3. GE-PSA Hg Monitor vs. OHM

A comparison between the gas-phase mercury concentration measured by the GE-PSA Hg monitor and OHM is presented in Figure 5-24. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

The correlation coefficient R2 of 0.986 indicates an excellent correlation between the gas-phase mercury concentration measured by the GE-PSA CMM and the OHM. The slope of the correlation line y of 1.1028 indicates that, the gas-phase mercury concentration measured by the GE-PSA CMM at Armstrong is, on average, 10.3 percent higher compared to the OHM results.

It also seems that the GE-PSA Hg CMM performed better when the low-Hg consistent quality Virginia coal was fired. For the low-Hg Virginia coal the monitor readings were very close to the OHM results. The GE-PSA Hg CMM readings were consistently higher when the high-Hg coal with variable composition, deli vered from the local mines, was fired. The Thermo Electron Hg CMM exhibited similar behavior (see Figure 5-23 and Table 5-14).

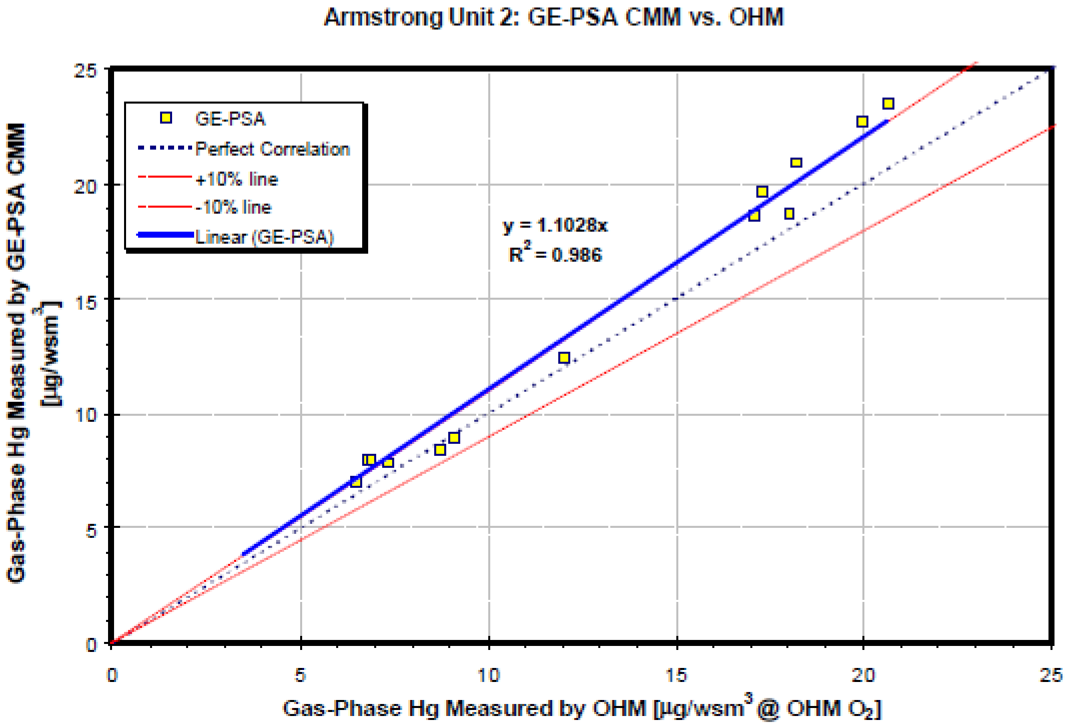


Figure 5 -24: Comparison of Total Gas-Phase Hg Concentration Measured by GE-PSA CMM and OHM: Test 3 Data Point Removed

Test statistics are summarized in Table 5-15. As the data show, the OHM precision is better compared to the GE-PSA CMM precision. Also, the precision was better for the low-Hg coal, compared to the high-Hg coal from local mines.

Table 5-15 GE-PSA vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		GE-PSA	OHM	GE-PSA	OHM	GE-PSA	OHM
Average Hg†	µg/wsm^3	19.5	17.7	8.1	7.8	13.7	12.4
Std. Dev.	µg/wsm^3	± 3.6	± 2.9	± 0.7	± 1.1	± 6.2	± 5.5
RSE	%	± 18.6	± 16.5	± 8.7	± 14.1	± 45.5	± 44.2
No. of Tests	NA	7	28	8	32	15	60
95% CI	µg/wsm^3	± 3.4	± 1.1	± 0.6	± 0.4	± 3.4	± 1.4
95% RCI	%	± 17.2	± 6.4	± 7.3	± 5.0	± 25.2	± 11.4
Bias Error	%	10.5		4.6		10.5	

The average value of B for all test points except Test 3, calculated from Equation 5-2, is 10.5 percent. This is very close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 10.5 percent. For the low-Hg coal, B is 4.6 percent.

5.5.4. Ohio Lumex Hg Monitor vs. OHM

The gas-phase mercury concentration measured by the Ohio Lumex semicontinuous IRM-915 MiniCEM Hg monitor is compared in Figure 5-25 to the OHM results. The data point corresponding to Test 3, that was affected by sootblowing , was removed from the analysis.

The correlation coefficient R2 of 0.9634 indicates an excellent correlation between the gas-phase mercury concentration measured by the Ohio Lumex Hg CEM and OHM. The slope of the correlation line y of 1.0547 indicates that, the gas-phase mercury concentration measured by the Ohio Lumex semi-continuous Hg CEM at Armstrong is, on average, 5.5 percent higher compared to the OHM results.

Test statistics are summarized in Table 5-16. As the data show, the OHM precision is better compared to the Ohio Lumex semi-continuous Hg CEM precision. Also, the precision was better for the low-Hg coal, compared to the high-Hg coal from local mines.

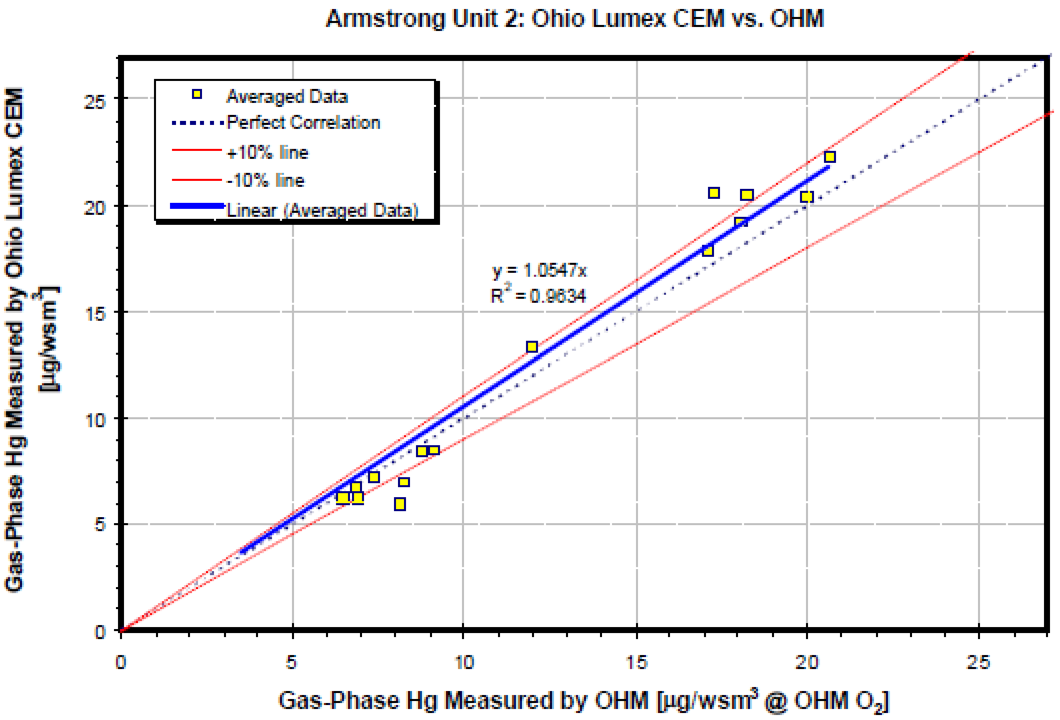


Figure 5-25: Comparison of Total Gas-Phase Hg Concentration Measured by Ohio Lumex CEM and OHM: Test 3 Data Point Removed

Table 5-16 Ohio Lumex MiniCEM vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Ohio Lumex	OHM	Ohio Lumex	OHM	Ohio Lumex	OHM
Average Hg^T	$\mu g/wsm^3$	19.2	17.7	7.0	7.8	13.1	12.4
Std. Dev.	$\mu g/wsm^3$	± 2.9	± 2.9	± 1.0	± 1.1	± 6.6	± 5.5
RSE	%	± 15.1	± 16.5	± 14.1	± 14.1	± 50.3	± 44.2
No. of Tests	NA	7	28	8	32	15	60
95% CI	$\mu g/wsm^3$	± 2.7	± 1.1	± 0.8	± 0.4	± 3.7	± 1.4
95% RCI	%	± 14.0	± 6.4	± 11.8	± 5.0	± 27.8	± 11.4
Bias Error	%	8.7		-9.4		6.2	

The average value of B for all test points except Test 3, calculated from Equation 5-2, is 6.2 percent. This is close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 8.7 percent. For the low-Hg coal, B is -9.4 percent.

5.5.5. Hg CEMs vs. OHM Comparison: Summary

The values of the bias error in the gas-phase Hg concentration measured by the mercury monitors and a Reference Method (OHM), calculated from Equation 5-2, are summarized in Table 5-17 and are also presented in graphical form in Figure 5-26.

Table 5-17 Hg CEM vs. OHM Bias

CEM Vendor	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
Tekran	- 4.2	- 3.1	- 10.4	± 44.2 Avg. ± 16.5 High-Hg coal ± 14.1 Low-Hg coal	± 11.4 Average ± 6.4 High-Hg Coal ± 5.0 Low-Hg Coal
Thermo Electron	+ 6.2	+ 7.8	- 2.3		
GE-PSA	+ 10.5	+ 10.5	+ 4.6		
Ohio Lumex	+ 6.2	+ 8.7	- 9.4		

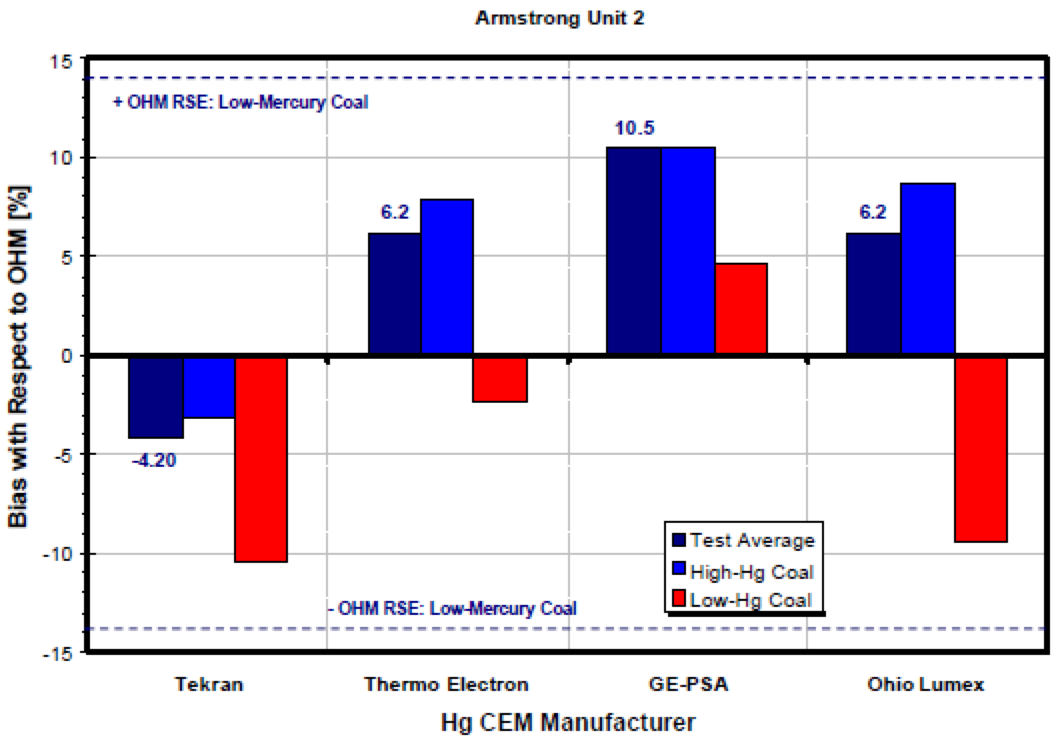


Figure 5-26: Hg CEM Bias Error with Respect to OHM

The average bias error in gas-phase Hg concentration measured by the Hg CEMs and OHM results ranges from -4.2 to + 10.5 percent. The bias error for high-Hg coal is in the -3.1 to 10.5 percent, while for the low-Hg coal it is in the -10.4 to 4.6 percent range.

It has to be noted that Hg CEM manufacturers use different equations for a mercury vapor pressure curve. Different vapor pressure curves are partially responsible for the difference in mercury concentration reported by different Hg CEMs.

The Relative Standard Error (RSE) of the OHM measurements at Armstrong and the high-Hg coal is ± 16.5 percent, while for the low-Hg coal it is ± 14.1 percent. The 95 percent relative confidence interval (RCI) is ± 6.4 percent for the high-Hg coal, and ± 5.0 percent for the low-Hg coal. The OHM RSE value, calculated from the low-Hg data set, was used to make conclusions concerning statistical significance of the calculated biases. As discussed in Section 5.3 (OHM Results), higher values of RSE, CI, and RCI obtained with the high-Hg coals are due to the variation in the coal mercury content, and are not due to the reduced precision of OHM.

The calculated bias errors and the ± RSE values for OHM obtained for the low- Hg coal data set are plotted in Figure 5-26. As the results show, the average bias errors for all Hg CEMs are contained within the ± RSE interval. Therefore, the bias errors for Hg CEMs, with respect to OHM determined at Armstrong, might not be statistically significant.

The HgT ± S values measured by OHM and Hg CEMs are presented in Figure 5- 27 for the high-Hg and low-Hg coals. The results show that, statistically, there is no difference between the HgT readings obtained by OHM and Hg CEMs.

A more stringent analysis involves comparison of the interval estimates for Hg T, i.e., the Hg T ± CI values measured by OHM and Hg CEMs. This comparison is presented in Figure 5-28 for the high-Hg and low-Hg coals. The results show that for the high-Hg coals the bias between OHM, GE-PSA CMM and Ohio Lumex Hg CEM could be statistically significant. For the low-Hg coals, the bias between OHM, Tekran CMM and Ohio Lumex CEM could be statistically significant.

5.6. Sorbent Trap Tests

The sorbent trap (ST) testing at Armstrong was conducted according to the Appendix K of 40 CFR Part 75 regulations in parallel to the OHM tests. The start and end times for the OHM and ST tests were coordinated to allow direct comparison of the results.

Sorbent traps have been developed and used to measure total Hg in flue gas from coal-fired units since 1990. A known volume of flue gas is drawn by a sampling train through a tube (sorbent trap) filled with a material that absorbs Hg. The traps are then analyzed either on site or in the laboratory to determine the Hg concentration in the stack flue gas. Most sorbent traps are designed to measure total Hg. Some traps, such as the Flue Gas Adsorbent Mercury Speciation Method (FAMS), developed by Frontier Geosciences, Inc., employs multiple sorbents to determine mercury speciation. Different versions of sampling trains were developed by the manufacturers.

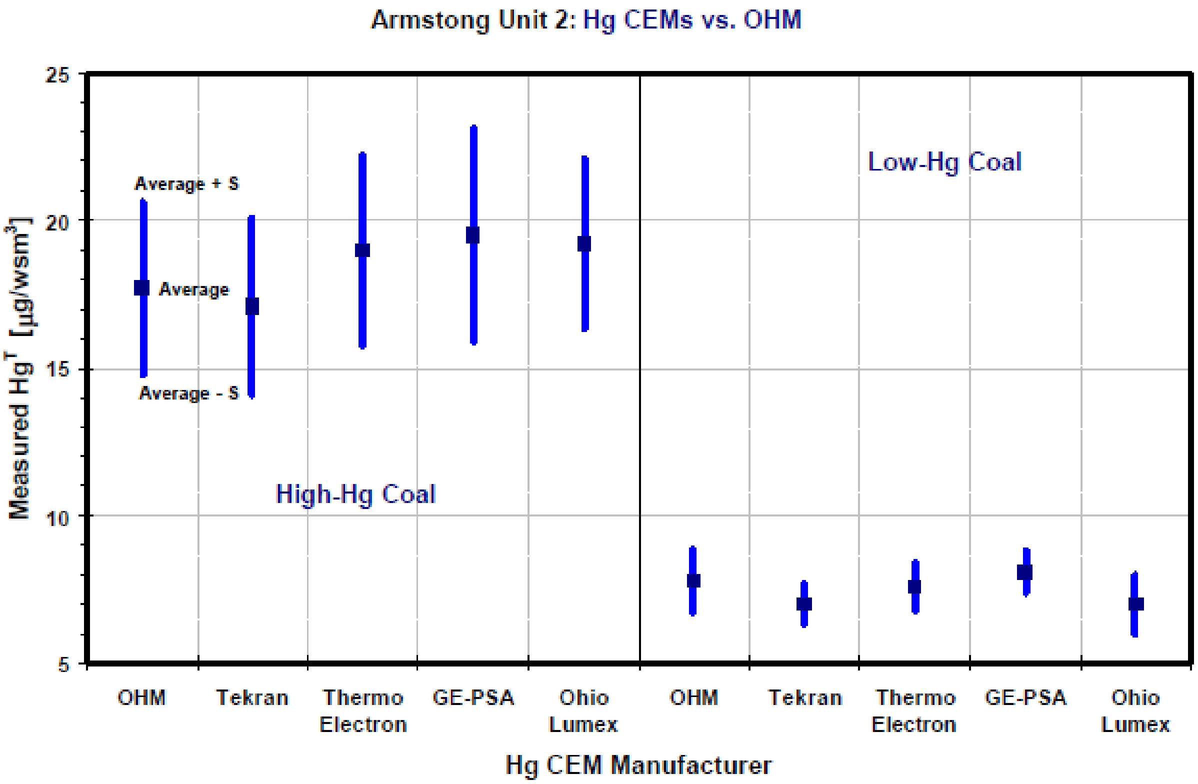


Figure 5-27: HgT ± S Values Measured by OHM and Hg CEMs Measured at Armstrong for High-Hg and Low-Hg Coals

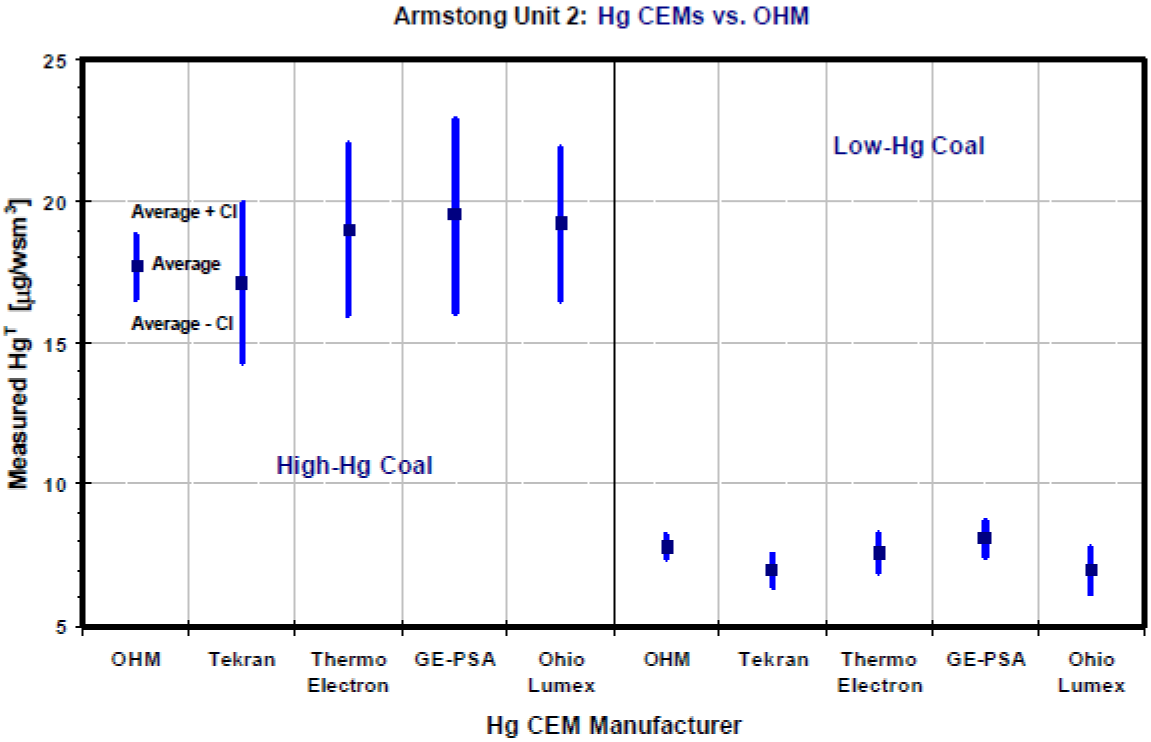


Figure 5 -28: HgT ± CI Values Measured by OHM and Hg CEMs Measured at Armstrong for High-Hg and Low-Hg Coals

Paired traps are required and must show relative agreement. Each trap is comprised of three sections. The first section is used for Hg measurement, the second one for quantification of the Hg breakthrough, and the third, spiked, section is used to demonstrate analytical proficiency. Under Appendix K, the sorbent trap breakthrough detected in the second section must be 5 percent or less of the first section mass. The relative deviation, RD, of the paired traps must be less or equal to 10 percent. For low average concentrations (1 mg/sm3), the recently proposed revisions (August 2006) to Part 75 allow for a relative deviation of less or equal to 20 percent. Spike recovery from the third trap section must be between 75 and 125 percent [4]. Also, Appendix K requires the results to be corrected for spike recovery.

The relative deviation (RD) of the paired traps is calculated from:

$$RD = |C1 - C2|/(C1 + C2) \times 100\% \quad \text{Eqn. 5-3}$$

Correction for spike recovery is calculated as:

$$Hg_{Corrected} = Hg_{Measured} \times R \text{ [ng]} \quad \text{Eqn. 5-4}$$

Where spike recovery, R, calculated as:

R = HgMeasured,Section 3 /HgPre-spiked,Section 3 x 100% Eqn. 5-5

Sampling trains provided by Ohio Lumex-Apex Instruments, CleanAir Engineering-CONSOL, and Frontier Geosciences Inc. (FGS) were located on the second, third, and fourth CEM platforms at Armstrong, as shown in Figure 3-7. The Ohio Lumex/Apex Instruments probe and a sampler and one of the FGS samplers were located on the second CEM platform, as shown in Figure 3-10. The rest of the FGS equipment was located on the third CEM Platform (Figure 3-11). FGS used four sampling probes and four samplers to obtain mercury flue gas concentration measurements from four mutually perpendicular sampling ports. This measurement location was also used to perform mercury stratification measurements, which were conducted at three radial locations by using sampling probes specially designed by FGS for the Armstrong test. The CleanAir-CONSOL equipment was located on the fourth, and hottest, CEM platform.

The Ohio Lumex sorbent traps were analyzed on site. The sorbent traps collected by CleanAir Engineering-CONSOL test team were analyzed in CONSOL's laboratory in Library, Pennsylvania. The FGS traps were shipped to California and analyzed in their laboratory.

5.6.1. Ohio Lumex – Apex Instruments

The Ohio Lumex raw sorbent trap data and mercury concentrations calculated from the data are summarized in Table 5-19. The relative deviation (RD) for all paired traps was less than 10 percent, while section 2 breakthrough was less than 10 ng (1–3 percent of section 1). The third sections of all traps were pre-spiked to 750 ng of Hg. The spike recovery R was in the 94 to 125 percent range. Therefore, all Hg measurements performed by Apex Instruments-Ohio Lumex team meet Appendix K requirements. Three traps broke at the beginning of the test. No other problems were encountered.

The calculated mercury concentrations , corrected and uncorrected for the spike, are presented in Table 5-18. Mercury content on the plug was also determined and the results are also presented. The Ohio Lumex-Apex Instruments results are also presented in a graphical form in Figures 5-29 to 5-35.

The mass of mercury measured on the first section is presented in Figure 5-29. The total Hg concentration, HgT, (gas-phase + particulate-bound) values corrected and uncorrected for spike, are presented in Figures 5-30 (individual trap values) and 5-31 (average values) on a dry basis. The average difference between the corrected and uncorrected values at Armstrong was less than 1 mg/dsm3, with the uncorrected values being higher.

Table 5-18 Ohio Lumex – Apex Instrument Sorbent Trap Data and Results

									Corrected for Spike		Uncorrected for Spike		Plug	Corrected for Spike		
Test Number	Sample Volume	Hg Mass in Section 1	RD	Hg Mass in Section 2	Section 3 Spike	Section 3 Recovered		Hg Mass in Section 1 Corr. for Recovery	Hg	Average Hg	Hg	Average Hg	Fraction of Section 1 on a Plug	Hg Excluding the Plug	Average Hg Excluding the Plug	COMMENTS
	dsm^3	ng	%	ng	ng	ng	%	ng	$\mu g/dsm^3$	$\mu g/dsm^3$	$\mu g/dsm^3$	$\mu g/dsm^3$	%	$\mu g/dsm^3$	$\mu g/dsm^3$	
2	0.05434	1,254	0.7	<10	750	846	113	1,112	20.46	19.22	23.08	22.77				Testing on Unit 1
	0.05509	1,237		<10	750	937	125	990	17.97		22.45					Testing on Unit 1
3	0.04723	822		<10	750	755	101	817	17.29	17.29	17.40	17.59	29	12.27	12.27	B Trap Broke!
	0.04742			<10	750	819	109						28	0.00		Plug not isolated?
4					750	793	106									Both Traps Broke!
					750	717	96									Both Traps Broke!
5	0.04985	669	2.4	<10	750	706	94	711	14.26	13.54	13.42	13.16	34	9.41	8.10	Plug not isolated?
	0.04947	638		<10	750	754	101	635	12.83		12.90		47	6.80		Plug not isolated?
6	0.04503	1,106	0.2	<10	750	918	122	904	20.07	20.43	24.56	24.81	3	19.47	18.98	
	0.04434	1,111		<10	750	904	121	922	20.79		25.06		11	18.50		
7	0.04538	879	2.5	<10	750	915	122	720	15.88	18.61	19.37	20.20	1	15.72	17.57	
	0.04396	925		<10	750	739	99	939	21.35		21.04		9	19.43		
8	0.04590	991	6.2	<10	750	735	98	1,011	22.03	20.77	21.59	20.85	11	19.61	17.90	
	0.04351	875		<10	750	773	103	849	19.51		20.11		17	16.20		
9	0.04312	1,150	1.4	<10	750	785	105	1,099	25.48	25.75	26.67	26.42	5	24.21	24.34	
	0.04276	1,119		<10	750	754	101	1,113	26.03		26.17		6	24.47		
10	0.04278	1,113	0.9	<10	750	791	105	1,055	24.67	24.63	26.02	26.04	5	23.43	23.27	
	0.04198	1,094		<10	750	795	106	1,032	24.59		26.06		6	23.11		
11	0.05349	582	7.3	<10	750	802	107	544	10.18	9.93	10.88	10.50	7	9.46	9.33	
	0.04967	503		<10	750	785	105	481	9.68		10.13		5	9.19		
12	0.04472	475	2.9	<10	750	746	99	478	10.68	10.73	10.62	10.54	16	8.97	9.61	
	0.04286	448		<10	750	727	97	462	10.78		10.45		5	10.24		
13	0.04328	370	3.6	<10	750	739	99	376	8.68	8.79	8.55	8.96	7	8.07	8.31	
	0.04249	398		<10	750	789	105	378	8.90		9.37		4	8.55		
14	0.04376	376	3.0	<10	750	824	110	342	7.82	7.59	8.59	8.47	6	7.35	7.02	
	0.04241	354		<10	750	851	113	312	7.36		8.35		9	6.69		
15	0.04610	420	4.2	<10	750	884	118	356	7.73	7.63	9.11	8.71	3	7.50	7.32	
	0.04642	386		<10	750	829	111	349	7.52		8.32		5	7.15		
16	0.04489	350	1.4	<10	750	798	106	329	7.33	7.63	7.80	7.78	8	6.74	7.22	
	0.04384	340		<10	750	733	98	348	7.94		7.76		3	7.70		
17	0.04190	402	1.0	<10	750	786	105	384	9.15	9.32	9.59	9.66	3	8.88	9.11	
	0.04213	410		<10	750	770	103	399	9.48		9.73		1	9.34		
18	0.04544	390	3.3	<10	750	816	109	358	7.89	7.74	8.58	8.38	1	7.81	7.59	
	0.04460	365		<10	750	809	108	338	7.59		8.18		3	7.36		

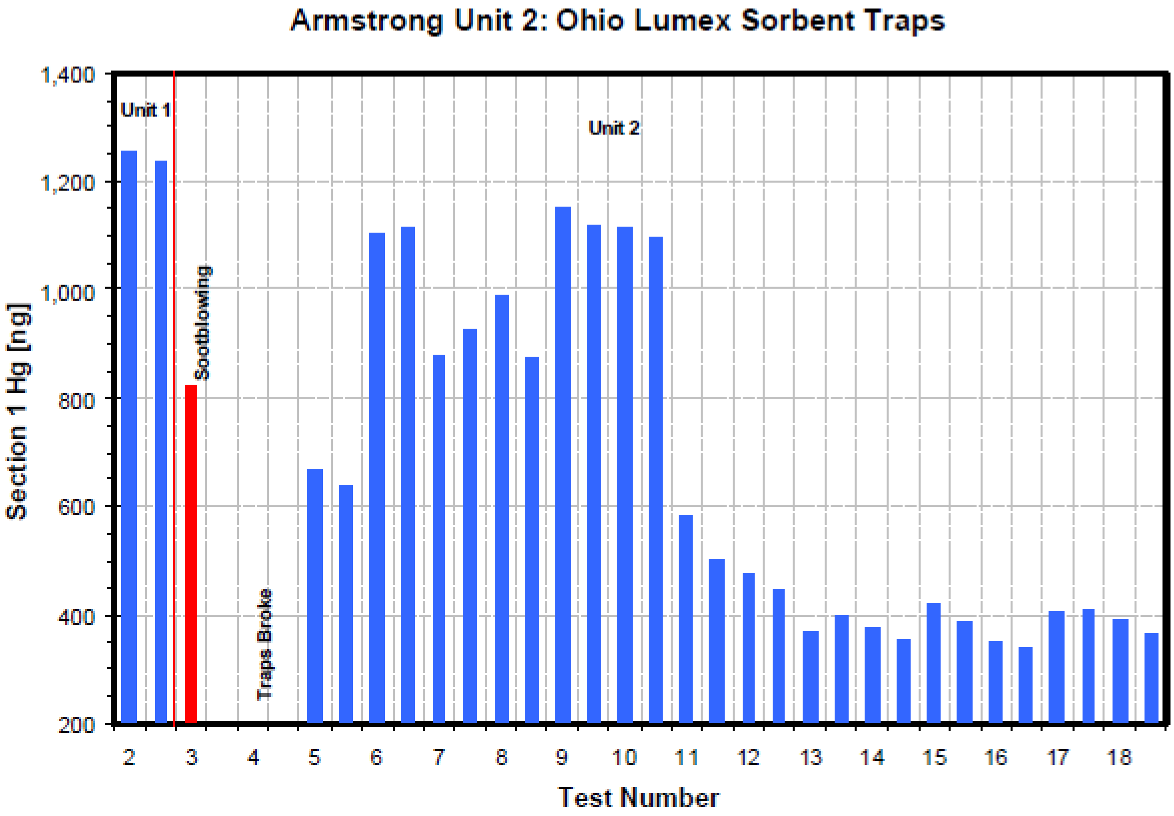


Figure 5-29: Mass of Hg Measured in Section 1: Ohio Lumex

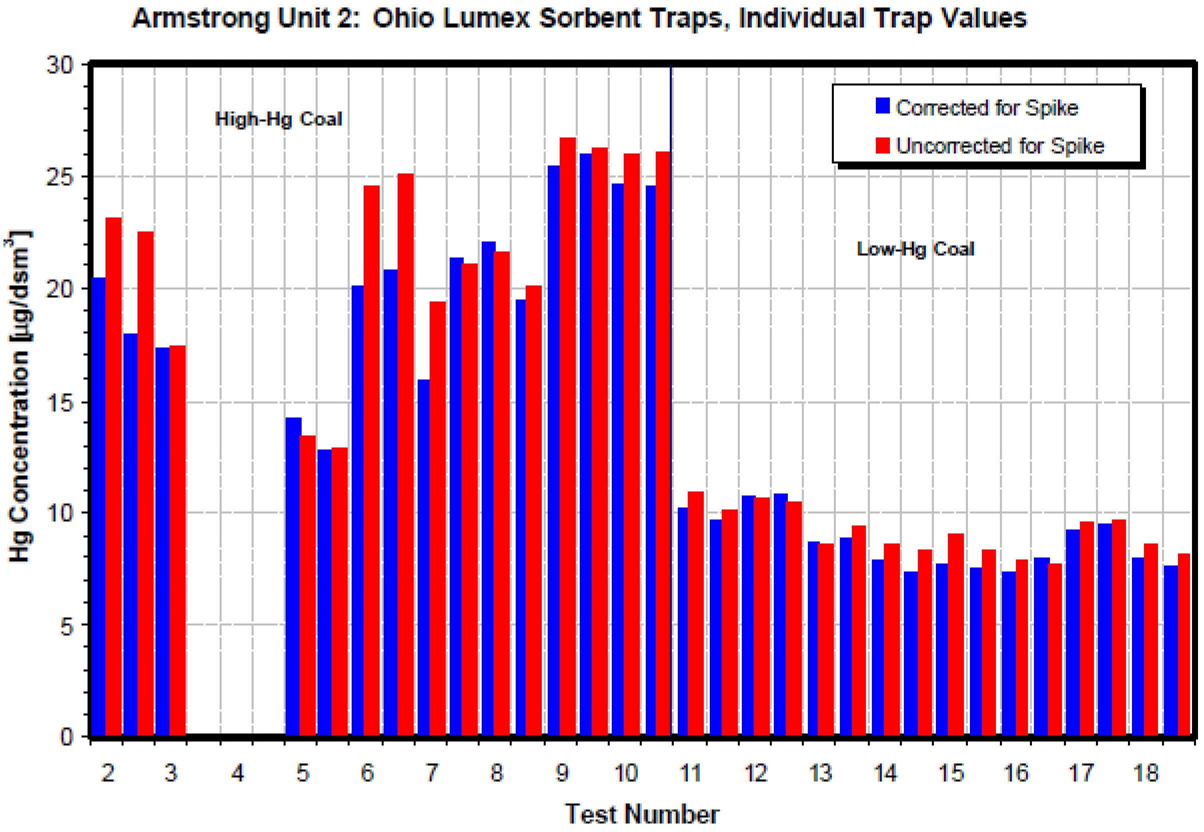


Figure 5 -30: Hg Concentration Values, Measured by Individual Traps, Corrected and Uncorrected for Spike: Ohio Lumex

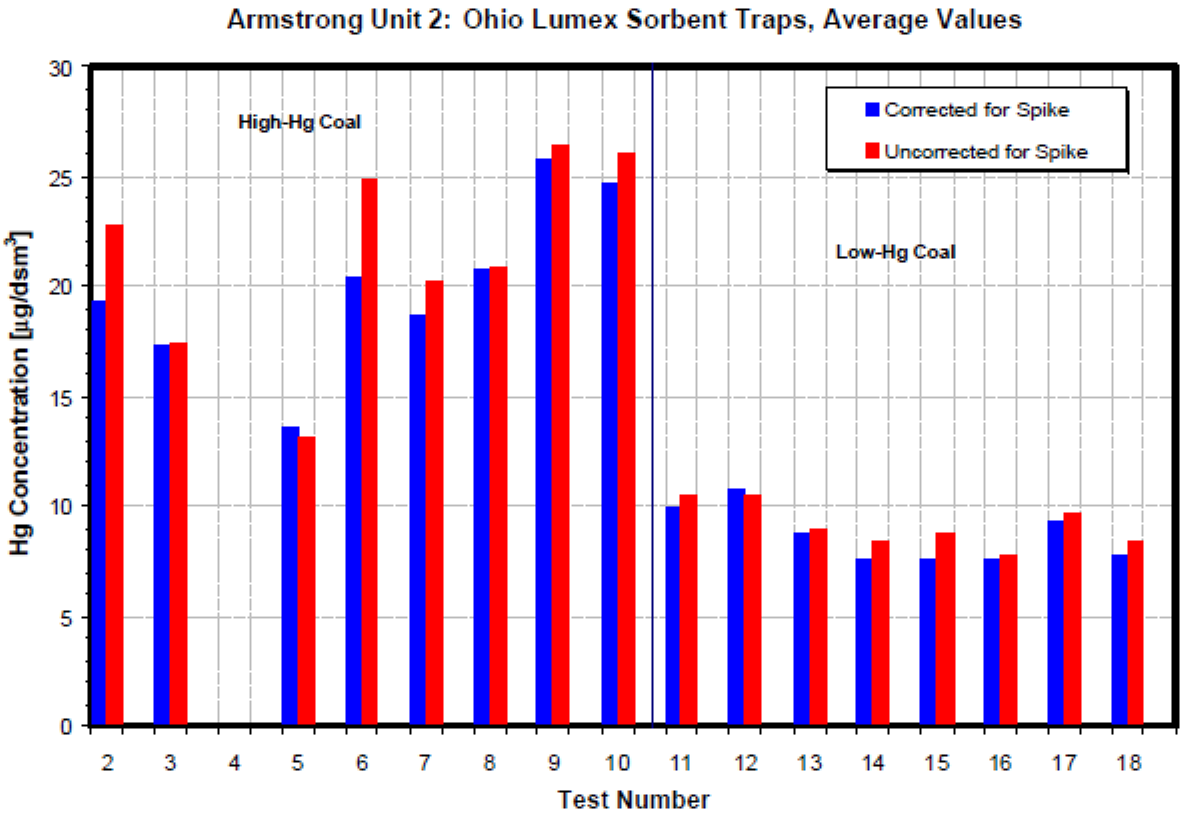


Figure 5-31: Average Hg Concentration Values Corrected and Uncorrected for Spike: Ohio Lumex

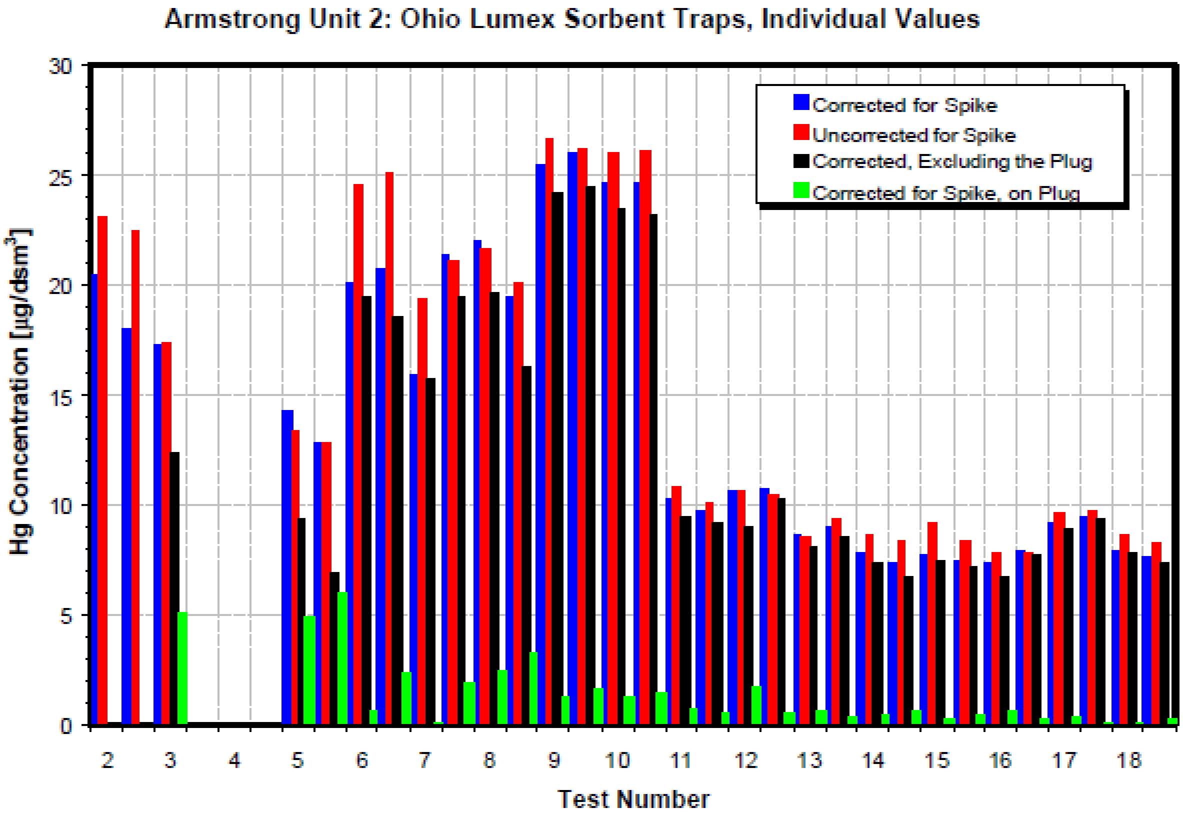


Figure 5-32: Individual Hg Concentration Values Corrected and Uncorrected for Spike, and Hg Concentration on the Plug: Ohio Lumex

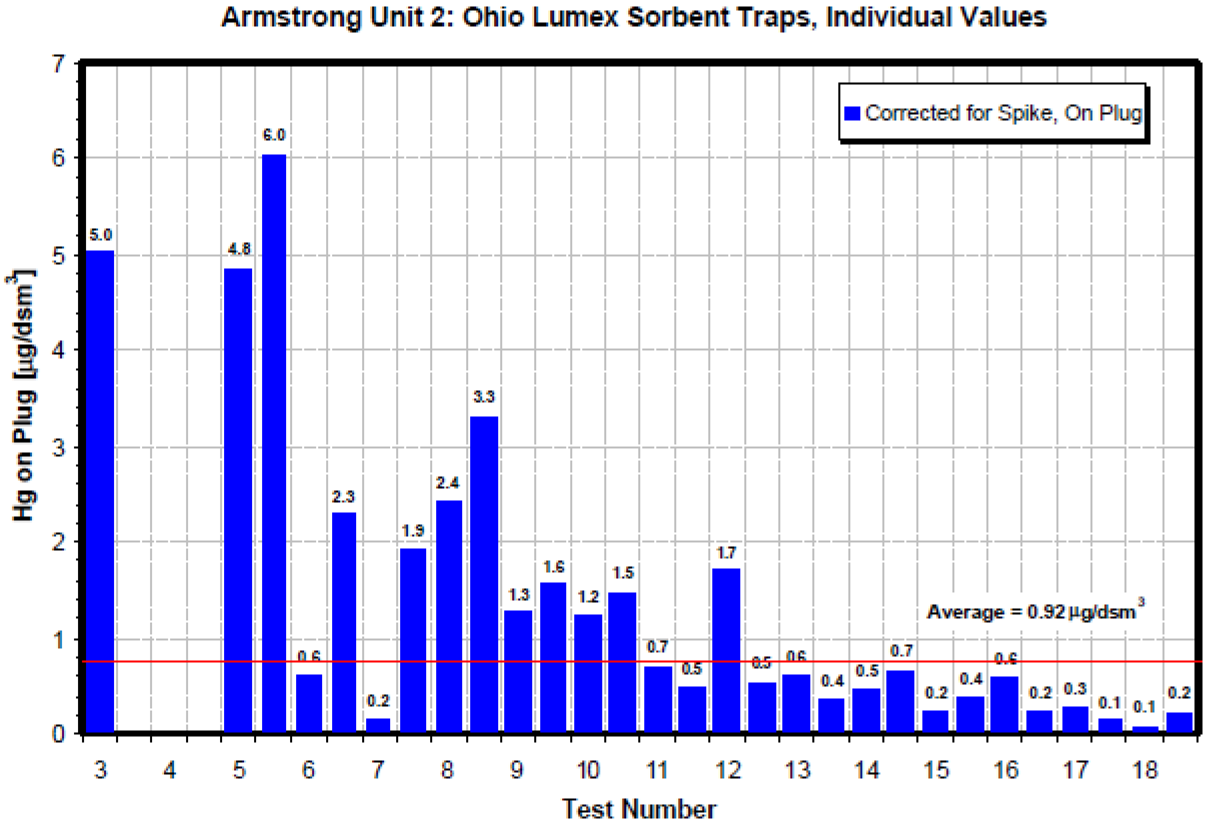


Figure 5-33: Hg Concentration on the Plug

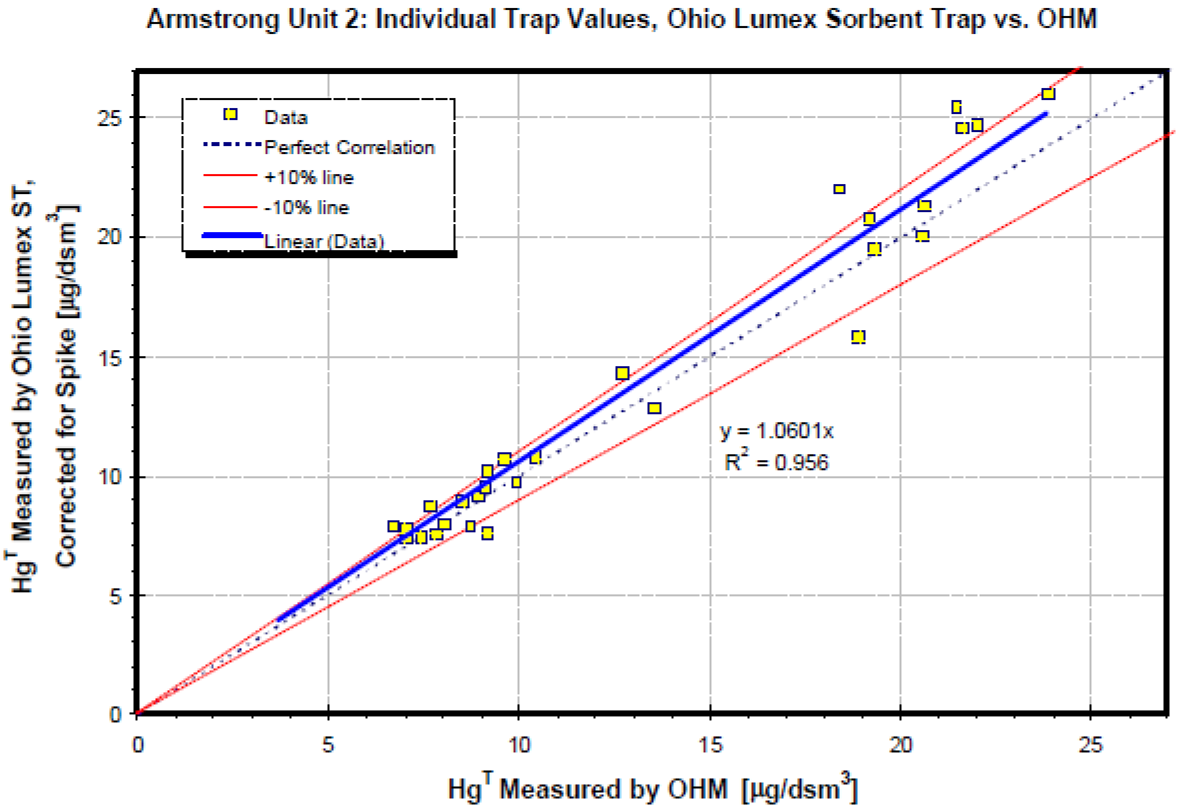


Figure 5-34: HgT Uncorrected for Spike Measured by Ohio Lumex-Apex Instruments vs. OHM

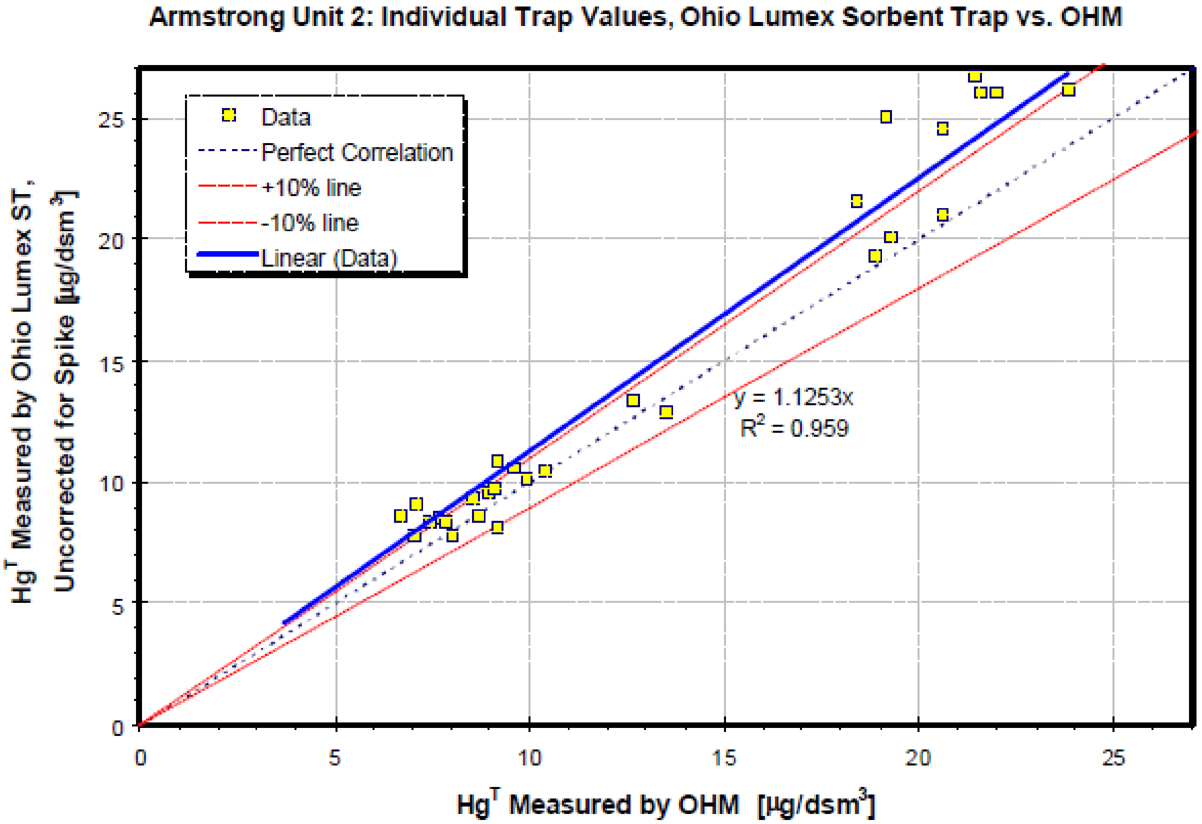


Figure 5 -35: HgT Uncorrected for Spike Measured by Ohio Lumex-Apex Instruments ST vs. OHM

Since Ohio Lumex traps were analyzed on site, it was requested that the amount of mercury collected on the plug be analyzed and reported separately. Mercury concentration, measured on the plug, is presented in Figures 5-32 and 5-33. On average, the plug contained less than 1 mg/dsm3 (approximately 6 percent) of total measured mercury. However, very high mercury concentrations (5-6 mg/dsm3, corresponding to 30 to 40 percent of the total mercury) were measured on the plug at the beginning of the test. It is unknown whether these high plug concentrations were caused by an error in the analysis procedure, or were due to combustion problems that generated high levels of unburned carbon (UC). The high UC levels on the plug would adsorb mercury from the flue gas stream to the traps.

A comparison between the total mercury concentration measured by the Ohio Lumex – Apex Instruments test team and HgT values measured by the Reference Method (OHM), are presented in Figure 5-34. The ST values are corrected for the spike. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

The correlation coefficient R2 of 0.956 indicates an excellent correlation between the HgT concentrations measured by the Ohio Lumex-Apex Instruments test team and OHM. The slope of the correlation line y of 1.0601 indicates that, the HgT concentration measured by the Ohio Lumex-Apex Instruments ST at Armstrong and corrected for the spike is, on average, 6.0 percent higher compared to the OHM results.

A comparison between the HgT values uncorrected for spike measured by the Ohio Lumex – Apex Instruments test team and the Hg T values measured by OHM, are presented in Figure 5-35. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

The correlation coefficient R2 remained virtually constant (0.959 vs. 0.956) when uncorrected for spike Hg T values were used. With the uncorrected-for-spike HgT values, the slope of the correlation line y increased from 1.0601 to 1.1253, indicating that the HgT values uncorrected for spike measured by the Ohio Lumex-Apex Instruments are, on average, 12.53 percent higher compared to the OHM results.

Test statistics are summarized in Tables 5-19a and 5-19b. The spike corrected results are compared to the OHM results in Table 5-19a, while Table 5-19b compares the uncorrected sorbent trap data to the OHM results. As the results show, precision of the OHM is better (smaller S, CI, and RCI) compared to the Appendix K results obtained by Ohio Lumex – Apex Instruments.

Table 5-19a Ohio Lumex-Apex Instruments Sorbent Trap Corrected for Spike vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Ohio Lumex	OHM	Ohio Lumex	OHM	Ohio Lumex	OHM
Average Hg^1	µg/wsm^3	**20.6**	**19.3**	**8.7**	**8.5**	**13.8**	**13.1**
Std. Dev.	µg/wsm^3	**± 4.4**	± 3.1	**± 1.2**	± 1.1	**± 6.7**	± 5.9
RSE	%	**± 21.3**	± 15.8	**± 13.8**	± 13	**± 48.6**	± 45.2
No. of Tests	NA	**12**	24	**16**	32	**28**	56
95% CI	µg/wsm^3	**± 2.8**	± 1.3	**± 0.6**	± 0.4	**± 2.6**	± 1.6
95% RCI	%	**± 13.6**	± 6.7	**± 7.4**	± 4.6	**± 18.9**	± 12.1
Bias Error	%	**6.6**		**2.5**		**5.1**	

Table 5-19b Ohio Lumex-Apex Instruments SorbentTrap Uncorrected for Spike vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Ohio Lumex	OHM	Ohio Lumex	OHM	Ohio Lumex	OHM
Average Hg^1	µg/wsm^3	**21.9**	**19.3**	**9.1**	**8.5**	**14.6**	**13.1**
Std. Dev.	µg/wsm^3	**± 4.8**	± 3.1	**± 1.0**	± 1.1	**± 7.2**	± 5.9
RSE	%	**± 22**	± 15.8	**± 11.1**	± 13	**± 49.2**	± 45.2
No. of Tests	NA	**12**	24	**16**	32	**28**	56
95% CI	µg/wsm^3	**± 3.1**	± 1.3	**± 0.5**	± 0.4	**± 2.8**	± 1.6
95% RCI	%	**± 14.0**	± 6.7	**± 5.9**	± 4.6	**± 19.1**	± 12.1
Bias Error	%	**13.3**		**7.9**		**11.3**	

The average value of bias error B for Tests 5 to 18, calculated from Equation 5-2, for the spike corrected data is 5.1 percent. This is relatively close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 6.6 percent. For the low-Hg coal, bias error is considerably smaller, only 2.5 percent. Also, measurement precision of both methods is much better for low-Hg coal.

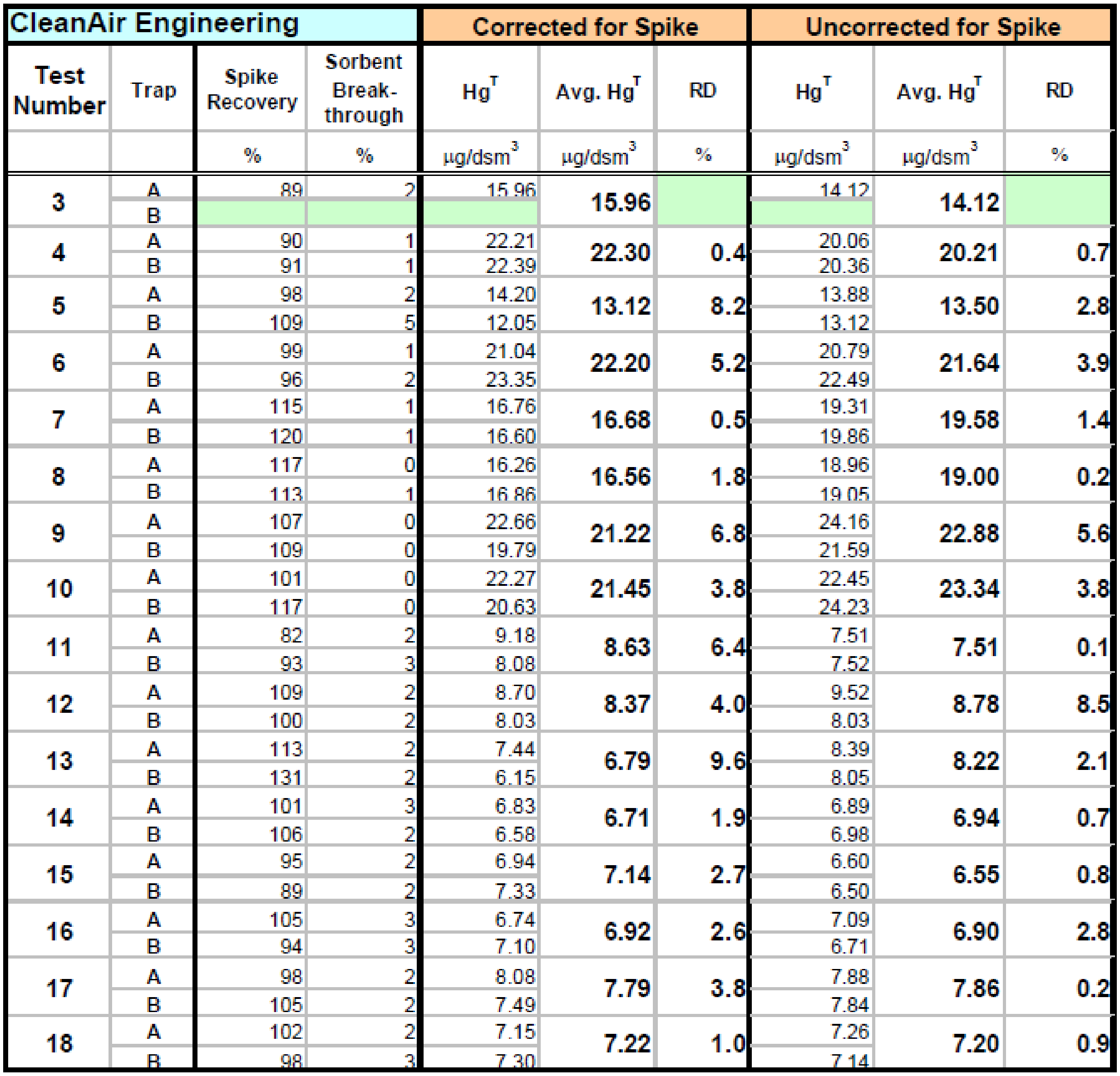
The average value of bias error B for Tests 5 to 18, calculated from Equation 5-2, for the uncorrected data is 11.3 percent. This is very close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is higher, 13.3 percent. For the low-Hg coal, the bias error is lower, 7.9 percent. Also, measurement precision of both methods is much better for the low-Hg coal compared to the high-Hg coal.

Also, comparing the results from Tables 5-19a and 5-19b, it can be concluded that correcting sorbent trap data, obtained by the Ohio Lumex-Apex Instruments test team at Armstrong, for spike did not have a significant effect on the precision of the Appendix K results.

5.6.2. CleanAir Engineering-CONSOL

The HgT concentrations expressed on a dry corrected and uncorrected basis, sorbent breakthrough, and RD values determined by CleanAir Engineering -CONSOL are summarized in Table 5-20. The average relative RD for all paired traps was smaller than 10 percent: 3.9 percent for the spike corrected HgT data, and 2.3 percent for uncorrected HgT data. The section 2 breakthrough was 1.8 percent, less than the maximum allowed value of 5 percent. The average spike recovery R was 103 percent, with only one trap exceeding the maximum allowed value of 125 percent (R = 131 for Trap B, Test 13). Therefore, all but one Hg measurements performed by the CleanAir Engineering-CONSOL team met the Appendix K requirements. One trap broke at the beginning of the test. No other problems were encountered.

Table 5-20 CleanAir Engineering -CONSOL Sorbent Trap Data and Results



CleanAir Engineering				Corrected for Spike			Uncorrected for Spike		
Test Number	Trap	Spike Recovery	Sorbent Break-through	Hg^T	Avg. Hg^T	RD	Hg^T	Avg. Hg^T	RD
		%	%	µg/dsm^3	µg/dsm^3	%	µg/dsm^3	µg/dsm^3	%
3	A	89	2	15.96	15.96		14.12	14.12	
	B								
4	A	90	1	22.21	22.30	0.4	20.06	20.21	0.7
	B	91	1	22.39			20.36		
5	A	98	2	14.20	13.12	8.2	13.88	13.50	2.8
	B	109	5	12.05			13.12		
6	A	99	1	21.04	22.20	5.2	20.79	21.64	3.9
	B	96	2	23.35			22.49		
7	A	115	1	16.76	16.68	0.5	19.31	19.58	1.4
	B	120	1	16.60			19.86		
8	A	117	0	16.26	16.56	1.8	18.96	19.00	0.2
	B	113	1	16.86			19.05		
9	A	107	0	22.66	21.22	6.8	24.16	22.88	5.6
	B	109	0	19.79			21.59		
10	A	101	0	22.27	21.45	3.8	22.45	23.34	3.8
	B	117	0	20.63			24.23		
11	A	82	2	9.18	8.63	6.4	7.51	7.51	0.1
	B	93	3	8.08			7.52		
12	A	109	2	8.70	8.37	4.0	9.52	8.78	8.5
	B	100	2	8.03			8.03		
13	A	113	2	7.44	6.79	9.6	8.39	8.22	2.1
	B	131	2	6.15			8.05		
14	A	101	3	6.83	6.71	1.9	6.89	6.94	0.7
	B	106	2	6.58			6.98		
15	A	95	2	6.94	7.14	2.7	6.60	6.55	0.8
	B	89	2	7.33			6.50		
16	A	105	3	6.74	6.92	2.6	7.09	6.90	2.8
	B	94	3	7.10			6.71		
17	A	98	2	8.08	7.79	3.8	7.88	7.86	0.2
	B	105	2	7.49			7.84		
18	A	102	2	7.15	7.22	1.0	7.26	7.20	0.9
	B	98	3	7.30			7.14		

The CleanAir Engineering-CONSOL results are also presented in a graphical form in Figures 5-36 to 5-41.

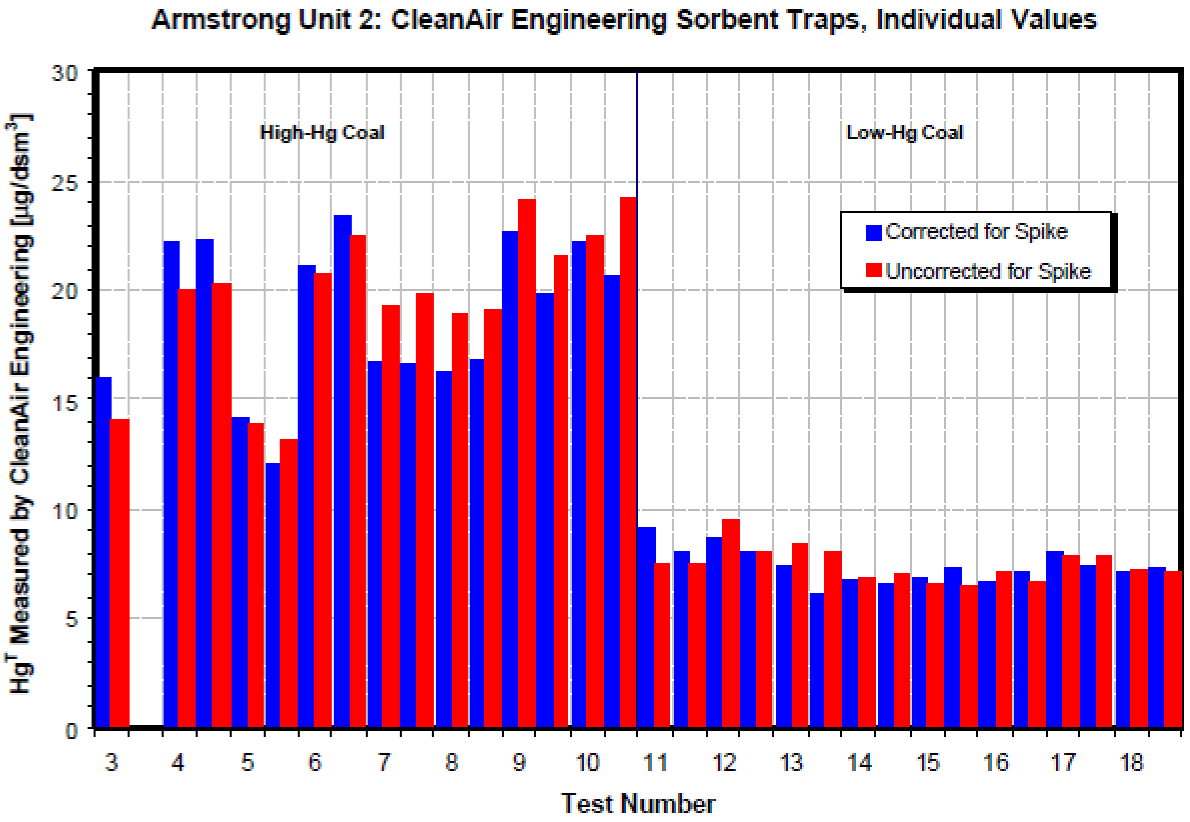


Figure 5 -36: Corrected and Uncorrected HgT Concentrations Measured by Individual CleanAir Engineering Sorbent Traps

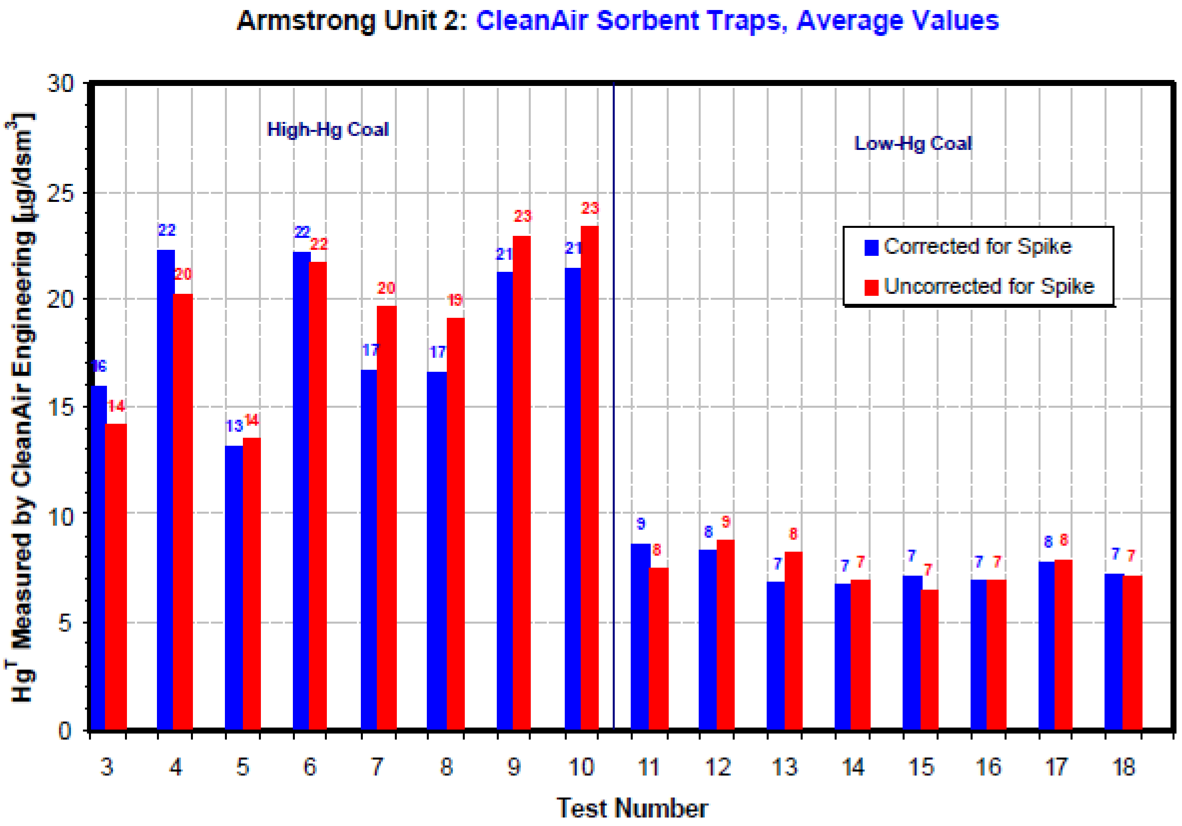


Figure 5-37: Average Corrected and Uncorrected HgT Concentrations Measured by CleanAir Engineering

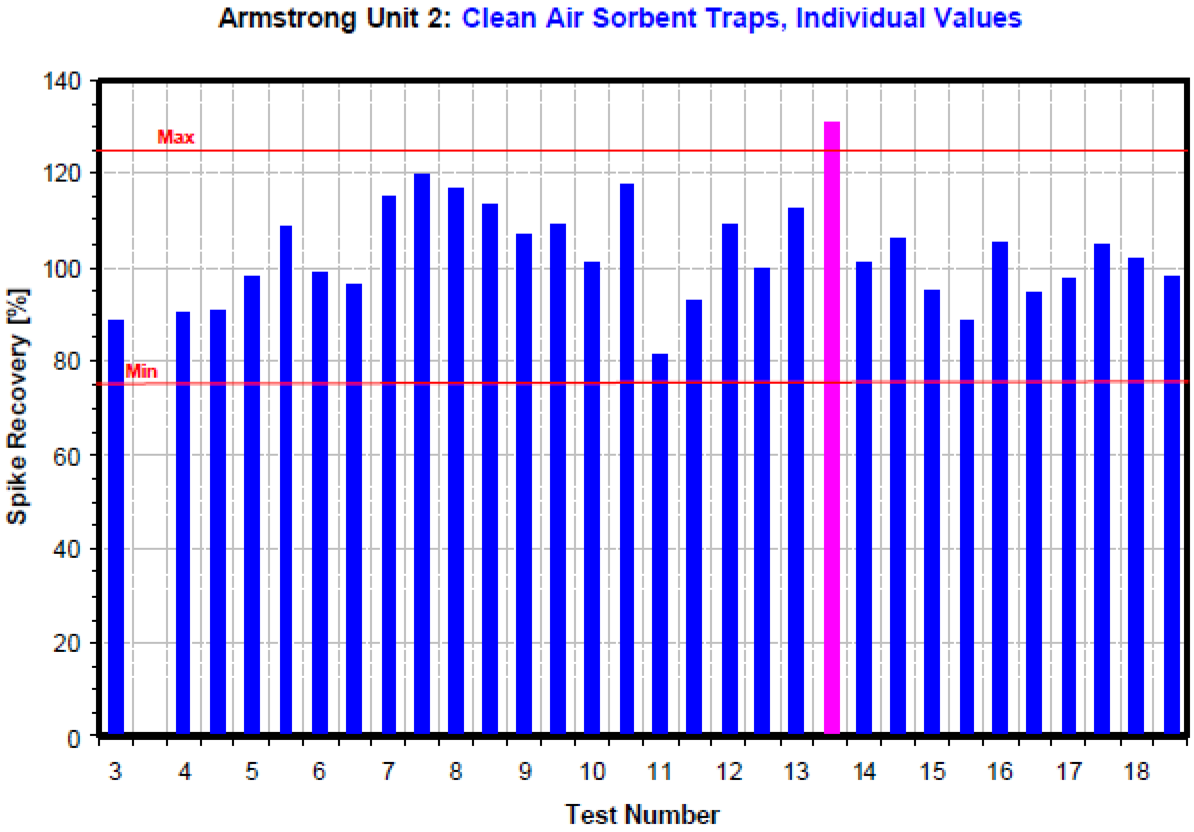


Figure 5-38: Spike Recovery for CleanAir Engineering Sorbent Traps

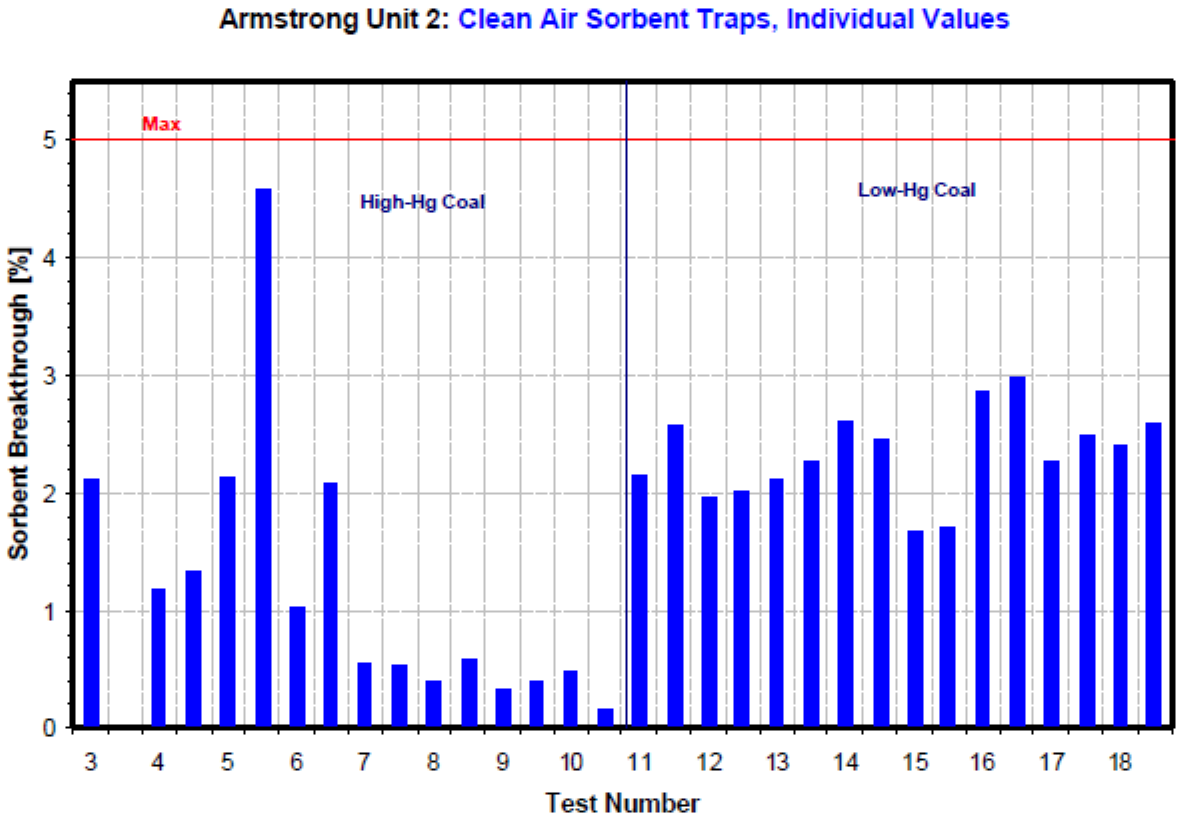


Figure 5-39: Sorbent Breakthrough for CleanAir Engineering Sorbent Traps

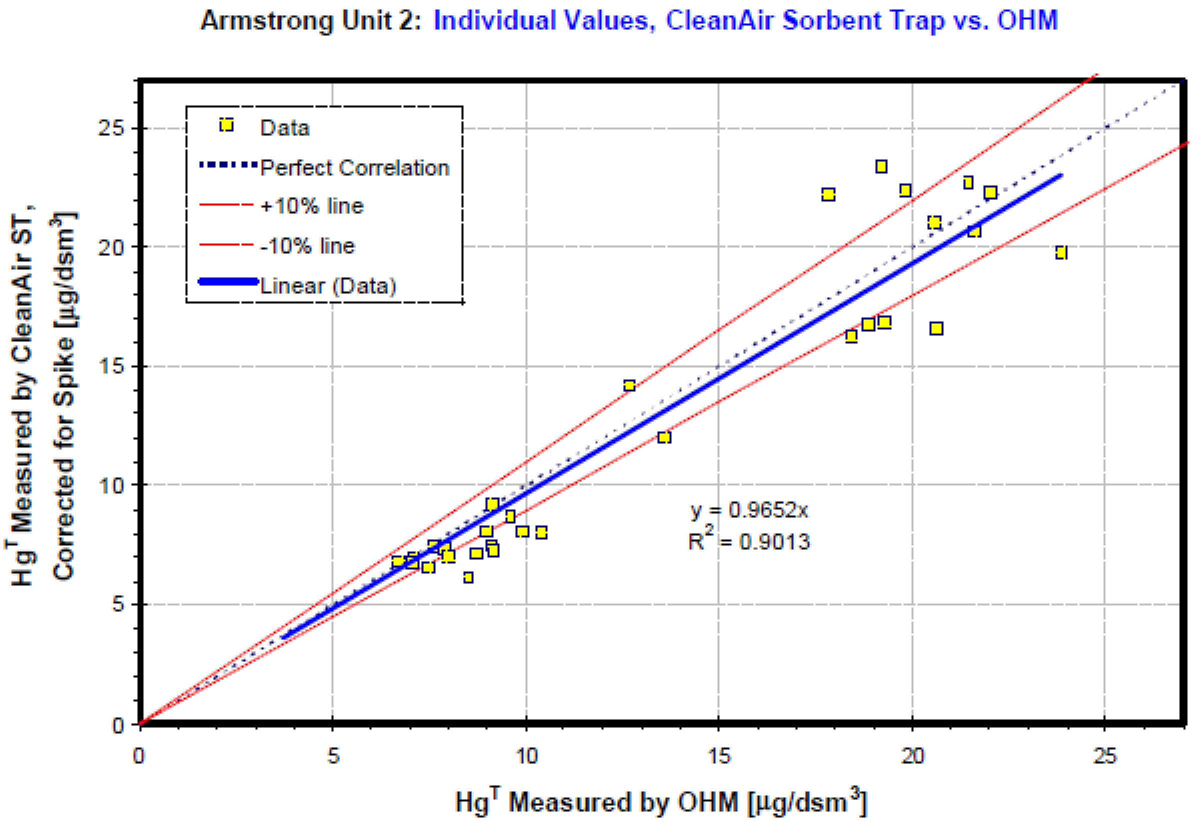


Figure 5-40: HgT corrected for spike measured by CleanAir Engineering ST vs. OHM

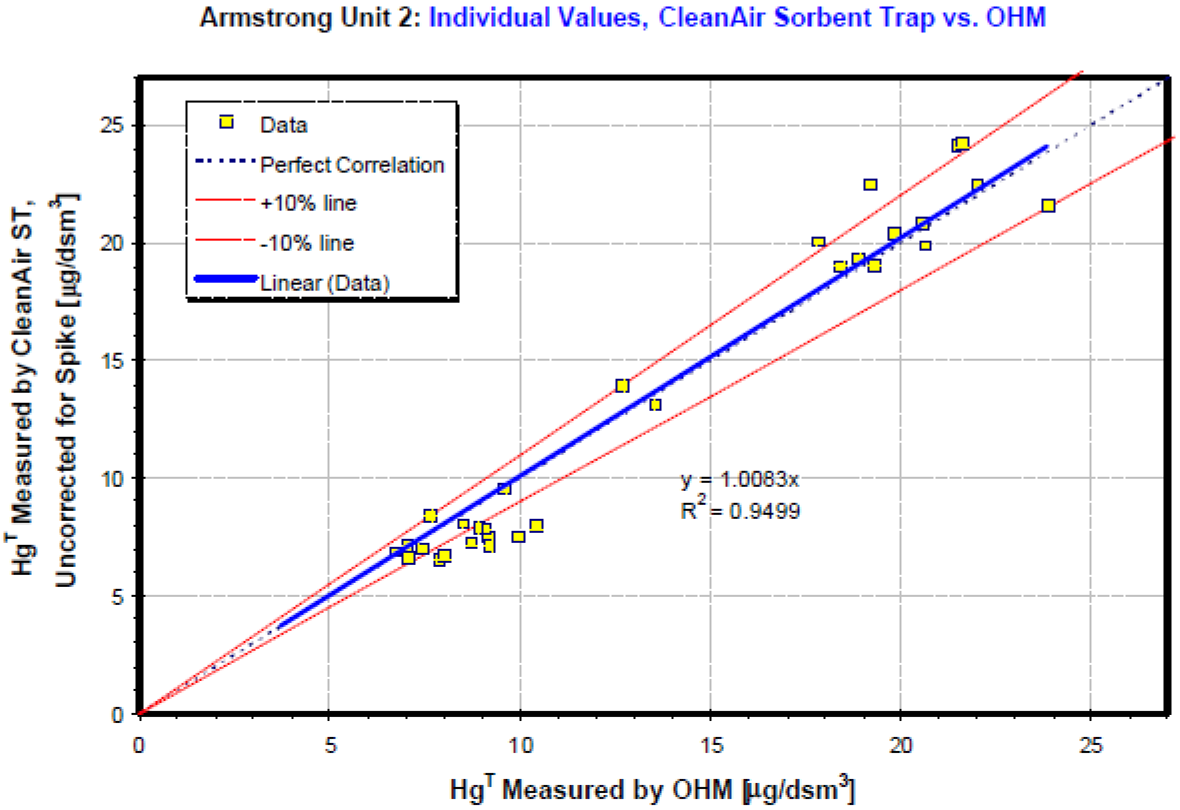


Figure 5-41: HgT Uncorrected for Spike Measured by CleanAir Engineering ST vs. OHM

The HgT values measured by individual sorbent traps expressed on a dry basis, corrected and uncorrected for the spike, are presented in Figure 5-36. The average difference between the corrected and uncorrected values is 0.4 mg/dsm3, with uncorrected values being higher.

The average HgT values, corrected and uncorrected for spike, are presented in Figure 5-37. Spike recovery for all tests is presented in Figure 5-38. For most of the tests, the uncorrected HgT values were higher compared to the corrected values, although for some of the tests the uncorrected values were lower.

The information on sorbent breakthrough is presented in Figure 5-39. The results from Figure 5-39 show that the average sorbent breakthrough for the low-Hg coal was higher compared to that of the high-Hg coal (2.3 vs. 1.2 percent), and also more uniform.

A comparison between the total mercury concentration measured by the CleanAir Engineering - CONSOL test team and HgT values measured by OHM, is presented in Figure 5-40. The HgT values, measured by sorbent traps, are corrected for the spike. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

The correlation coefficient R2 of 0.9013 indicates a very good correlation between the HgT concentrations measured by the CleanAir Engineering – CONSOL test team and OHM. The slope of the correlation line y of 0.9652 indicates that the HgT concentration measured by CleanAir Engineering at Armstrong and corrected for spike is, on average, 3.5 percent lower compared to the OHM results.

Also, variation in HgT concentration values measured with the low-Hg coal was considerably lower compared to those of the high-Hg coals where data scatter was considerable.

A comparison between the HgT values uncorrected for spike, measured by CleanAir Engineering – CONSOL, and the HgT values measured by OHM is presented in Figure 5-41. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

For the uncorrected Hg T values, correlation coefficient R2 improved compared to the corrected values (0.9499 vs. 0.9013). The slope of the correlation line y increased from 0.9652 to 1.0083, indicating that the uncorrected HgT values measured by CleanAir-CONSOL were very close to the OHM values.

Test statistics are summarized in Tables 5-21a and 5-21b. The spike corrected results are compared to the OHM results in Table 5-21a, while Table 5-21b compares the uncorrected sorbent trap data to the OHM results. As the results show, the precision of the OHM is better (smaller S, CI, and RCI) compared to the Appendix K results obtained by CleanAir-CONSOL.

Table 5-21a CleanAir Engineering Sorbent Trap Corrected for Spike vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Clean Air	OHM	Clean Air	OHM	Clean Air	OHM
Average Hg^T	$\mu g/wsm^3$	**19.1**	**19.3**	**7.4**	**8.5**	**12.9**	**13.5**
Std. Dev.	$\mu g/wsm^3$	**± 3.6**	± 3.1	**± 0.8**	± 1.1	**± 6.4**	± 5.9
RSE	%	**± 18.8**	± 15.9	**± 10.7**	± 13	**± 49.7**	± 43.8
No. of Tests	NA	**14**	28	**16**	32	**30**	60
95% CI	$\mu g/wsm^3$	**± 2.1**	± 1.2	**± 0.4**	± 0.4	**± 2.3**	± 1.5
95% RCI	%	**± 10.8**	± 6.2	**± 5.7**	± 4.6	**± 18.1**	± 11.3
Bias Error	%	**-1.0**		**-12.0**		**-4.7**	

Table 5-21b CleanAir Engineering Sorbent Trap Uncorrected for Spike vs. OHM Comparison

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		Clean Air	OHM	Clean Air	OHM	Clean Air	OHM
Average Hg[1]	µg/wsm³	**20.0**	**19.3**	**7.5**	**8.5**	**13.3**	**13.5**
Std. Dev.	µg/wsm³	**± 3.3**	± 3.1	**± 0.8**	± 1.1	**± 6.7**	± 5.9
RSE	%	**± 16.3**	± 15.9	**± 10.4**	± 13	**± 50.3**	± 43.8
No. of Tests	NA	**14**	28	**16**	32	**30**	60
95% CI	µg/wsm³	**± 1.9**	± 1.2	**± 0.4**	± 0.4	**± 2.5**	± 1.5
95% RCI	%	**± 9.4**	± 6.2	**± 5.6**	± 4.6	**± 18.4**	± 11.3
Bias Error	%	**3.9**		**-11.4**		**-1.2**	

The average value of bias error B for Tests 4 to 18 for the spike corrected data is -4.7 percent. This is relatively close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is -1 percent. For the low-Hg coal, bias error is considerably higher and negative, -12 percent. The data scatter for the low-Hg coal is much smaller compared to the high-Hg coal, resulting in smaller values of S, RSE, CI, and RCI.

The average value of the bias error B for Tests 4 to 18 for the uncorrected data is -1.2 percent. This is relatively close to the bias error estimated from the slope y of thecorrelation line. The bias error for the high-Hg coal is 3.9 percent. For the low-Hg coal, the bias error is higher and negative, -11.4 percent. Also, measurement precision of both methods is much better for the low-Hg coal compared to the high-Hg coal.

Also, by comparing the results from Tables 5-21a and 5-21b, it can be concluded that correcting the sorbent trap data, obtained at Armstrong by the CleanAir Engineering-CONSOL test team, for spike did not have a significant effect on the precision of the Appendix K results.

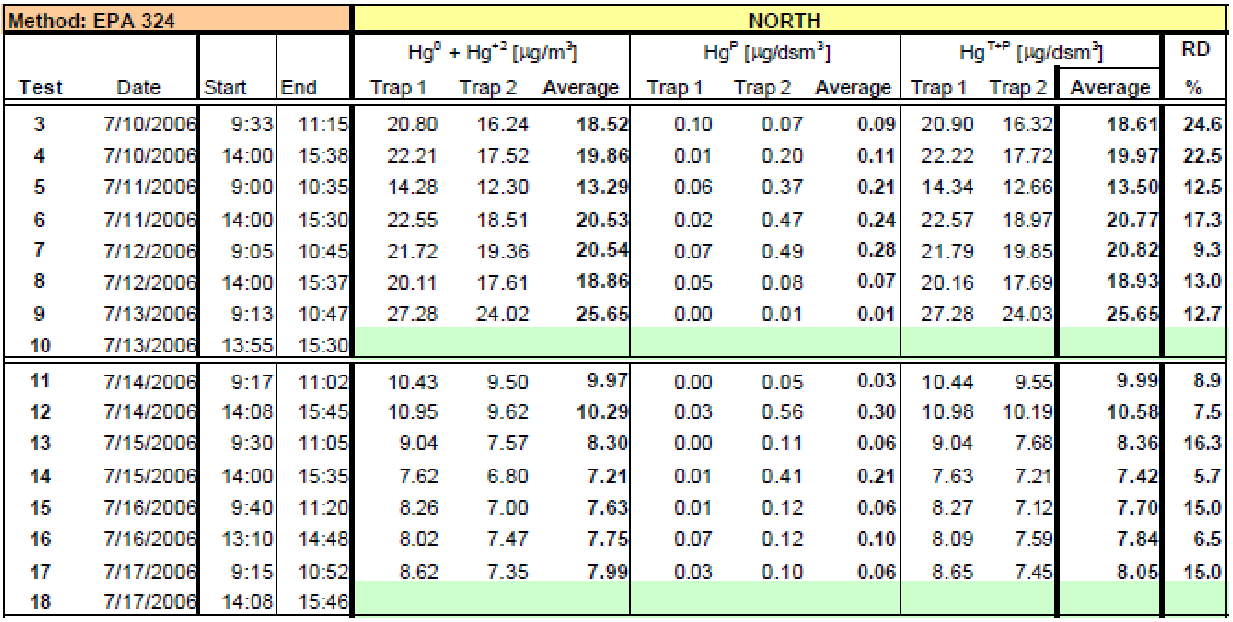
5.6.3. Frontier Geosciences

Frontier Geosciences, Inc . used the Mercury in Flue Gas via Frontier-Sorbent Total Mercury Method (FSTM) (EPA Method), and Mercury Speciation in Flue Gas via Flue Gas Adsorbent Mercury Speciation Method (FAMS), to measure total mercury and mercury speciation at Armstrong. It has to be noted that Method 324 allows for the use of single traps for general monitoring but requires paired traps when the method is used to determine compliance. Two-section traps are specified to determine if there is significant breakthrough of Hg through the sorbent material. The method also requires periodic spike recovery testing. Method 324 was never finalized.

As described in Section 3.3 of this report, Frontier obtained flue gas samples from the North and South ports located on the 3rd CEM platform at Armstrong (see Figures 3-7 and 3-11).

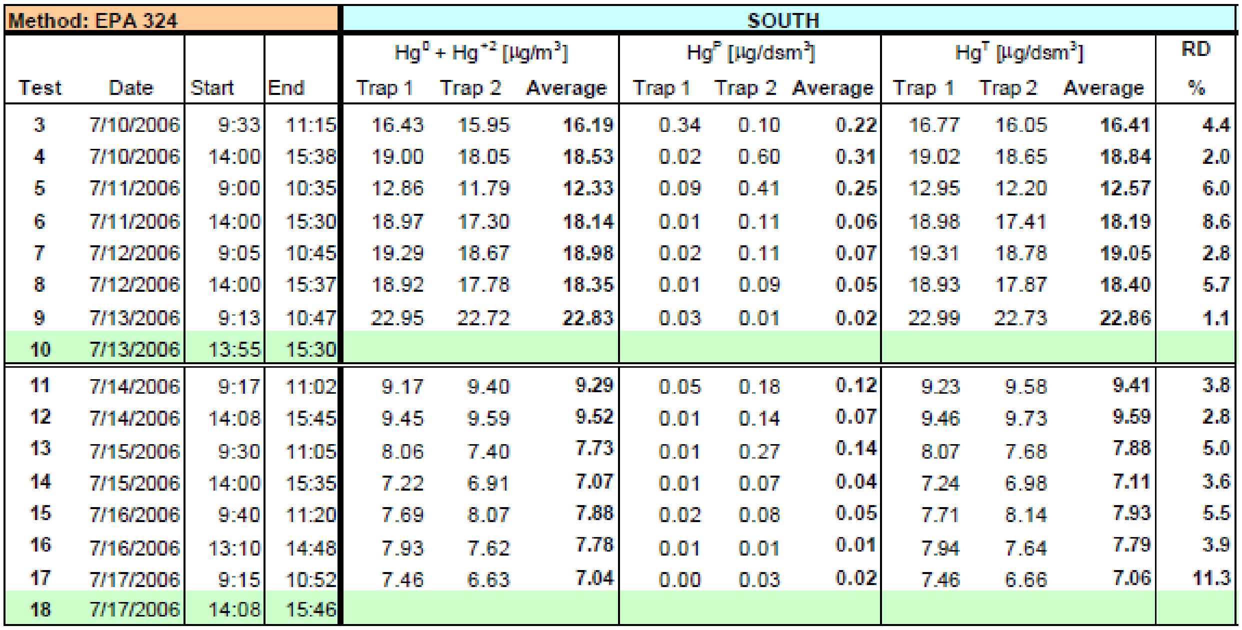
5.6.3.1. FSTM (EPA Method 324 – No Spiking) Results. The gas-phase, particle-bound, and total Hg concentration values, measured by FSTM in the North and South ports, expressed on a dry basis and corrected for blanks, are summarized in Table 5-22a (North Port), and Table 5-22b (South Port). The stack average values are summarized in Table 5-23.

Table 5-22a Gas-Phase, Particle -Bound, and Total Hg Concentration Measured by FSTM in the North Port



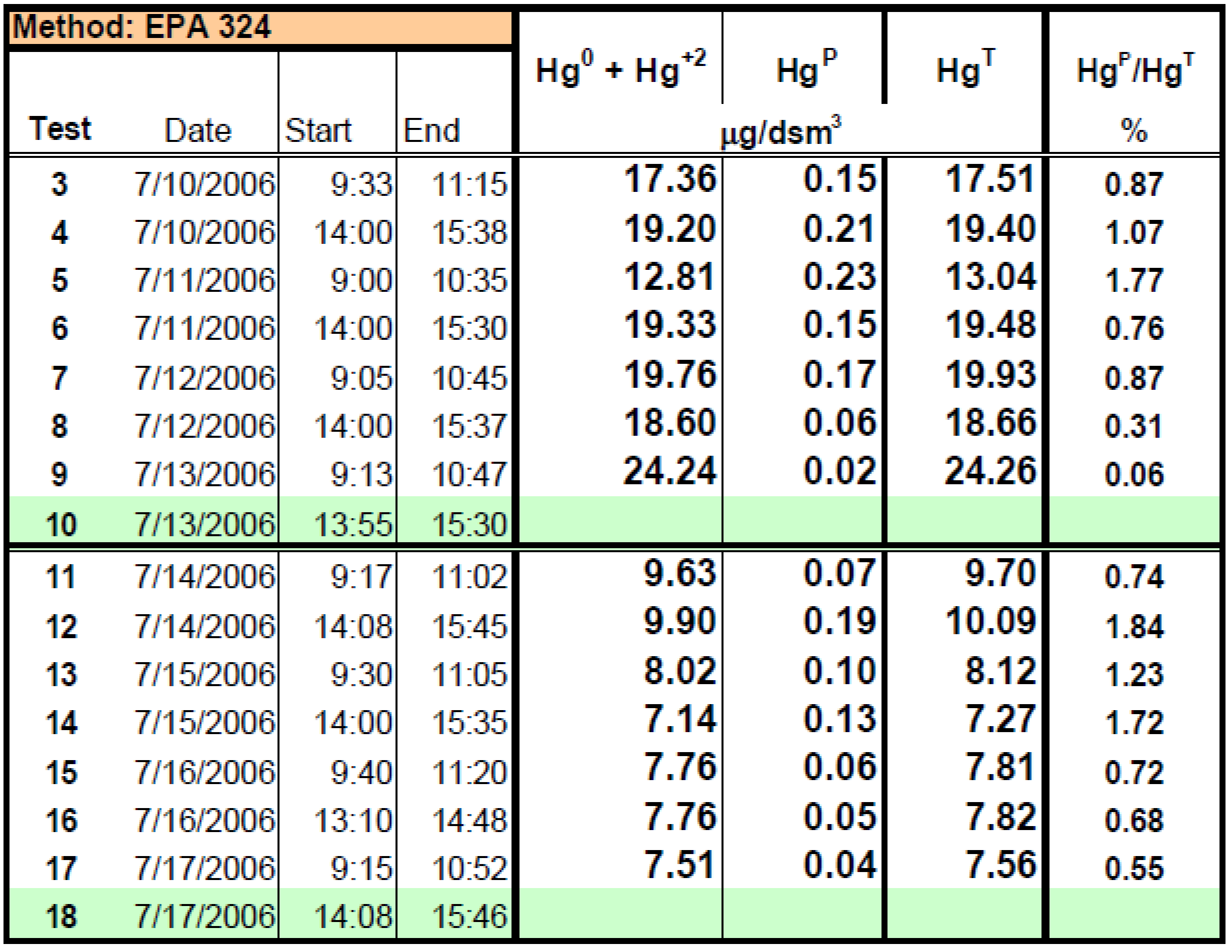
Method: EPA 324				NORTH									
				$Hg^0 + Hg^{+2}$ [µg/m³]			Hg^P [µg/dsm³]			Hg^{T+P} [µg/dsm³]			RD
Test	Date	Start	End	Trap 1	Trap 2	Average	Trap 1	Trap 2	Average	Trap 1	Trap 2	Average	%
3	7/10/2006	9:33	11:15	20.80	16.24	**18.52**	0.10	0.07	**0.09**	20.90	16.32	**18.61**	**24.6**
4	7/10/2006	14:00	15:38	22.21	17.52	**19.86**	0.01	0.20	**0.11**	22.22	17.72	**19.97**	**22.5**
5	7/11/2006	9:00	10:35	14.28	12.30	**13.29**	0.06	0.37	**0.21**	14.34	12.66	**13.50**	**12.5**
6	7/11/2006	14:00	15:30	22.55	18.51	**20.53**	0.02	0.47	**0.24**	22.57	18.97	**20.77**	**17.3**
7	7/12/2006	9:05	10:45	21.72	19.36	**20.54**	0.07	0.49	**0.28**	21.79	19.85	**20.82**	**9.3**
8	7/12/2006	14:00	15:37	20.11	17.61	**18.86**	0.05	0.08	**0.07**	20.16	17.69	**18.93**	**13.0**
9	7/13/2006	9:13	10:47	27.28	24.02	**25.65**	0.00	0.01	**0.01**	27.28	24.03	**25.65**	**12.7**
10	7/13/2006	13:55	15:30										
11	7/14/2006	9:17	11:02	10.43	9.50	**9.97**	0.00	0.05	**0.03**	10.44	9.55	**9.99**	**8.9**
12	7/14/2006	14:08	15:45	10.95	9.62	**10.29**	0.03	0.56	**0.30**	10.98	10.19	**10.58**	**7.5**
13	7/15/2006	9:30	11:05	9.04	7.57	**8.30**	0.00	0.11	**0.06**	9.04	7.68	**8.36**	**16.3**
14	7/15/2006	14:00	15:35	7.62	6.80	**7.21**	0.01	0.41	**0.21**	7.63	7.21	**7.42**	**5.7**
15	7/16/2006	9:40	11:20	8.26	7.00	**7.63**	0.01	0.12	**0.06**	8.27	7.12	**7.70**	**15.0**
16	7/16/2006	13:10	14:48	8.02	7.47	**7.75**	0.07	0.12	**0.10**	8.09	7.59	**7.84**	**6.5**
17	7/17/2006	9:15	10:52	8.62	7.35	**7.99**	0.03	0.10	**0.06**	8.65	7.45	**8.05**	**15.0**
18	7/17/2006	14:08	15:46										

Table 5 -22b Gas-Phase, Particle -Bound, and Total Hg Concentration Measured by FSTM in the South Port



Method: EPA 324				SOUTH									
				Hg^0 + Hg^{+2} [µg/m^3]			Hg^P [µg/dsm^3]			Hg^T [µg/dsm^3]			RD
Test	Date	Start	End	Trap 1	Trap 2	Average	Trap 1	Trap 2	Average	Trap 1	Trap 2	Average	%
3	7/10/2006	9:33	11:15	16.43	15.95	**16.19**	0.34	0.10	**0.22**	16.77	16.05	**16.41**	**4.4**
4	7/10/2006	14:00	15:38	19.00	18.05	**18.53**	0.02	0.60	**0.31**	19.02	18.65	**18.84**	**2.0**
5	7/11/2006	9:00	10:35	12.86	11.79	**12.33**	0.09	0.41	**0.25**	12.95	12.20	**12.57**	**6.0**
6	7/11/2006	14:00	15:30	18.97	17.30	**18.14**	0.01	0.11	**0.06**	18.98	17.41	**18.19**	**8.6**
7	7/12/2006	9:05	10:45	19.29	18.67	**18.98**	0.02	0.11	**0.07**	19.31	18.78	**19.05**	**2.8**
8	7/12/2006	14:00	15:37	18.92	17.78	**18.35**	0.01	0.09	**0.05**	18.93	17.87	**18.40**	**5.7**
9	7/13/2006	9:13	10:47	22.95	22.72	**22.83**	0.03	0.01	**0.02**	22.99	22.73	**22.86**	**1.1**
10	7/13/2006	13:55	15:30										
11	7/14/2006	9:17	11:02	9.17	9.40	**9.29**	0.05	0.18	**0.12**	9.23	9.58	**9.41**	**3.8**
12	7/14/2006	14:08	15:45	9.45	9.59	**9.52**	0.01	0.14	**0.07**	9.46	9.73	**9.59**	**2.8**
13	7/15/2006	9:30	11:05	8.06	7.40	**7.73**	0.01	0.27	**0.14**	8.07	7.68	**7.88**	**5.0**
14	7/15/2006	14:00	15:35	7.22	6.91	**7.07**	0.01	0.07	**0.04**	7.24	6.98	**7.11**	**3.6**
15	7/16/2006	9:40	11:20	7.69	8.07	**7.88**	0.02	0.08	**0.05**	7.71	8.14	**7.93**	**5.5**
16	7/16/2006	13:10	14:48	7.93	7.62	**7.78**	0.01	0.01	**0.01**	7.94	7.64	**7.79**	**3.9**
17	7/17/2006	9:15	10:52	7.46	6.63	**7.04**	0.00	0.03	**0.02**	7.46	6.66	**7.06**	**11.3**
18	7/17/2006	14:08	15:46										

Table 5-23 Average Gas-Phase, Particle-Bound, and Total Hg Concentration Measured by FSTM



Method: EPA 324				$Hg^0 + Hg^{+2}$	Hg^P	Hg^T	Hg^P/Hg^T
Test	Date	Start	End	µg/dsm^3			%
3	7/10/2006	9:33	11:15	17.36	0.15	17.51	0.87
4	7/10/2006	14:00	15:38	19.20	0.21	19.40	1.07
5	7/11/2006	9:00	10:35	12.81	0.23	13.04	1.77
6	7/11/2006	14:00	15:30	19.33	0.15	19.48	0.76
7	7/12/2006	9:05	10:45	19.76	0.17	19.93	0.87
8	7/12/2006	14:00	15:37	18.60	0.06	18.66	0.31
9	7/13/2006	9:13	10:47	24.24	0.02	24.26	0.06
10	7/13/2006	13:55	15:30				
11	7/14/2006	9:17	11:02	9.63	0.07	9.70	0.74
12	7/14/2006	14:08	15:45	9.90	0.19	10.09	1.84
13	7/15/2006	9:30	11:05	8.02	0.10	8.12	1.23
14	7/15/2006	14:00	15:35	7.14	0.13	7.27	1.72
15	7/16/2006	9:40	11:20	7.76	0.06	7.81	0.72
16	7/16/2006	13:10	14:48	7.76	0.05	7.82	0.68
17	7/17/2006	9:15	10:52	7.51	0.04	7.56	0.55
18	7/17/2006	14:08	15:46				

The average relative difference, RD, for all paired traps and North and South ports was 9 percent. The North port RD values were higher (13.3 percent) compared to the South port RD values (4.7 percent). The RD values for Tests 3, 4, 6, 13, 15, and 17 conducted in the North port were higher than 10 percent. In the South port, the RD value for Test 17 was higher than the EPA limit. The discrepancy in RD values for the North and South ports points to a measurement or sampling problem at the North port.

After eliminating test points with RD > 10 percent, the average RD for the North port decreased to 9.5 percent, and for the South port to 4.2 percent. The average RD for the stack decreased to 6.9 percent.

The particulate-bound mercury, measured by FSTM at Armstrong, was approximately 0.9 percent of the total measured Hg.

The FSTM results are also presented in a graphical form in Figures 5-42 to 5-47.

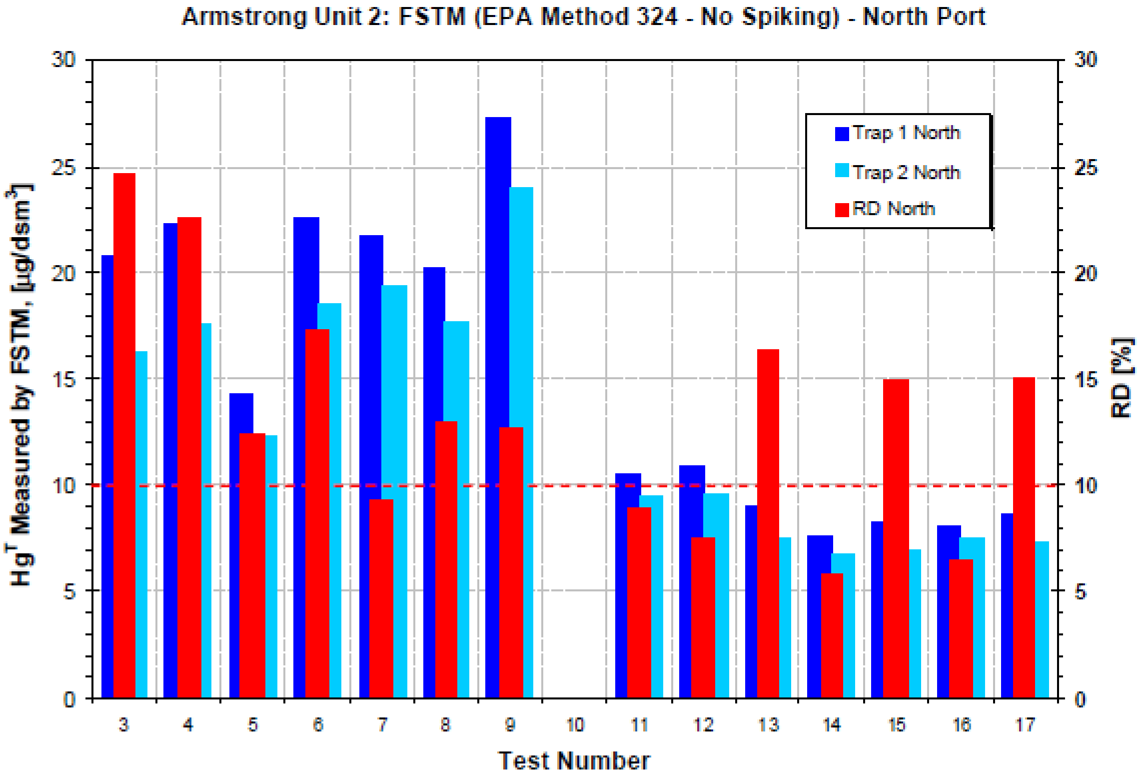


Figure 5-42: Total Hg Measured by FSTM (EPA Method 324): North Port

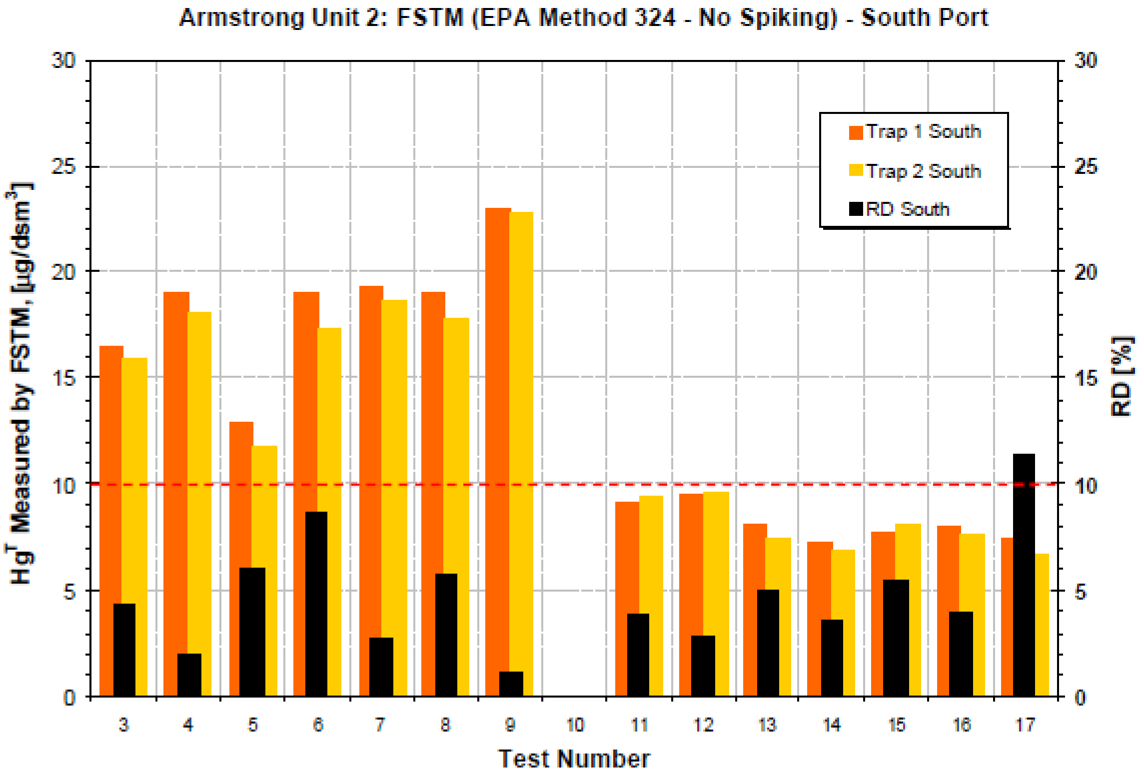


Figure 5-43: Total Hg Measured by FSTM (EPA Method 324): South Port

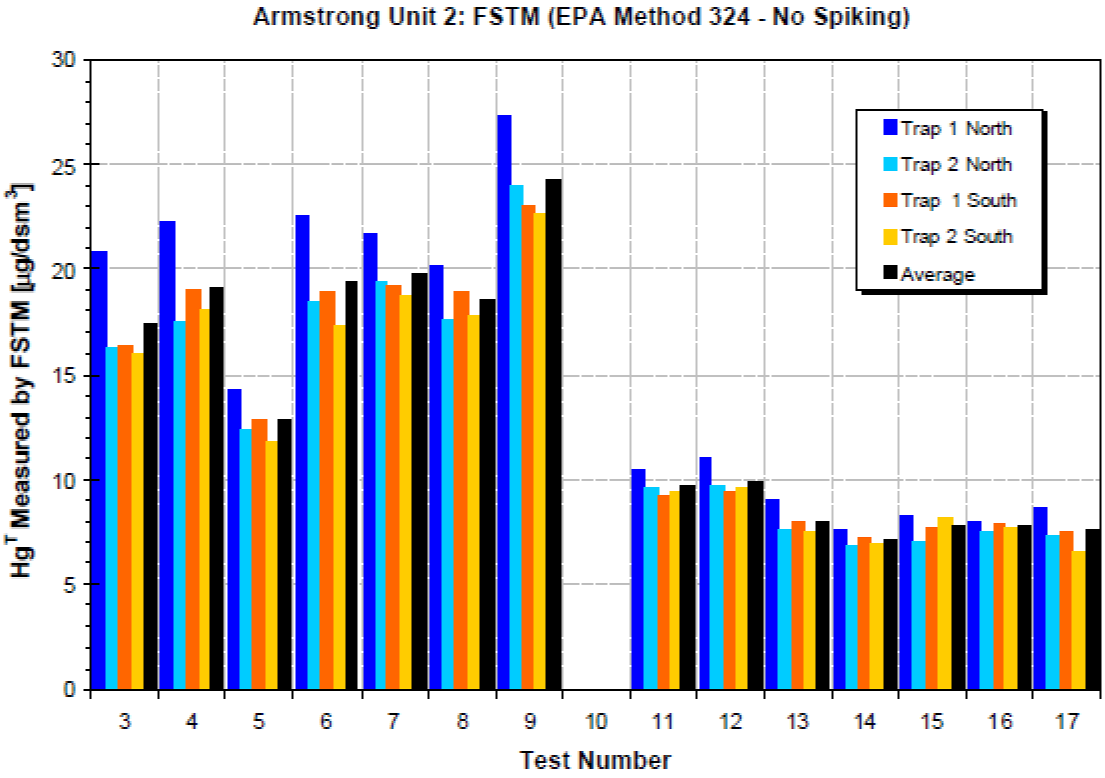


Figure 5-44: Total Hg Measured by FSTM (EPA Method 324)

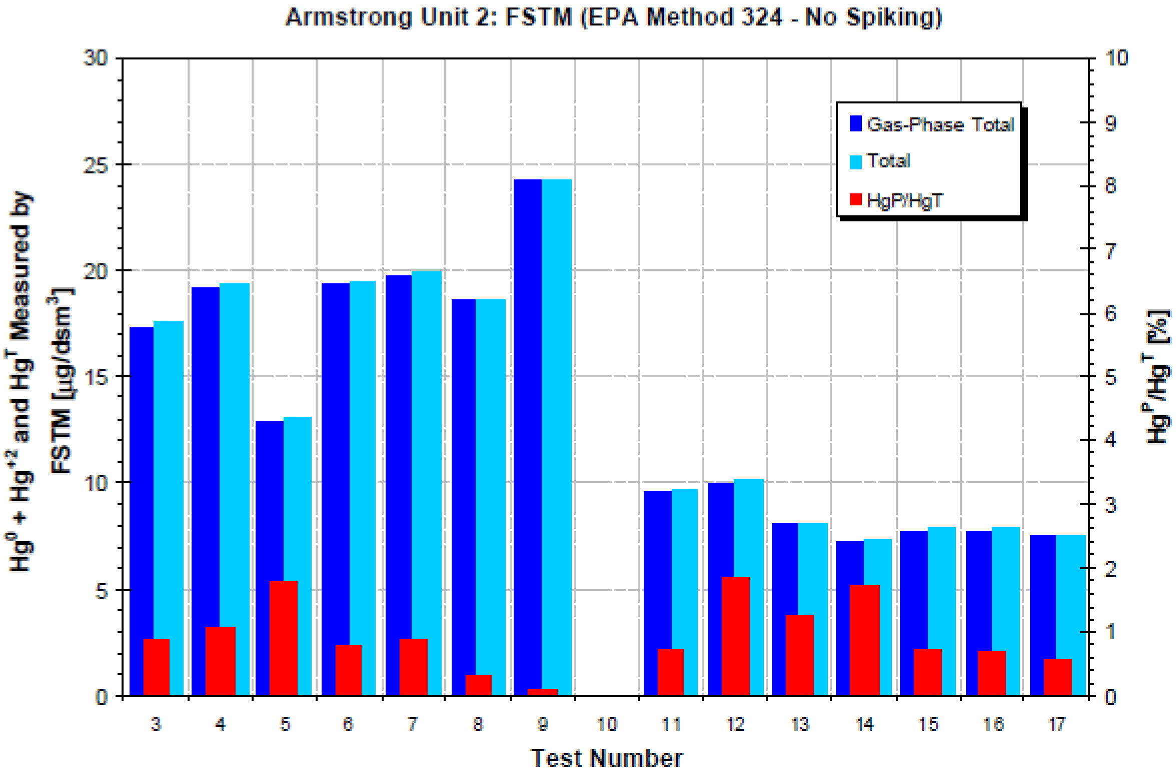


Figure 5-45: Gas-Phase, Particulate, and Total Hg Measured by FSTM

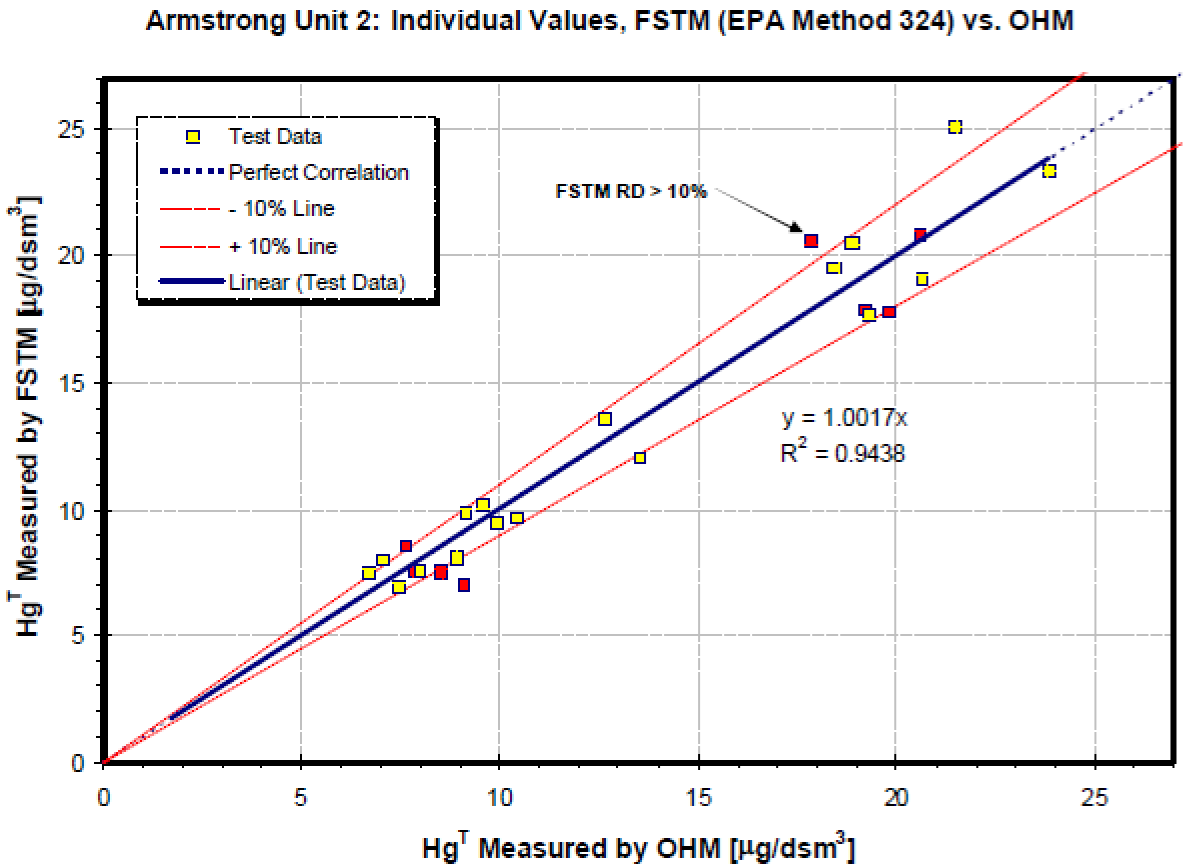


Figure 5-46: Total Hg Measured by FSTM vs. OHM – All Test Points

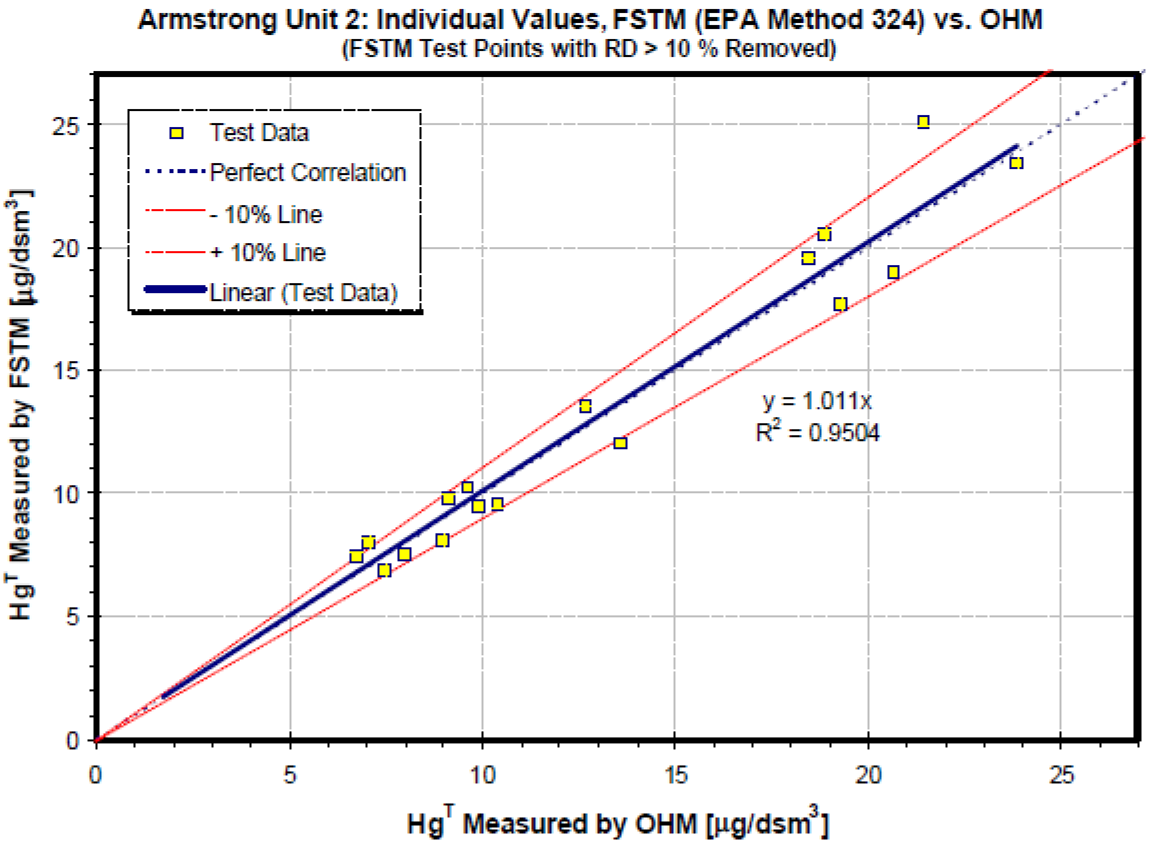


Figure 5-47: Total Hg Measured by FSTM vs. OHM – Test Points

The total Hg concentration, measured by FSTM in the North and South ports, and corresponding trap-to-trap RD values are presented in Figures 5-42 and 5-43. As discussed earlier, RD values for the seven test points from the North port and one test point from the South port exceeded 10 percent, pointing to a potential measurement or sampling problem at the North port. The North and South port values, and the stack average values (Average of North and South port results), are presented in Figure 5-44.

It has to be noted that no FSTM testing was performed during Tests 10 and 18 since the North and South ports were used to measure mercury stratification using specially designed probes.

The gas-phase, total, and particulate mercury is shown in Figure 5-45. The particulate mercury, measured by FSTM, was less than 1 percent of total.

A comparison between the total mercury concentration measured FSTM and HgT values measured by OHM, are presented in Figure 5-46. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis.

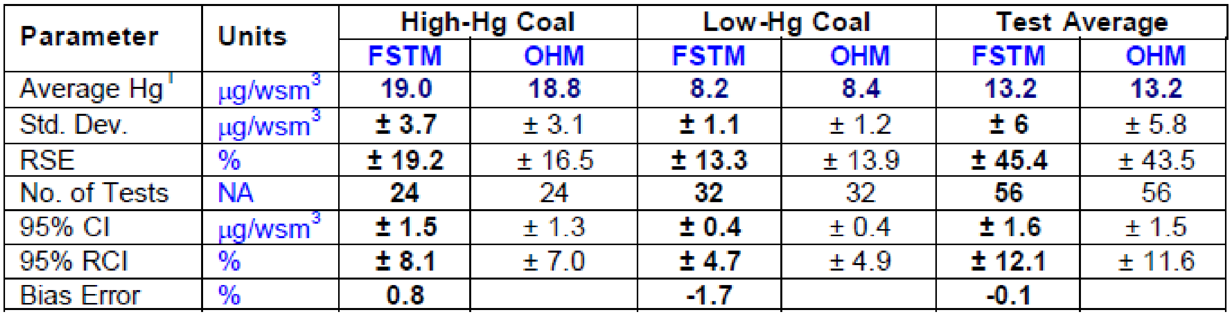
The correlation coefficient R2 of 0.9438 indicates a very good correlation between the HgT concentrations measured by FSTM and OHM. The slope of the correlation line y of 1.0017 indicates that the Hg T concentration measured by FSTM at Armstrong is, on average, approximately 0.2 percent higher compared to the OHM results. Also, variation in HgT concentration measured with the low-Hg coal was lower compared to the high-Hg coals.

The data points indicated by red squares denote tests with the trap-to-trap RD > 10 percent. Figure 5-47 shows a comparison between the FSTM and OHM for the FSTM test points with RD < 10 percent. The results show an improvement in correlation coefficient and a small change in slope, i.e., from 1.0017 to 1.011.

In conclusion, when only the test points with RD < 10 percent are considered, the total Hg concentration values, measured by FSTM at Armstrong are on average 1 percent higher compared to the OHM results.

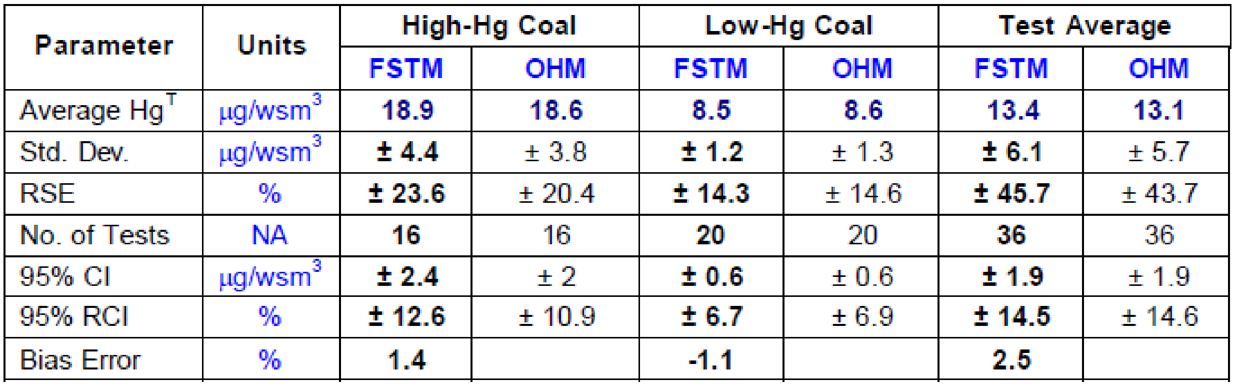
Test statistics are summarized in Tables 5-24a and Table 5-24b. The FAMS results for all test points, except for 3, 10, and 18 are compared to the OHM data in Table 5-24a. A comparison of the FSTM and OHM results for test points 3, 10, and 18 and for all tests points having RD > 10 percent is given in Table 5-24b. As the results show, precision of the OHM and FSTM methods is comparable. Also, the precision was better for the low-Hg coal, compared to the high-Hg coal.

Table 5-24a FSTM vs. OHM Comparison: Tests 3, 10, and 18 Excluded



Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		FSTM	OHM	FSTM	OHM	FSTM	OHM
Average Hg[1]	μg/wsm^3	**19.0**	**18.8**	**8.2**	**8.4**	**13.2**	**13.2**
Std. Dev.	μg/wsm^3	**± 3.7**	± 3.1	**± 1.1**	± 1.2	**± 6**	± 5.8
RSE	%	**± 19.2**	± 16.5	**± 13.3**	± 13.9	**± 45.4**	± 43.5
No. of Tests	NA	**24**	24	**32**	32	**56**	56
95% CI	μg/wsm^3	**± 1.5**	± 1.3	**± 0.4**	± 0.4	**± 1.6**	± 1.5
95% RCI	%	**± 8.1**	± 7.0	**± 4.7**	± 4.9	**± 12.1**	± 11.6
Bias Error	%	**0.8**		**-1.7**		**-0.1**	

Table 5-24b FSTM vs. OHM Comparison: Tests 3, 4, 6, 10, 13, 15, 18 Excluded



Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		FSTM	OHM	FSTM	OHM	FSTM	OHM
Average Hg^T	$\mu g/wsm^3$	**18.9**	**18.6**	**8.5**	**8.6**	**13.4**	**13.1**
Std. Dev.	$\mu g/wsm^3$	**± 4.4**	± 3.8	**± 1.2**	± 1.3	**± 6.1**	± 5.7
RSE	%	**± 23.6**	± 20.4	**± 14.3**	± 14.6	**± 45.7**	± 43.7
No. of Tests	NA	**16**	16	**20**	20	**36**	36
95% CI	$\mu g/wsm^3$	**± 2.4**	± 2	**± 0.6**	± 0.6	**± 1.9**	± 1.9
95% RCI	%	**± 12.6**	± 10.9	**± 6.7**	± 6.9	**± 14.5**	± 14.6
Bias Error	%	**1.4**		**-1.1**		**2.5**	

The average value of the bias B for all test points except Test 3, 10, and 18, calculated from Equation 5-2, is -0.1 percent. This is close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 0.8 percent. For the low-Hg coal, the bias error is -1.7 percent.

The average value of the bias B for all test points except Test 3, 4, 6, 10, 13, 15, and 18 is 2.5 percent. This is close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 1.4 percent. For the low-Hg coal, the bias error is -1.1 percent.

By analyzing results from Tables 5-24a and 5-24b, it can be concluded that excluding test points with RD > 10% did not result in an improvement in bias error or test precision.

5.6.3.2. FAMS Results. In addition to using FSTM, Frontier Geosciences, Inc. also used the Mercury Speciation in Flue Gas via Flue Gas Adsorbent Mercury Speciation Method (FAMS) to measure mercury speciation at Armstrong. The flue gas samples were obtained from the North and South ports located on the 3rd CEM platform at Armstrong. A schematic representation of the three-section FAMS trap is presented in Figure 4-35.

The elemental, oxidize, particle -bound, and total Hg concentration values, measured by FAMS in the North and South ports, expressed on a dry basis and corrected for blanks, are summarized in Table 5-25a (North Port), and Table 5-25b (South Port). The stack average values are summarized in Table 5-26.

The average relative difference, RD, for all paired traps and both ports (North and South) was 5.7 percent. The North port RD values were slightly lower (5.3 percent) compared to the South port RD values (6.2 percent). The RD value for Test 14 and the North port was higher than 10 percent. For the South port, the RD values for Tests 5, 11 and 14 were higher than the EPA limit.

Table 5-25a Elemental, Oxidized, Particle-Bound, and Total Hg Concentrations Measured by FAMS in the North Port

Method: FAMS				NORTH PORT												
				Hg^{0} [µg/m^{3}]			Hg^{+2} [µg/m^{3}]			Hg^{P} [µg/dsm^{3}]			Hg^{T} [µg/dsm^{3}]			RD
Test	Date	Start	End	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	**%**
3	7/10/2006	9:33	11:15	1.07	1.02	**1.04**	17.53	17.78	**17.65**	0.36	0.27	**0.31**	18.96	19.06	**19.01**	**0.5**
4	7/10/2006	14:00	15:38	2.58	3.19	**2.88**	17.62	16.12	**16.87**	0.10	0.03	**0.07**	20.31	19.34	**19.82**	**4.9**
5	7/11/2006	9:00	10:35	0.94	1.15	**1.04**	12.55	11.34	**11.95**	0.14	0.12	**0.13**	13.63	12.61	**13.12**	**7.8**
6	7/11/2006	14:00	15:30	1.30	0.98	**1.14**	18.07	17.24	**17.66**	0.16	0.55	**0.36**	19.54	18.77	**19.16**	**4.0**
7	7/12/2006	9:05	10:45	1.32	1.38	**1.35**	17.23	15.69	**16.46**	0.25	0.21	**0.23**	18.80	17.28	**18.04**	**8.4**
8	7/12/2006	14:00	15:37	1.85	2.44	**2.15**	17.24	16.67	**16.96**	0.03	0.12	**0.08**	19.12	19.24	**19.18**	**0.6**
9	7/13/2006	9:13	10:47	2.78	2.92	**2.85**	23.46	23.08	**23.27**	0.02	0.01	**0.01**	26.25	26.00	**26.13**	**1.0**
10	7/13/2006	13:55	15:30													
11	7/14/2006	9:17	11:02	1.59	1.91	**1.75**	7.30	7.88	**7.59**	0.35	0.07	**0.21**	9.24	9.86	**9.55**	**6.5**
12	7/14/2006	14:08	15:45	1.50	1.51	**1.50**	7.64	7.98	**7.81**	0.17	0.08	**0.13**	9.31	9.57	**9.44**	**2.8**
13	7/15/2006	9:30	11:05	1.33	1.49	**1.41**	7.10	7.32	**7.21**	0.05	0.05	**0.05**	8.48	8.85	**8.67**	**4.2**
14	7/15/2006	14:00	15:35	1.39	1.51	**1.45**	6.48	5.13	**5.80**	0.02	0.07	**0.04**	7.89	6.70	**7.30**	**16.3**
15	7/16/2006	9:40	11:20	1.39	1.62	**1.50**	6.71	6.89	**6.80**	0.01	0.06	**0.03**	8.11	8.57	**8.34**	**5.5**
16	7/16/2006	13:10	14:48	1.44	1.52	**1.48**	7.04	6.46	**6.75**	0.12	0.08	**0.10**	8.59	8.06	**8.33**	**6.4**
17	7/17/2006	9:15	10:52	1.58	1.68	**1.63**	5.93	6.25	**6.09**	0.08	0.05	**0.07**	7.59	7.99	**7.79**	**5.0**
18	7/17/2006	14:08	15:46													

Table 5-25b Elemental, Oxidized, Particle-bound, and Total Hg Concentrations Measured by FAMS in the South Port

Method: FAMS				SOUTH PORT												
				Hg^{0} [µg/m^{3}]			Hg^{+2} [µg/m^{3}]			Hg^{P} [µg/dsm^{3}]			Hg^{T} [µg/dsm^{3}]			RD
Test	Date	Start	End	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	Trap 1	Trap 2	**Average**	**%**
3	7/10/2006	9:33	11:15	1.09	0.61	**0.85**	18.24	18.14	**18.19**	0.31	0.11	**0.21**	19.64	18.87	**19.25**	**4.0**
4	7/10/2006	14:00	15:38	3.44	3.32	**3.38**	16.49	16.91	**16.70**	0.06	0.08	**0.07**	20.00	20.31	**20.15**	**1.5**
5	7/11/2006	9:00	10:35	0.99	1.17	**1.08**	12.73	11.13	**11.93**	0.12	0.02	**0.07**	13.85	12.33	**13.09**	**11.6**
6	7/11/2006	14:00	15:30	1.31	1.65	**1.48**	19.65	17.67	**18.66**	0.84	1.09	**0.97**	21.79	20.42	**21.10**	**6.5**
7	7/12/2006	9:05	10:45	1.63	2.34	**1.98**	17.69	17.57	**17.63**	0.04	0.66	**0.35**	19.36	20.56	**19.96**	**6.0**
8	7/12/2006	14:00	15:37	1.85	2.44	**2.15**	17.24	16.67	**16.96**	0.03	0.12	**0.08**	19.12	19.24	**19.18**	**0.6**
9	7/13/2006	9:13	10:47	2.65	2.28	**2.46**	20.36	19.72	**20.04**	0.01	0.01	**0.01**	23.03	22.00	**22.51**	**4.5**
10	7/13/2006	13:55	15:30													
11	7/14/2006	9:17	11:02	1.22	1.86	**1.54**	6.15	6.55	**6.35**	0.03	0.06	**0.04**	7.41	8.47	**7.94**	**13.4**
12	7/14/2006	14:08	15:45	1.42	2.06	**1.74**	7.62	7.21	**7.41**	0.02	0.05	**0.03**	9.05	9.32	**9.19**	**2.9**
13	7/15/2006	9:30	11:05	1.41	1.42	**1.41**	6.52	6.87	**6.69**	0.10	0.17	**0.14**	8.04	8.45	**8.24**	**5.0**
14	7/15/2006	14:00	15:35	1.81	1.12	**1.46**	6.46	5.35	**5.91**	0.07	0.64	**0.36**	8.34	7.11	**7.73**	**15.9**
15	7/16/2006	9:40	11:20	0.79	1.37	**1.08**	6.16	5.86	**6.01**	0.06	0.12	**0.09**	7.00	7.35	**7.17**	**4.8**
16	7/16/2006	13:10	14:48	1.57	1.62	**1.59**	5.93	6.22	**6.07**	0.05	0.05	**0.05**	7.55	7.89	**7.72**	**4.5**
17	7/17/2006	9:15	10:52	1.73	1.86	**1.80**	5.69	5.00	**5.34**	0.02	0.19	**0.11**	7.44	7.05	**7.25**	**5.3**
18	7/17/2006	14:08	15:46													

Table 5-26 Average Elemental, Oxidized, Particle-Bound, and Total Hg Concentrations Measured by FAMS

Method: FAMS				Hg^0	Hg^{+2}	Hg^P	Hg^T	Hg^P/Hg^T
Test	Date	Start	End	µg/dsm³				%
3	7/10/2006	9:33	11:15	0.95	17.92	0.26	19.13	1.38
4	7/10/2006	14:00	15:38	3.13	16.79	0.07	19.99	0.34
5	7/11/2006	9:00	10:35	1.06	11.94	0.10	13.10	0.78
6	7/11/2006	14:00	15:30	1.31	18.16	0.66	20.13	3.29
7	7/12/2006	9:05	10:45	1.67	17.04	0.29	19.00	1.51
8	7/12/2006	14:00	15:37	2.15	16.96	0.08	19.18	0.39
9	7/13/2006	9:13	10:47	2.66	21.65	0.01	24.32	0.05
10	7/13/2006	13:55	15:30					
11	7/14/2006	9:17	11:02	1.65	6.97	0.13	8.74	1.46
12	7/14/2006	14:08	15:45	1.62	7.61	0.08	9.31	0.86
13	7/15/2006	9:30	11:05	1.41	6.95	0.09	8.45	1.10
14	7/15/2006	14:00	15:35	1.46	5.86	0.20	7.51	2.65
15	7/16/2006	9:40	11:20	1.29	6.41	0.06	7.76	0.78
16	7/16/2006	13:10	14:48	1.54	6.41	0.07	8.02	0.93
17	7/17/2006	9:15	10:52	1.71	5.72	0.09	7.52	1.15
18	7/17/2006	14:08	15:46					

After eliminating all test points with RD > 10 percent, the average RD for the North port decreased to 4.4 percent, and for the South port to 4.2 percent. The average RD for the stack decreased to 4.3 percent.

The average Hg0, Hg+2, HgP, and HgT concentrations measured by FAMS at Armstrong are summarized in Table 5-26. The average elemental mercury represents 12.3 percent of total, oxidized represents mercury 86.6 percent of total, and particulate bound mercury represents 1.1 percent of total. For comparison purposes, the average elemental mercury measured by OHM represents approximately 20 percent of the total mercury.

The FAMS results are also presented in a graphical form in Figures 5 -48 to 5-53.

The total Hg concentration, measured by FAMS in the North and South ports, and the corresponding trap-to-trap RD values are presented in Figures 5-48 and 5-49. As discussed earlier, RD values for one test point from the North port and three test points from the South port exceeded 10 percent. The North and South port values, and the stack average values (Average of North and South port results), are presented in Figure 5-50. Mercury speciation is shown in Figure 5-51. The average value of particulate mercury, measured by FAMS, was less than 1 percent of the total mercury.

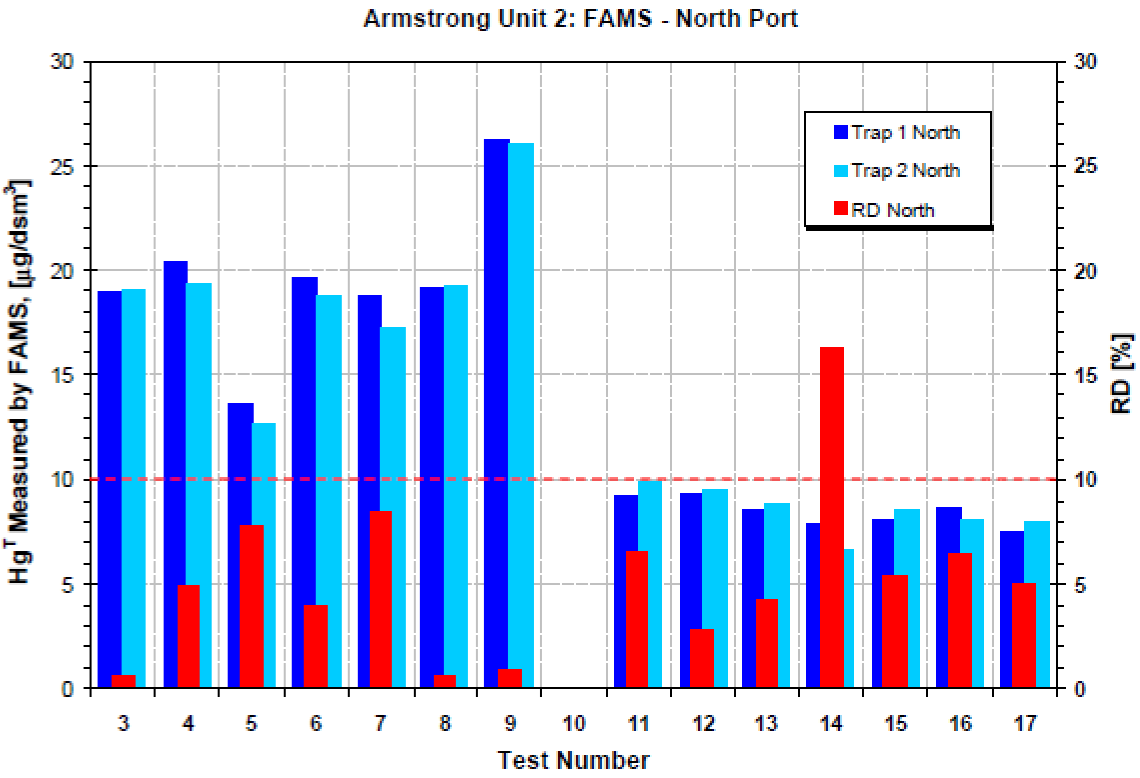


Figure 5-48: Total Hg Measured by FAMS: North Port

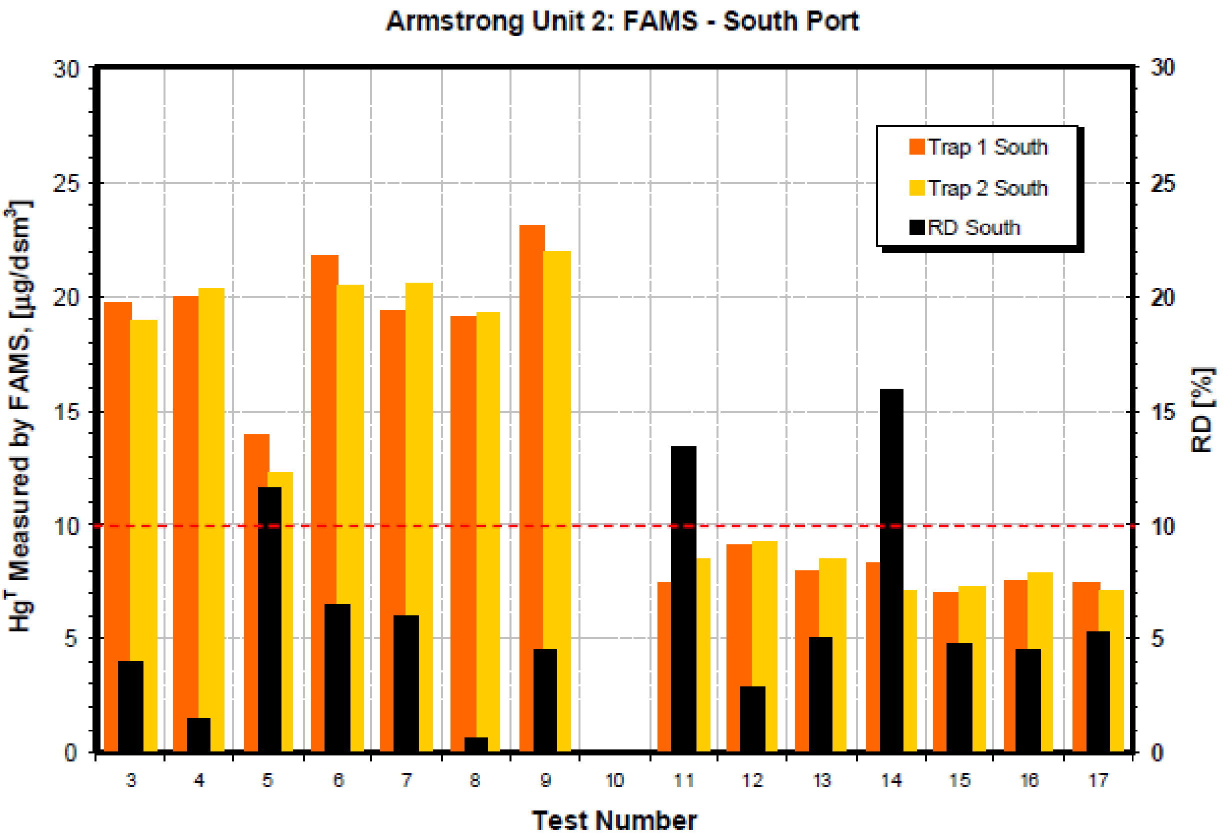


Figure 5-49: Total Hg Measured by FAMS: South Port

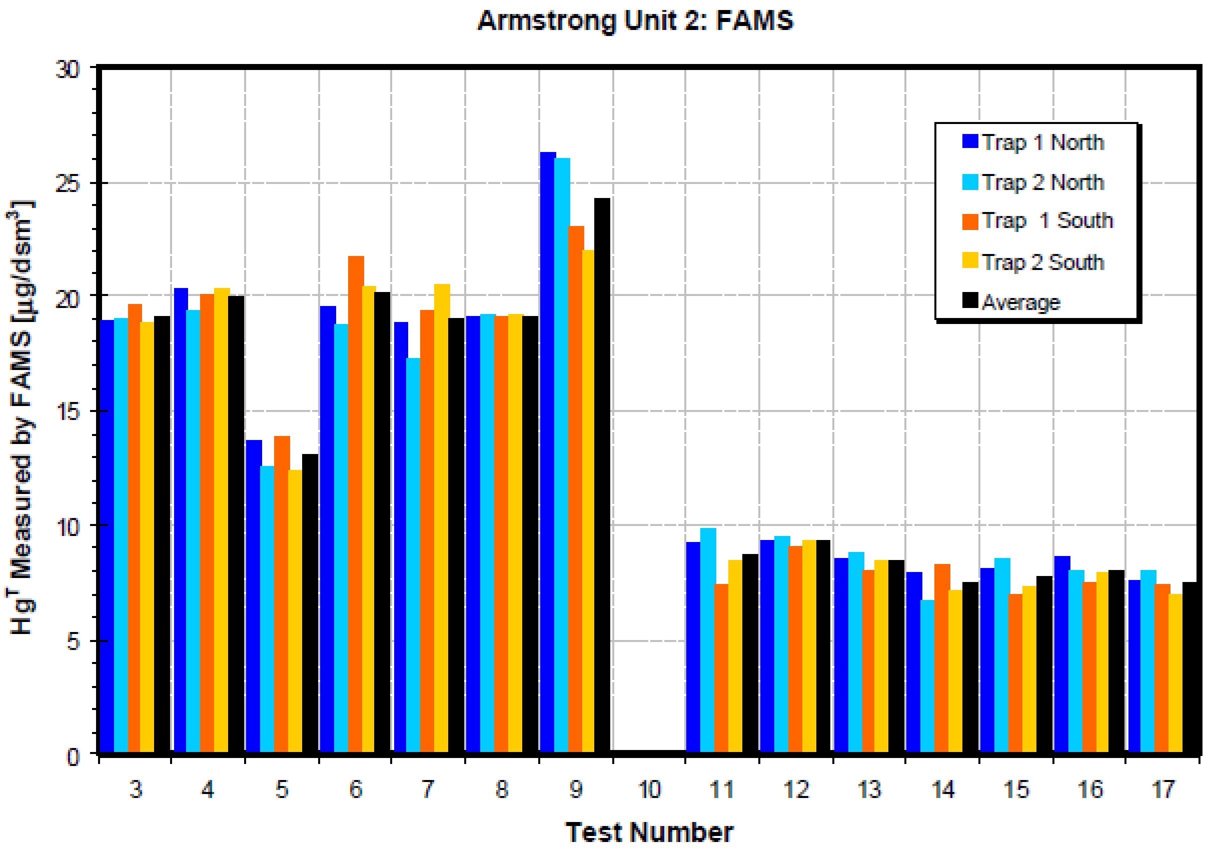


Figure 5-50: Total Hg Measured by FAMS

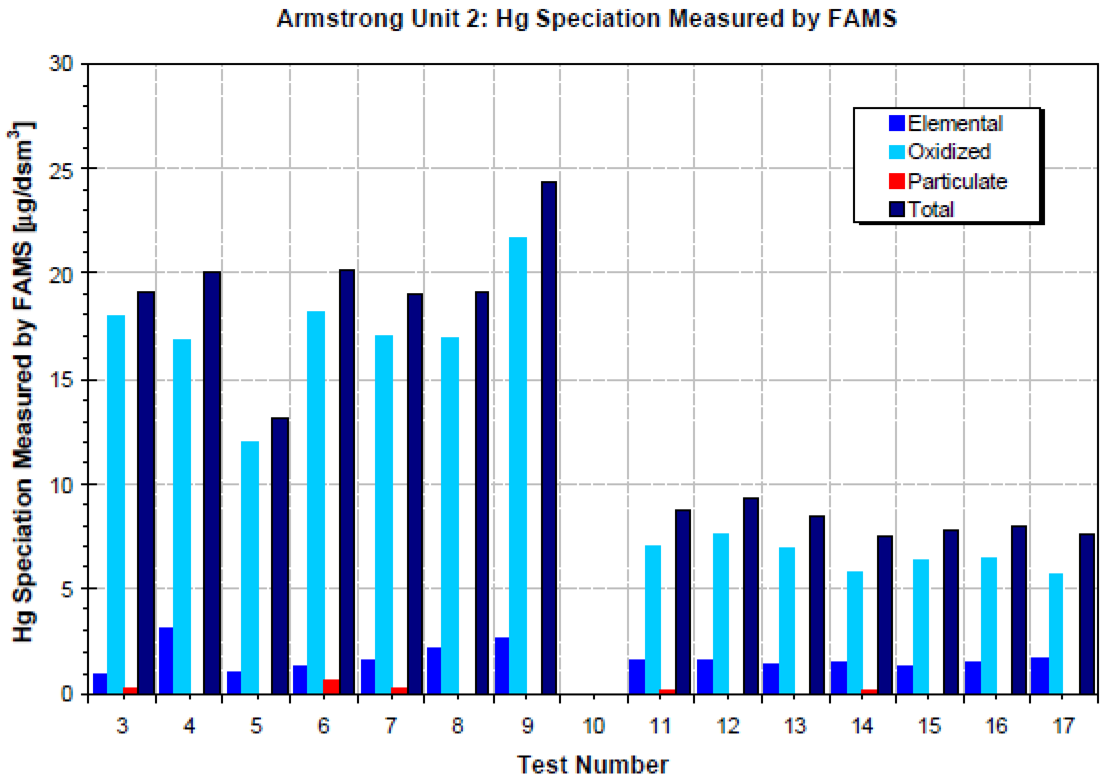


Figure 5-51: Hg Speciation Measured by FAMS

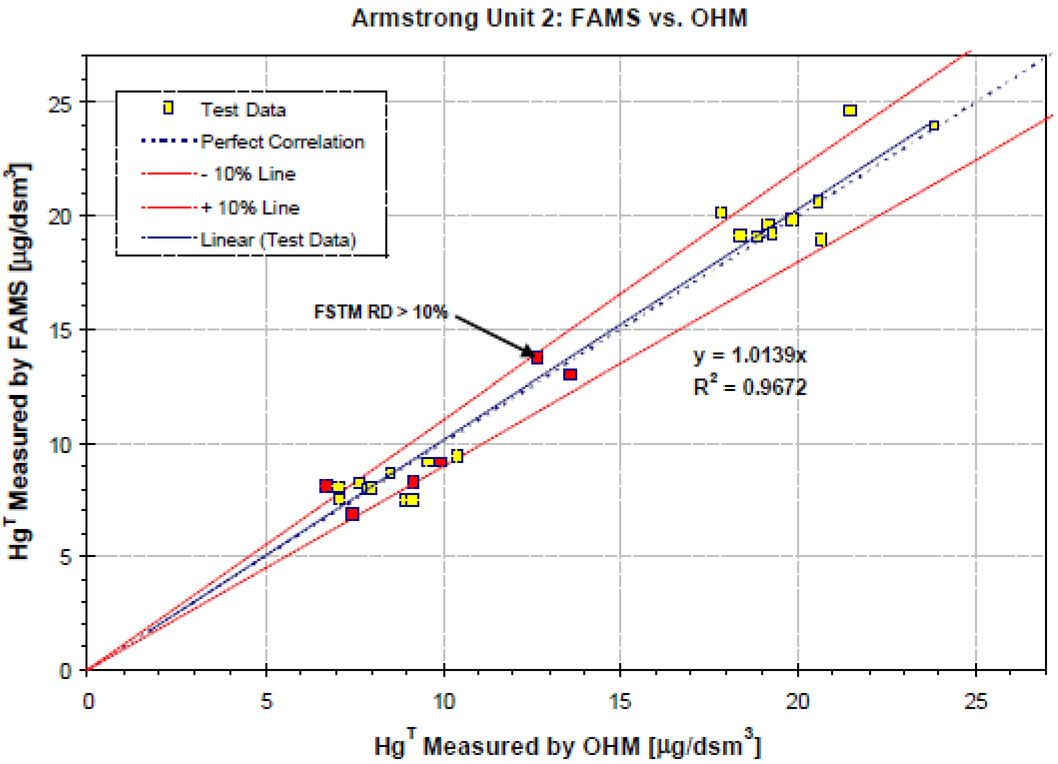


Figure 5-52: Total Hg Measured by FAMS vs. OHM – All Test Points

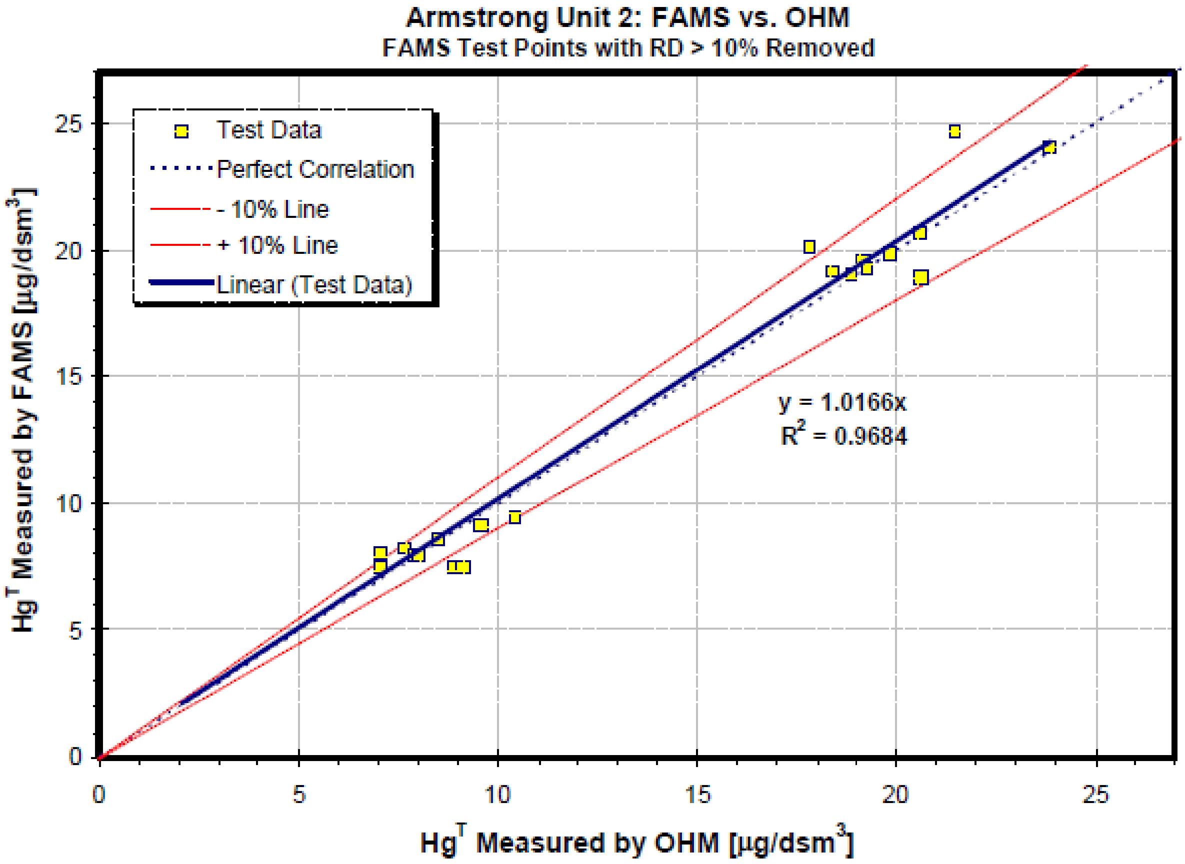


Figure 5-53: Total Hg Measured by FAMS vs. OHM: Test Points with RD > 10% excluded

No FAMS testing was performed during Tests 10 and 18 since the North and South ports were used to measure mercury stratification using specially designed probes.

A comparison of the total mercury concentration measured the FAMS and OHM is presented in Figure 5-52. The data point corresponding to Test 3 that was affected by sootblowing was removed from the analysis. The data points indicated by red squares denote the tests with the trap-to-trap RD > 10 percent.

The correlation coefficient R2 of 0.9672 indicates a very good correlation between the HgT concentration values measured by FAMS and OHM. The slope of the correlation line y of 1.0139 indicates that the HgT concentration measured by FAMS at Armstrong is, on average, approximately 1.4 percent higher compared to the OHM results. Variation in the HgT concentration values measured for the low-Hg coal was lower compared to the high-Hg coal variation.

Figure 5-53 shows a comparison between the FAMS and OHM for the FAMS test points having RD < 10 percent. The results show that correlation coefficient remained virtually constant, while the slope y changed slightly from 1.0139 to 1.0166. Therefore, when only the FAMS test points having RD < 10 percent are considered, the HgT concentration, measured by FAMS at Armstrong was on average 1.7 percent higher compared to the OHM results.

Test statistics are summarized in Tables 5-27a and 5-27b. The FAMS results for all test points, except for 3, 10, and 18 are compared to the OHM data in Table 5-27a. A comparison of the FAMS and OHM results for test points 3, 10, and 18 and for all tests points having RD>10 percent is given in Table 5-27b. As the results show, precision of the OHM and FAMS methods is comparable. Also, the precision was better for the low-Hg coal, compared to the high-Hg coal precision.

Table 5-27a FAMS vs. OHM Comparison: Tests 3, 10, and 18 are Excluded

Parameter	**Units**	**High-Hg Coal**		**Low-Hg Coal**		**Test Average**	
		FAMS	**OHM**	**FAMS**	**OHM**	**FAMS**	**OHM**
Average Hg^T	$\mu g/wsm^3$	**19.3**	**18.8**	**8.2**	**8.4**	**13.3**	**13.2**
Std. Dev.	$\mu g/wsm^3$	**± 3.4**	± 3.1	**± 0.7**	± 1.2	**± 6**	± 5.8
RSE	%	**± 17.4**	± 16.5	**± 8.8**	± 13.9	**± 45.3**	± 43.5
No. of Tests	NA	**24**	24	**28**	32	**52**	56
95% CI	$\mu g/wsm^3$	**± 1.4**	± 1.3	**± 0.3**	± 0.4	**± 1.7**	± 1.5
95% RCI	%	**± 7.4**	± 7.0	**± 3.3**	± 4.9	**± 12.6**	± 11.6
Bias Error	%	**2.6**		**-2.4**		**0.9**	

Table 5-27b FAMS vs. OHM Comparison: Tests 3, 5, 10, 11, 14, and 18 Excluded

Parameter	**Units**	**High-Hg Coal**		**Low-Hg Coal**		**Test Average**	
		FAMS	**OHM**	**FAMS**	**OHM**	**FAMS**	**OHM**
Average Hg^T	$\mu g/wsm^3$	**20.5**	**20.0**	**8.2**	**8.4**	**14.4**	**14.2**
Std. Dev.	$\mu g/wsm^3$	**± 2.1**	± 1.7	**± 0.7**	± 1.1	**± 6.5**	± 6.1
RSE	%	**± 10.1**	± 8.7	**± 8.3**	± 13.1	**± 45.2**	± 43
No. of Tests	NA	**20**	20	**20**	20	**44**	40
95% CI	$\mu g/wsm^3$	**± 1**	± 0.8	**± 0.3**	± 0.5	**± 2**	± 1.9
95% RCI	%	**± 4.7**	± 4.1	**± 3.9**	± 6.1	**± 13.6**	± 13.6
Bias Error	%	**2.6**		**-2.5**		**1.1**	

The average value of the bias B for all test points except Test 3, 10, and 18 is 0.9 percent. This is close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 2.6 percent. For the low-Hg coal, the bias error is -2.4 percent.

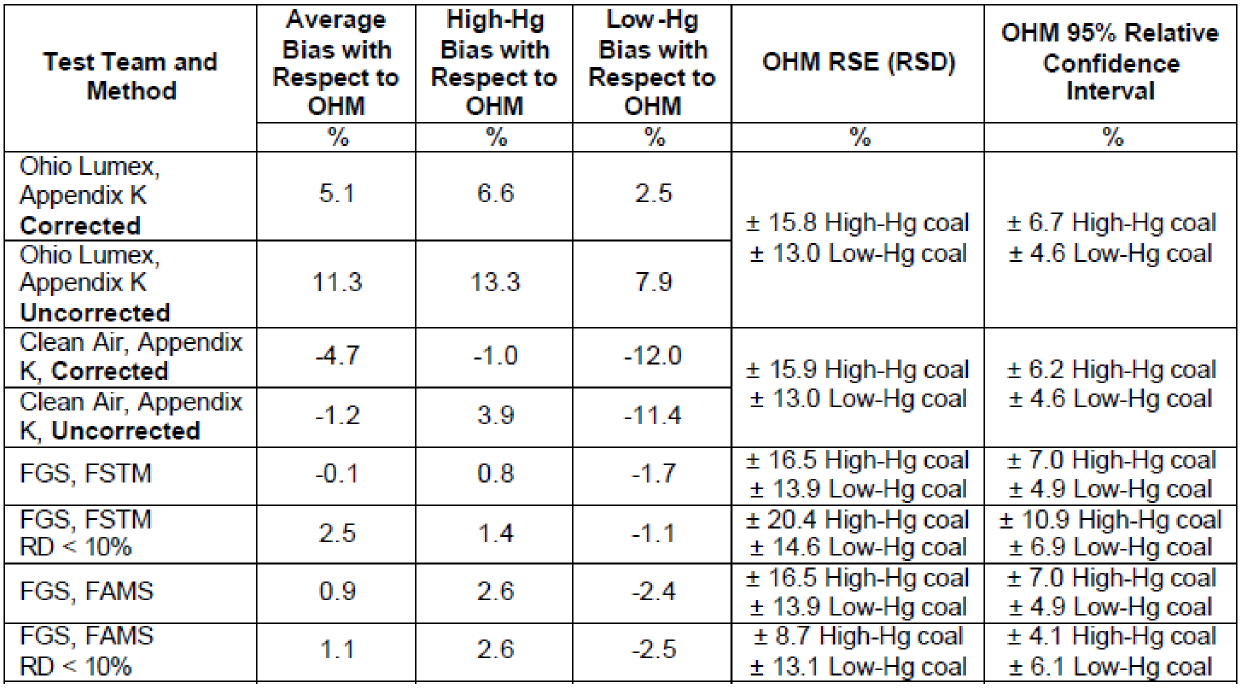
The average value of the bias B for all test points except Test 3, 5, 10, 11, 14, and 18 is 1.1 percent. This is close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 2.6 percent. For the low-Hg coal, the bias error is -2.5 percent.

By analyzing results from Tables 5-27a and 5-27b, it can be concluded that excluding test points with RD > 10% did result in an improvement in bias error and test precision for the high-Hg coal.

5.6.4. Sorbent Trap vs. OHM Comparison: Summary

The values of the bias error B in HgT concentration measured by the Sorbent Trap Methods and a Reference Method (OHM), calculated from Equation 5-2, are summarized in Table 5-28, and are also presented in graphical form in Figure 5-54.

Table 5-28 HgT Bias: Sorbent Traps vs. OHM



Test Team and Method	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
Ohio Lumex, Appendix K **Corrected**	5.1	6.6	2.5	± 15.8 High-Hg coal ± 13.0 Low-Hg coal	± 6.7 High-Hg coal ± 4.6 Low-Hg coal
Ohio Lumex, Appendix K **Uncorrected**	11.3	13.3	7.9		
Clean Air, Appendix K, **Corrected**	-4.7	-1.0	-12.0	± 15.9 High-Hg coal ± 13.0 Low-Hg coal	± 6.2 High-Hg coal ± 4.6 Low-Hg coal
Clean Air, Appendix K, **Uncorrected**	-1.2	3.9	-11.4		
FGS, FSTM	-0.1	0.8	-1.7	± 16.5 High-Hg coal ± 13.9 Low-Hg coal	± 7.0 High-Hg coal ± 4.9 Low-Hg coal
FGS, FSTM RD < 10%	2.5	1.4	-1.1	± 20.4 High-Hg coal ± 14.6 Low-Hg coal	± 10.9 High-Hg coal ± 6.9 Low-Hg coal
FGS, FAMS	0.9	2.6	-2.4	± 16.5 High-Hg coal ± 13.9 Low-Hg coal	± 7.0 High-Hg coal ± 4.9 Low-Hg coal
FGS, FAMS RD < 10%	1.1	2.6	-2.5	± 8.7 High-Hg coal ± 13.1 Low-Hg coal	± 4.1 High-Hg coal ± 6.1 Low-Hg coal

The average bias error in HgT concentration, measured by sorbent trap methods and OHM, ranges from –4.7 to 11.3 percent. The bias error for the high-Hg coal is within the -1 to 13.3 percent range while, for the low-Hg coal, B is within the -12 to 7.9 percent range.

For Armstrong data, not correcting measured HgT concentrations for spike has resulted in higher reported HgT concentrations. The spike correction, therefore, has

affected bias error with respect to OHM. The values of the bias error for the Sorbent Trap methods tested at Armstrong, with respect to OHM, are presented in Figure 5-54. Three values of the bias error are shown: test average, high-Hg coal, and low-Hg coal value. For the Ohio Lumex results, not correcting for spike has resulted in an increase in the bias error; for the CleanAir Engineering results, the bias error for uncorrected results has decreased. The lowest bias error was achieved by Frontier Geosciences' FSTM and FAMS methods.

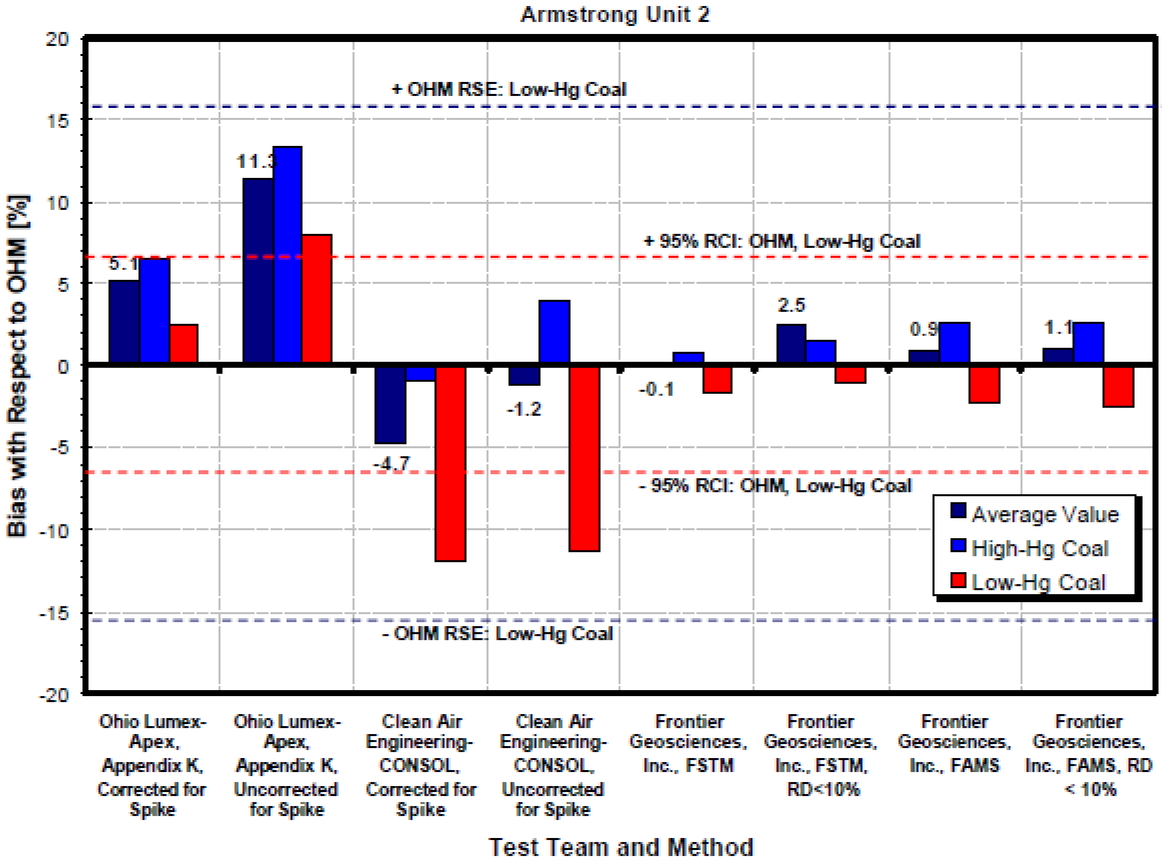


Figure 5-54: Sorbent Trap Bias Error with Respect to OHM

The relative standard deviation (RSE) intervals and 95 percent relative confidence intervals (RCI) for the OHM results calculated from the low-Hg coal data are also plotted in Figure 5-54.

As the results show, the test average values of bias error for all Sorbent Trap methods are contained within the ± RSE interval of the Reference Method (OHM) determined for the low-Hg coals. Using the ± RSE interval as the criterion, it can be concluded that bias errors for the Sorbent Trap methods with respect to the Reference Method, determined at Armstrong, might not be statistically significant.

The HgT ± S values measured by OHM and Sorbent Trap methods are presented in Figure 5-55 for the high-Hg coal. The HgT ± S values for the low-Hg coals are given in Figure 5-56. The results show that, statistically, there is no difference between HgT readings obtained by OHM and Hg CEMs.

The results from Figure 5-55 show that for the high-Hg coals, there is no statistically significant difference between the OHM and Sorbent Trap results. For the low-Hg coals, only the CleanAir Engineering results are close to the HgT – S limit, but are still contained within the Average OHM reading ± S interval. This indicates that for the low-Hg coals there is no statistically significant difference between the OHM and Sorbent Trap methods readings.

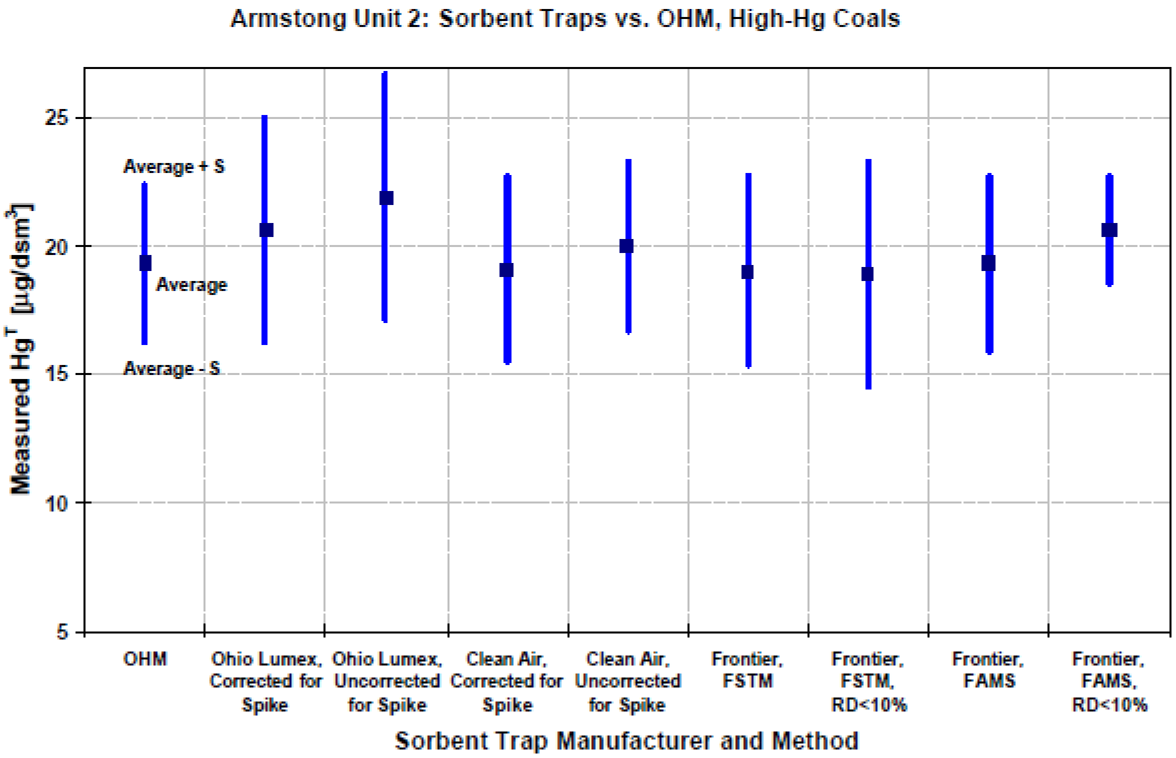


Figure 5-55: HgT ± S Values Measured by the OHM and Sorbent

However, as shown in Figure 5-54, values of the bias error for two Sorbent Trap methods (uncorrected Ohio Lumex, and corrected and uncorrected CleanAir Engineering results for low-Hg coal) fall outside of the 95 percent ± RCI for the Reference Method (OHM) determined for the low-Hg coals. Using the ± RCI as the criterion, it can be concluded that bias errors for the uncorrected Ohio Lumex results and CleanAir Engineering results for the low-Hg coals might be statistically significant. A more detailed analysis is needed to determine significance of bias errors for these two cases.

A more detailed analysis involved comparison of the interval estimates for HgT, i.e., the Hg T ± 95% CI values measured by the OHM and Sorbent Trap methods. This comparison is presented in Figure 5-57 for the high-Hg coal, and in Figure 5-58 for the low-Hg coals.

The results obtained for the high-Hg coal show that the bias between the results obtained from the Sorbent Trap methods and OHM is not statistically significant. For the low-Hg coals, the bias between the uncorrected Ohio Lumex results and corrected and uncorrected CleanAir Engineering results and OHM could be statistically significant.

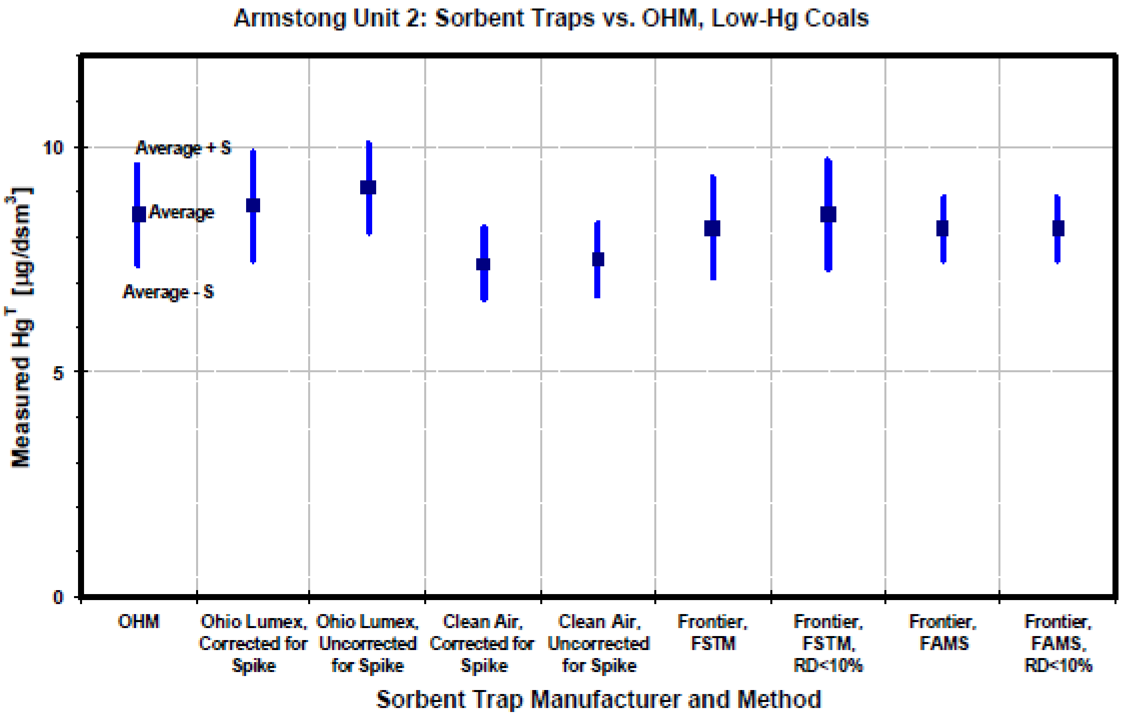


Figure 5-56: HgT ± S Values Measured by the OHM and Sorbent Trap Methods for the Low-Hg Coals

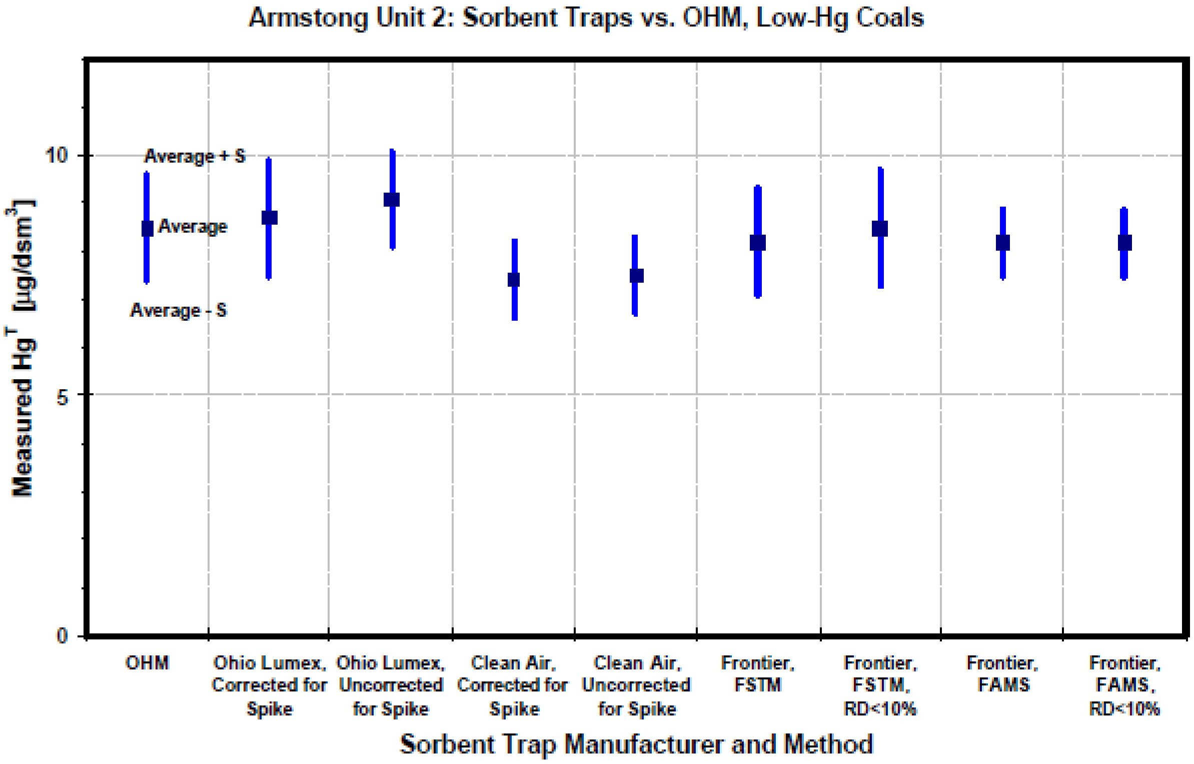


Figure 5-57: HgT ± 95% CI Values Measured by OHM and Sorbent

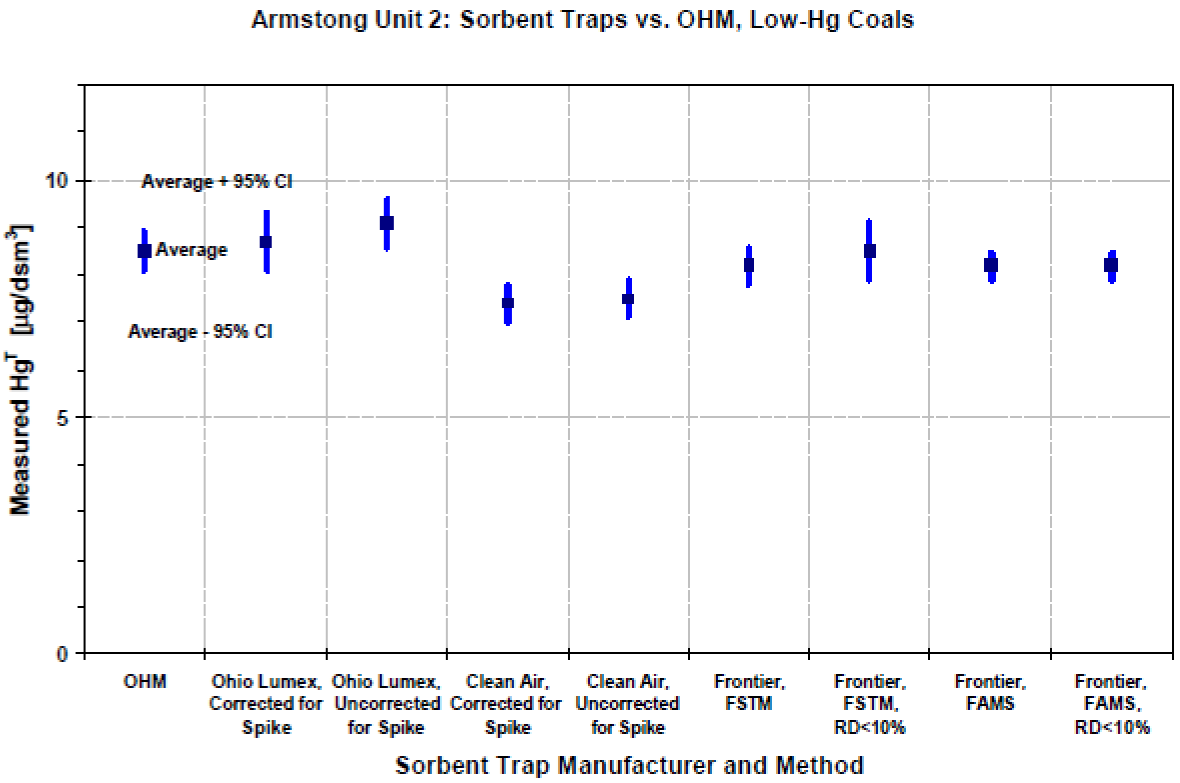


Figure 5-58: HgT ± 95% CI Values Measured by OHM and Sorbent Trap

As discussed earlier, correcting Ohio Lumex and CleanAir Engineering results for spike has resulted in higher reported HgT values. However, spike correction had a mixed effect on measurement precision of these methods, which has in some cases improved after the correction, while in some cases it got worse.

5.7. EN-13211 Manual Method for Total Mercury

The EN-13211 manual method for measurement of total mercury and sampling equipment are described in Section 4.1.2 of this report. The test results from Armstrong are summarized in Tables 5-29 and 5-30. The total gas-phase (Hg+2 and Hg0) and particulate-bound (HgP) mercury concentrations, measured by two EU trains located in two mutually perpendicular test ports (see Figure 3-9), are presented in Table 5-29 on a dry basis. Tests 1 and 2 were performed on Unit 1, Tests 3 – 10 were conducted on Unit 2 with the high-Hg coal from local mines, Tests 11 – 18 were conducted on Unit 2 with the low-Hg Virginia coal. A three-point traverse according to the EPA Equal Area Method (EAM) was used to obtain a composite mercury sample. Heavy metals were measured concurrently with mercury during Tests 5 and 8. The PM testing was performed in parallel with mercury measurements during Tests 15 and 16.

The relative difference (RD) in HgT concentration measured by Trains A and B, located in two adjacent, but perpendicular, test ports is also presented. It has to be noted that RD values, presented in Table 5-29, represent a relative difference between two sampling trains located at two test ports. The average value of RD is 6.4 percent. After excluding the Test 3 results, which were affected by sootblowing, and Test 4 results, where RD exceeded 10 percent, the average RD value decreased to 4.5 percent.

Mercury concentration data, obtained on a dry basis, were corrected to a wet basis using the flue gas moisture data from Table 5-8, and are presented in Table 5-30.

After converting HgT results to a wet basis, the average RD value decreased to 5.5 percent. After excluding the Test 3 results, which were affected by sootblowing, and Test 4 results, where RD exceeded 10 percent, the average RD value decreased to 4.5 percent.

Table 5-29 EN-13211 Test Results Expressed on a Dry Basis

EN-13211 - DRY BASIS

TEST				Dry-Gas Phase Only				Dry-Particulates				Dry-Total				
Unit	Pg	Test Number	OHM Train	Train A	Train B	Average	Stack Average	Train A	Train B	Average	Stack Average	Train A	Train B	Average	Average	RD
	MW			µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	µg/dsm³	%
1		1	1		8.31	8.31	8.31		0.030	0.030	0.030		8.34	8.34	8.34	
			2			8.31			0.030	0.030				8.34		
1	68	2	1		12.07	12.07	10.90		0.040	0.040	0.037		12.11	12.11	10.94	
			2		9.73	9.73		0.030	0.040	0.035			9.77	9.77		
2	75	3	1	7.00	9.81	8.40	8.40	0.030	0.030	0.030	0.030	7.03	9.84	8.43	8.43	16.7
			2			8.40				0.030				8.43		
2	168	4	1	18.88	13.80	16.34	16.34	0.030	0.030	0.030	0.030	18.91	13.83	16.37	16.37	15.5
			2			16.34		0.030	0.030	0.030				16.37		
2	121	5	1		9.42	9.42	9.42		0.030	0.030	0.030		9.45	9.45	9.45	
			2			9.42			0.030	0.030				9.45		
2	167	6	1	20.36	19.71	20.03	20.03	0.050	0.030	0.040	0.040	20.41	19.74	20.07	20.07	1.7
			2			20.03		0.050	0.030	0.040				20.07		
2	170	7	1	15.23	18.09	16.66	16.66	0.050	0.060	0.055	0.055	15.28	18.15	16.71	16.71	8.6
			2			16.66		0.050	0.060	0.055				16.71		
2	166	8	1		19.53	19.53	19.53		0.060	0.060	0.060		19.59	19.59	19.59	
			2			19.53			0.060	0.060				19.59		
2	170	9	1	26.56	24.81	25.69	25.69	0.050	0.040	0.045	0.045	26.61	24.85	25.73	25.73	3.4
			2			25.69		0.050	0.040	0.045				25.73		
2	170	10	1	15.23	16.54	15.88	15.88	0.030	0.040	0.035	0.035	15.26	16.58	15.92	15.92	4.2
			2			15.88		0.030	0.040	0.035				15.92		
2	175	11	1	9.81	9.78	9.80	9.80	0.030	0.030	0.030	0.030	9.84	9.81	9.83	9.83	0.1
			2			9.80		0.030	0.030	0.030				9.83		
2	175	12	1	10.30	10.61	10.45	10.45	0.040	0.030	0.035	0.035	10.34	10.64	10.49	10.49	1.5
			2			10.45		0.040	0.030	0.035				10.49		
2	174	13	1	8.59	9.95	9.27	9.27	0.030	0.040	0.035	0.035	8.62	9.99	9.31	9.31	7.4
			2			9.27		0.030	0.040	0.035				9.31		
2	175	14	1	7.64	7.92	7.78	7.78	0.030	0.060	0.045	0.045	7.67	7.98	7.83	7.83	2.0
			2			7.78		0.030	0.060	0.045				7.83		
2	176	15	1	6.88	5.97	6.42	6.42	0.040	0.050	0.045	0.045	6.92	6.02	6.47	6.47	6.9
			2			6.42		0.040	0.050	0.045				6.47		
2	176	16	1	6.31	7.54	6.92	6.92	0.040	0.050	0.045	0.045	6.35	7.59	6.97	6.97	8.9
			2			6.92		0.040	0.050	0.045				6.97		
2	174	17	1													
			2													
2	174	18	1													
			2													

Table 5-30 EN-13211 Test Results Expressed on a Wet Basis

EN-13211 WET BASIS																
TEST				Wet-Gas Phase Only				Wet-Particulates				Wet-Total				
Unit	Pg	Test Number	OHM Train	Port 2	Port 4	Average	Stack Average	Port 2	Port 4	Average	Stack Average	Port 2	Port 4	Average	Average	RD
	MW			µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	µg/wsm³	%
1		1	1		7.69	7.69	7.69		0.0277	0.0277	0.0277		7.71	7.71	7.71	
			2			7.69				0.0277				7.71		
1	68	2	1		11.15	11.15	10.02		0.0368	0.0368	0.0368		11.13	11.13	10.05	
			2		8.90	8.90			0.0368	0.0368			8.98	8.98		
2	75	3	1	6.48	9.09	7.78	7.78	0.0278	0.0278	0.0278	0.0278	6.51	9.11	7.81	7.81	16.7
			2			7.78				0.0278				7.81		
2	168	4	1	17.36	12.69	15.02	15.02	0.0276	0.0276	0.0276	0.0276	17.39	12.72	15.05	15.05	15.5
			2			15.02				0.0276				15.05		
2	121	5	1		8.66	8.66	8.66		0.0276	0.0276	0.0276		8.69	8.69	8.69	
			2			8.66				0.0276				8.69		
2	167	6	1	18.74	18.14	18.44	18.44	0.0460	0.0276	0.0368	0.0368	18.78	18.16	18.47	18.47	1.7
			2			18.44				0.0368				18.47		
2	170	7	1	13.95	16.57	15.26	15.26	0.0458	0.0550	0.0504	0.0504	14.00	16.63	15.31	15.31	8.6
			2			15.26				0.0504				15.31		
2	166	8	1		17.76	17.76	17.76		0.0546	0.0546	0.0546		17.82	17.82	17.82	
			2			17.76				0.0546				17.82		
2	170	9	1	24.27	22.67	23.47	23.47	0.0457	0.0365	0.0411	0.0411	24.31	22.70	23.51	23.51	3.4
			2			23.47				0.0411				23.51		
2	170	10	1	13.97	15.18	14.58	14.58	0.0275	0.0367	0.0321	0.0321	14.00	15.22	14.61	14.61	4.2
			2			14.58				0.0321				14.61		
2	175	11	1	9.00	8.98	8.99	8.99	0.0275	0.0275	0.0275	0.0275	9.03	9.01	9.02	9.02	0.1
			2			8.99				0.0275				9.02		
2	175	12	1	9.41	9.70	9.56	9.56	0.0366	0.0274	0.0320	0.0320	9.45	9.73	9.59	9.59	1.5
			2			9.56				0.0320				9.59		
2	174	13	1	7.88	9.12	8.50	8.50	0.0275	0.0367	0.0321	0.0321	7.90	9.16	8.53	8.53	7.4
			2			8.50				0.0321				8.53		
2	175	14	1	7.05	7.30	7.18	7.18	0.0277	0.0553	0.0415	0.0415	7.07	7.36	7.22	7.22	2.0
			2			7.18				0.0415				7.22		
2	176	15	1	6.33	5.50	5.91	5.91	0.0368	0.0460	0.0414	0.0414	6.37	5.54	5.96	5.96	6.9
			2			5.91				0.0414				5.96		
2	176	16	1	5.81	6.95	6.38	6.38	0.0369	0.0461	0.0415	0.0415	5.85	6.99	6.42	6.42	8.9
			2			6.38				0.0415				6.42		
2	174	17	1													
			2													
2	174	18	1													
			2													

The HgT results, obtained by Sampling Trains A and B located in two different ports, stack-average value, and port-to-port RD are also presented in a graphical form in Figure 5-59.

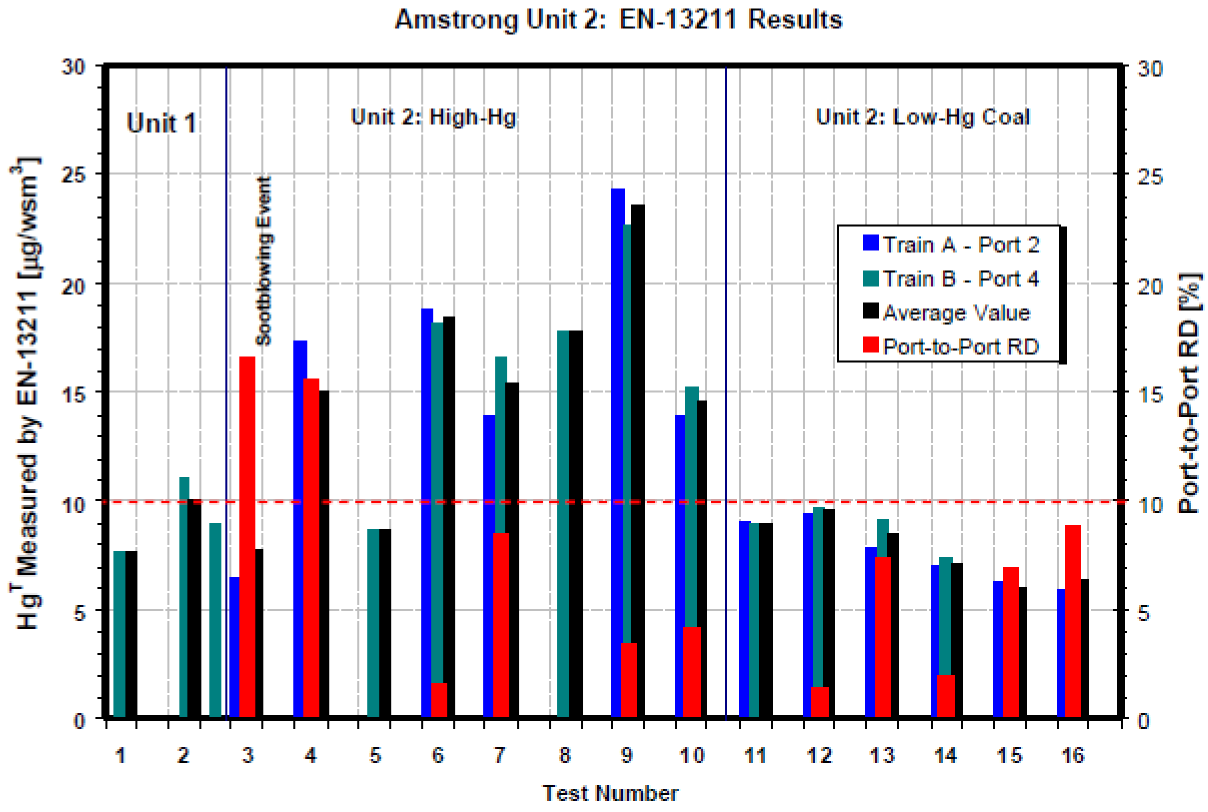


Figure 5-59: EN-13211 Results

For statistical calculations, test data was divided into two sets: the high-Hg and low-Hg coal sets. The Unit 1 and Test 3 test data were omitted from the analysis. The results are summarized in Table 5-31. The average HgT concentration for the high-Hg coal data set is 16.2 mg/wsm3, S is 4.5 mg/wsm3, RSE is 27.8 percent, and 95 percent CI is ± 2.6 mg/wsm3. For the low-Hg coal data set, the average HgT concentration is 7.8 mg/wsm3, S is 1.5 mg/dsm3, RSE is 18.9 percent, and 95 percent CI is ± 0.9 mg/wsm3.

Table 5-31 Test Statistics: EN-13211

Data Set	Average Hg^T	Standard Deviation	Relative Standard Error, RSE	95% Confidence Interval
	µg/wsm^3	µg/wsm^3	%	µg/wsm^3
High-Hg coal	**16.2**	**4.5**	**27.8**	**± 2.6**
Low-Hg coal	**7.8**	**1.5**	**18.9**	**± 0.9**

A comparison between the total mercury concentration values measured by EN- 13211 and OHM, and expressed on a dry basis, is presented in Figure 5-60. The data point corresponding to the Test 3 that was affected by sootblowing was removed from the analysis. Also, Test points 5 and 10 were removed due to inconsistencies in the measured flue gas volume.

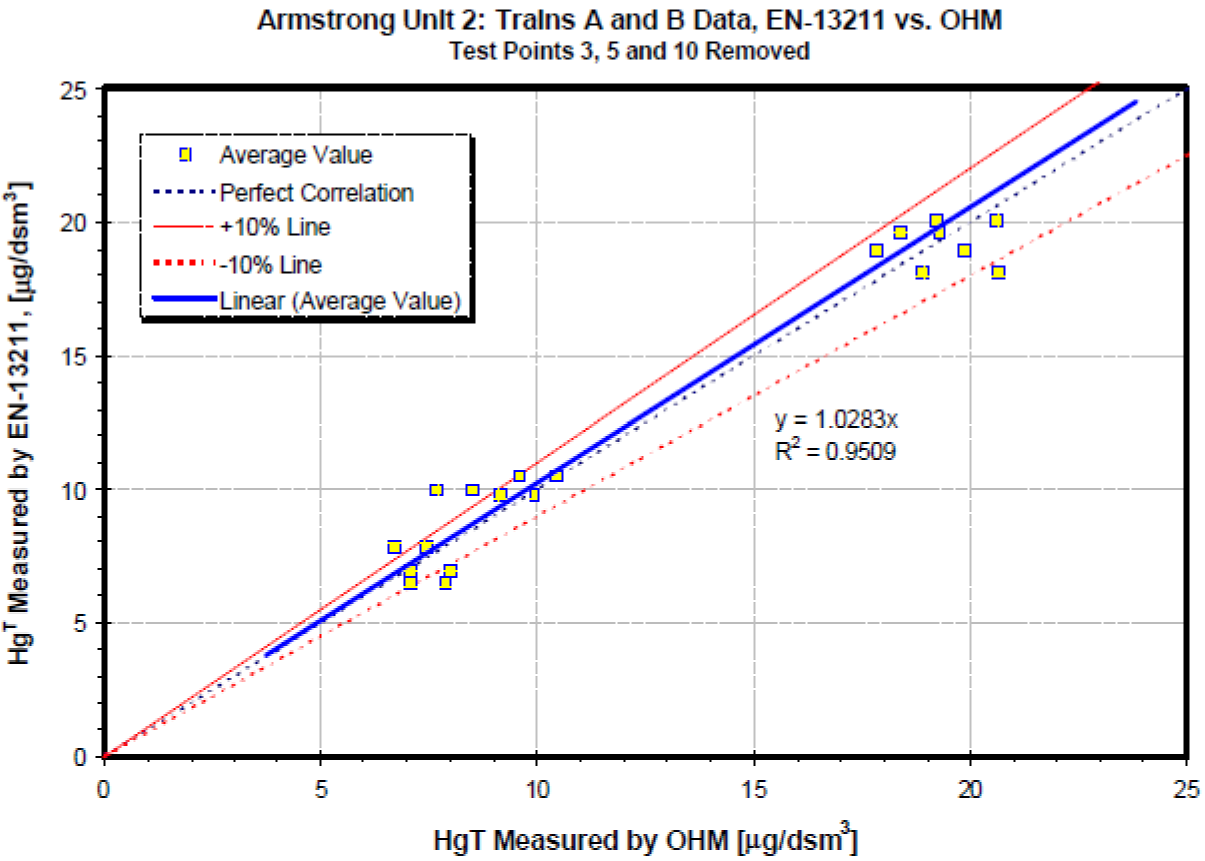


Figure 5-60: EN-13211 vs. OHM: Dry Basis

The correlation coefficient R2 of 0.951 indicates a very good correlation between the HgT concentrations measured by the EN-13211 Sampling Trains A and B and two paired OHM trains. The slope of the correlation line y of 1.0283 indicates that the HgT concentration measured by at Armstrong by EN-13211 is, on average, 2.8 percent higher compared to the OHM results. Variation in the HgT concentration values measured for the low-Hg coal was considerably lower compared to the high-Hg coals.

A comparison between the total mercury concentration values measured by EN- 13211 and OHM, and expressed on a wet basis, is presented in Figure 5-61. Test points 3, 5, and 10 were removed from the analysis. The results are virtually identical to the dry basis results.

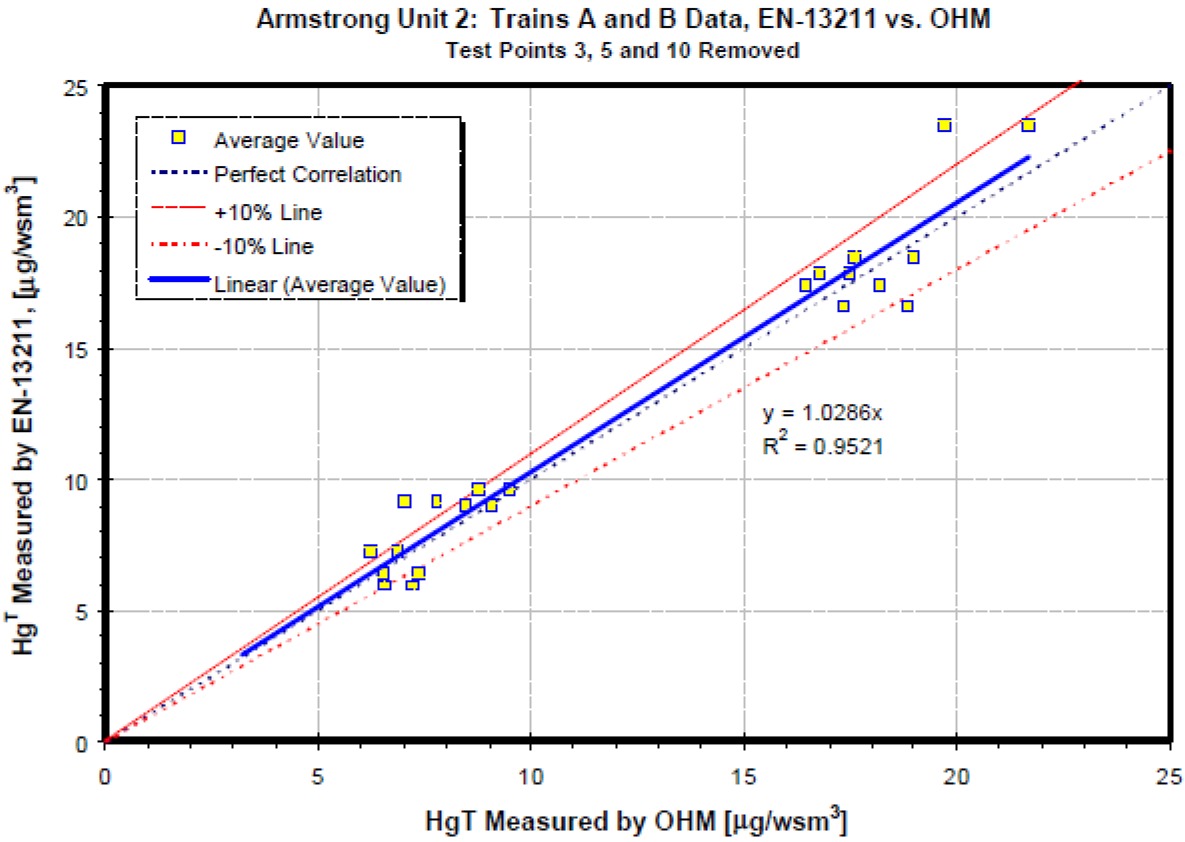


Figure 5-61: EN-13211 vs. OHM: Wet Basis

5.7.1. EN-13211 vs. OHM Comparison

A comparison of the EN-13211 and OHM test data is summarized in Table 5-32 where average HgT values, standard deviations, RSE, and 95 percent absolute and relative CI of both methods are presented.

Table 5-32 EN-13211 vs. OHM Comparison: Test Points 3, 5, and 10 Excluded

Parameter	Units	High-Hg Coal		Low-Hg Coal		Test Average	
		EN-13211	OHM	EN-13211	OHM	EN-13211	OHM
Average Hg^T	μg/wsm^3	**20.5**	**20.0**	**8.6**	**8.3**	**14**	**13.6**
Std. Dev.	μg/wsm^3	**± 2.8**	± 1.7	**± 1.6**	± 1.2	**± 6.5**	± 6.1
RSE	%	**± 13.9**	± 8.7	**± 19.1**	± 14.8	**± 46.1**	± 44.5
No. of Tests	NA	**7**	20	**11**	24	**18**	44
95% CI	μg/wsm^3	**± 2.6**	± 0.8	**± 1.1**	± 0.5	**± 3.2**	± 1.8
95% RCI	%	**± 12.9**	± 4.1	**± 12.8**	± 6.3	**± 22.9**	± 13.4
Bias Error	%	**2.5**		**3.8**		**2.9**	

The results show that the average HgT value measured by both methods was very close (within 0.5 mg/wsm3) for both the high-Hg and low-Hg coals. The precision of the OHM was better but this could be attributed to a larger number of samples that were obtained by the OHM compared to EN-13211 (two paired trains vs. two single trains).

The average value of the EN-13211 bias with respect to OHM is 2.9 percent. This is very close to the bias error estimated from the slope y of the correlation line. The bias error for the high-Hg coal is 2.5 percent. For the low-Hg coal, the bias error is larger, 3.8 percent.

The values of the bias error in HgT concentration measured by EN-13211 and the OHM, calculated from Equation 5-2, are summarized in Table 5-33. The results show that bias error B is contained within the ± RSE and ± RCI intervals of the OHM, meaning that the bias error between EN-13211 and OHM is not statistically significant.

Table 5-33 Hg CEM vs. OHM Bias

Reference Method	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
EN-13211	2.9	2.5	3.8	± 8.7 High-Hg coal ± 14.8 Low-Hg coal	± 4.1 High-Hg Coal ± 6.3 Low-Hg Coal

In summary, EN-13211 performed very well and, on average, produced almost identical values compared to OHM. This means that Hg emission rates measured by the Reference Methods in the USA and European Union are, from the practical point of view, identical and Global trading (if it ever becomes a reality), would be fair and unbiased, as far as measurement accuracy is concerned.

5.8. Heavy Metals

The heavy metal emissions were measured at Armstrong by employing EPA Method 29 and EN-14385 flux derived method. A separate sampling train was required to obtain flue gas samples according to the Method 29. Heavy metals sampling according to EN-14385 was conducted in parallel to the Hg sampling.

Unfortunately, the impinger solutions, collected by EN-14385 were displaced and never found. Only the Method 29 samples were analyzed. Therefore, it was not possible to compare the EU and U.S. methods for heavy metal emission measurement. The Method 29 results are summarized in Table 5-34.

5.9. Particulate Matter (PM)

EPA Method 5B and VDI Impaction Method were used to measure particulate matter (PM) emissions at Armstrong. A separate sampling train was required to obtain flue gas samples according to the EPA Method 5B (Section 4.1.3). The PM sampling according to the VDI Impaction Method was conducted in parallel to the Hg sampling (see Section 4.1.4.). Results are summarized in Figures 5-62 and 5-63.

The PM2.5, PM10 and total PM concentrations, measured by the EPA Method 5B and VDI Impaction Method, are presented in Figure 5-62. While the there is a good agreement between the PM2.5 and PM10 results, the total PM concentration measured by EPA Method 5B is significantly higher compared to the VDI method. This discrepancy in total PM could be explained by the filter breakthrough on the VDI probe. It has to be noted that the VDI method is designed for one hour of sampling, while the EPA Method 5B requires two hours of sampling to collect a representative sample. To facilitate a direct comparison between the EU and U.S. methods, sampling was performed over a two hour period. This has resulted in overloading of the paper filter in the VDI probe and filter breakthrough.

The measured PM concentration presented by particle size ranges is given in Figure 5-63. The results show that at Armstrong the largest fraction of the particles is smaller than 2.5 m. The biggest discrepancy between the EPA Method 5B and VDI Impaction Method occurred with the smallest particles due to the paper filter breakthrough.

Table 5-34 Method 29 Results

	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg
Sample	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Method 29 Blank 72206	0.0010	0.1224	-0.0024	0.6364	0.0001	0.0001	0.0257	0.0003	0.0001	0.0015	0.0000	0.0136	0.0097	0.0138
71106 Method 29-1 1-1	0.0006	0.1755	0.0032	1.6	0.0028	0.0000	0.3982	0.0003	0.0000	0.0033	0.0028	0.1229	0.1650	0.0703
71106 Method 29-1 1-2	0.0003	0.1560	0.0030	1.5	0.0028	0.0000	0.3849	0.0004	0.0002	0.0030	0.0032	0.1245	0.1611	0.0662
Method 29-2	0.0004	0.1246	-0.0024	1.6	0.0019	0.0000	0.1756	0.0034	0.0000	0.0013	0.0017	0.0368	0.2375	0.0251
Method 29-1 1-1	0.0044	0.1177	0.0036	1.7	0.0064	0.0000	0.1761	0.0007	0.0003	0.0040	0.0016	0.1123	0.0725	0.0307
Method 29-1 1-2	0.0045	0.1155	0.0034	1.7	0.0063	0.0000	0.1814	0.0007	-0.0004	0.0037	0.0016	0.1112	0.0704	0.0315
71206 Method 29-2	0.0537	0.2154	0.0113	1.6	0.0030	0.0000	0.2548	0.0005	0.0006	0.0230	0.0048	0.2450	0.1354	0.0541

	Mn	Mo	Na	Ni	Pb	Sb	Se	Sr	Th	Tl	U	V	Zn
Sample	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Method 29 Blank 72206	0.0370	0.0017	0.0377	0.0020	0.0014	0.3249	0.0005	0.0075	0.0048	-0.0001	0.0006	-0.0002	0.0054
71106 Method 29-1 1-1	0.1331	0.0013	3.8863	0.0052	0.0016	0.0644	0.0513	0.0072	0.0037	0.0083	-0.0008	-0.0004	0.0469
71106 Method 29-1 1-2	0.1323	0.0016	3.7467	0.0046	0.0010	0.0046	0.0480	0.0058	0.0032	0.0102	-0.0004	-0.0001	0.0464
Method 29-2	0.3481	0.0011	0.6766	0.0047	0.0001	-0.0168	0.0735	0.0045	0.0021	0.0176	0.0007	-0.0003	0.0260
Method 29-1 1-1	0.0454	0.0012	18.8	0.0054	0.0001	0.0159	0.0782	0.0038	0.0029	0.0088	0.0038	-0.0002	0.0455
Method 29-1 1-2	0.0462	0.0012	19.2	0.0062	0.0008	-0.0131	0.0833	0.0036	0.0010	0.0089	0.0002	-0.0003	0.0466
71206 Method 29-2	0.0313	0.0035	1.4	0.0328	0.0017	0.0081	0.0739	0.0030	0.0030	-0.0010	-0.0004	-0.0001	0.0719

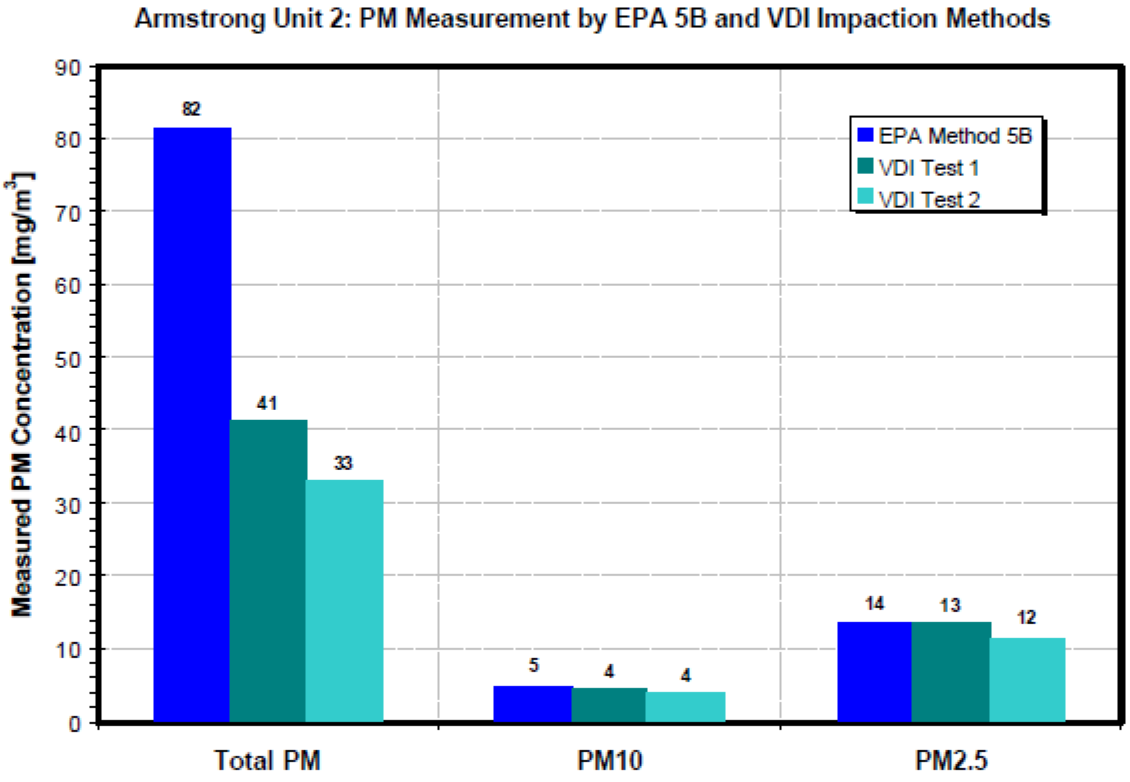


Figure 5-62: PM Concentration Measured by EPA Method 5B and VDI Impaction Method

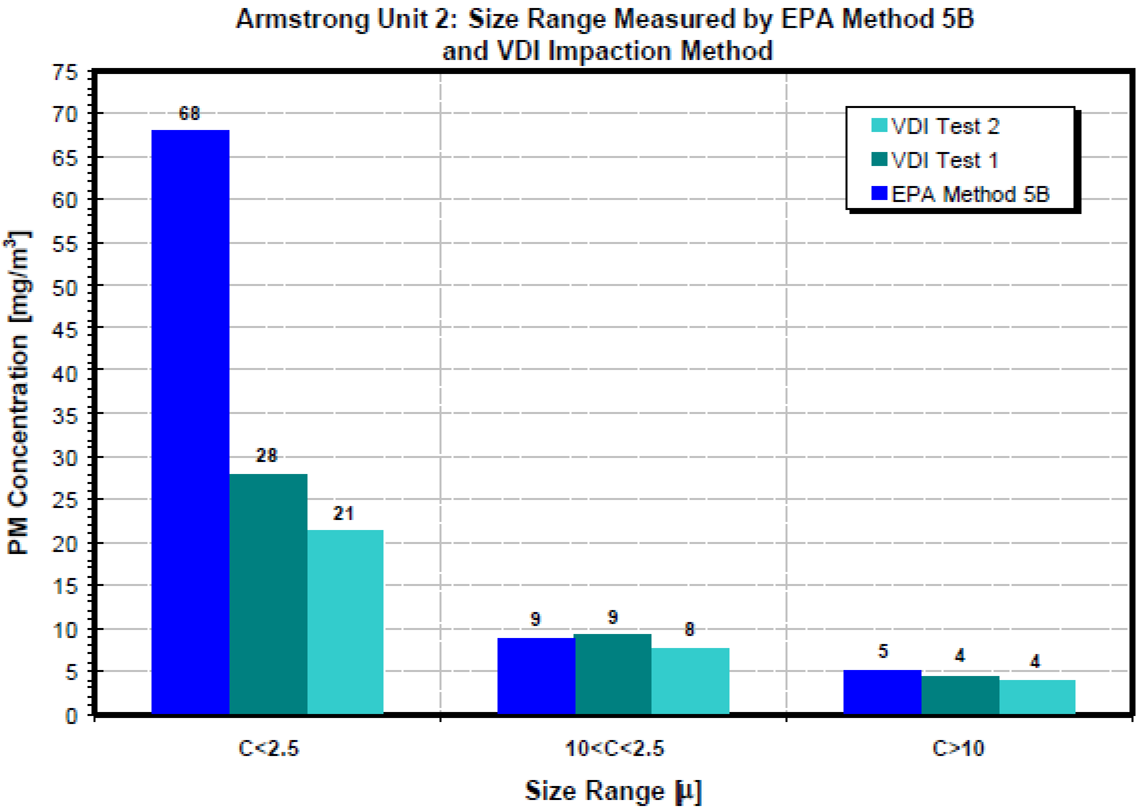


Figure 5 -63: PM Concentration bySize Ranges Measured by EPA Method 5B and VDI Impaction Method

6. STRATIFICATION TESTING

The Instrumental Reference Method (IRM), recently developed by the U.S. EPA, when used for mercury emission testing (i.e., to determine compliance with an emission standard or limit) or for RATA testing, requires mercury measurements to be obtained from multiple traverse points. Mercury stratification tests may be conducted to determine whether the number of traverse points may be reduced. In either case, determination of spatial stratification of mercury in power plant stacks is needed.

Although measurement of spatial stratification is a common requirement for many reference methods, spatial stratification of mercury is particularly difficult to measure. This is because temporal variations in mercury concentration interfere with stratification measurements. Temporal variations in mercury concentration occur as mercury content in the coal and plant operating conditions vary in time.

Two methods for measuring a true spatial stratification of mercury in power plant stacks were developed and field -tested at Armstrong. The first method termed, “The Background Correction Method” uses a heated sampling probe connected to a portable mercury analyzer. Mercury concentration is measured at discrete points by traversing the sampling probe along the stack radius. The true spatial stratification is determined by subtracting the background mercury concentration, measured by a permanently installed Hg monitor, from the traverse measurements.

The second method, termed the "Sorbent Trap Array Method" uses an array of sorbent traps located at various radial distances from the stack wall. In this arrangement, temporal variation in Hg concentration equally affects all sorbent traps. By comparing the differences in concentration values measured by individual sorbent traps, the temporal variation part cancels out and the resulting difference represents a true spatial stratification.

6.1. Background Correction Method

After much brainstorming, a sampling train for the Hg T traverse was assembled on site from the U.S. and EU components, and represents a collaborative effort of Dr. Nenad Sarunac of Lehigh University's ERC, Dr. Domenico Cipriano of CESI RICERCA, and Joseph Siperstein, M.Sc. of Ohio Lumex. A schematic of the sampling train is provided in Figure 6-1. A titanium heated sampling probe developed by CESI RICERCA was connected directly to the Ohio Lumex RA 915 CEM spectrometer via a heated line, also supplied by Ohio Lumex. The flue gas sample was condensed in an ice-bath condenser. Suction was provided by a small unheated pump located at the end of the sampling train.

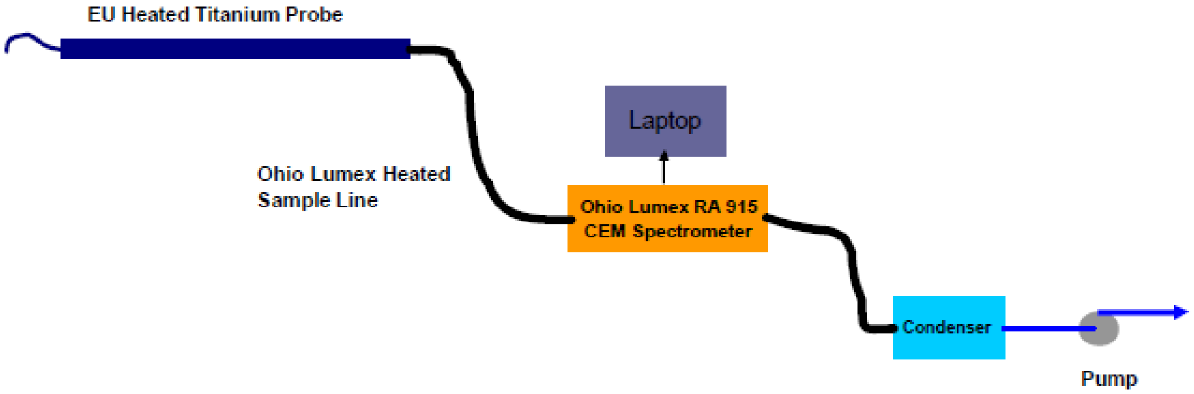


Figure 6-1: Sampling Train for Mercury Traverse: Total Mercury

The sampling rate was determined by the pump capacity and was not isokinetic. This did not affect HgT concentrations measured by the RA 915 CEM spectrometer since this instrument is insensitive to the sampling rate. Photographs of the system components are presented in Figure 6-2.

A schematic of the Background Correction Method is presented in Figure 6-3. As implied by its name, the method is based on subtracting the background mercury concentration, measured by a permanently installed Hg monitor, from the traverse measurements. The difference, DHgT, represents a true spatial Hg stratification.

Six stratification tests were performed at Armstrong on July 17, 2006, where HgT concentration was measured at three points along the stack radius. The results are summarized in Figures 6-4 and 6-5. Deviation in total mercury from the mean value, corrected for background (representing spatial stratification), is presented in Figure 6-4 as a function of dimensionless radial distance from the stack wall. The results show that spatial stratification in Hg T measured at Armstrong is within ± 4 percent. According to the EPA criteria for stratification, this represents a non-stratified condition.

Figure 6-2: Sampling Train for Hg T Traverse: System Components

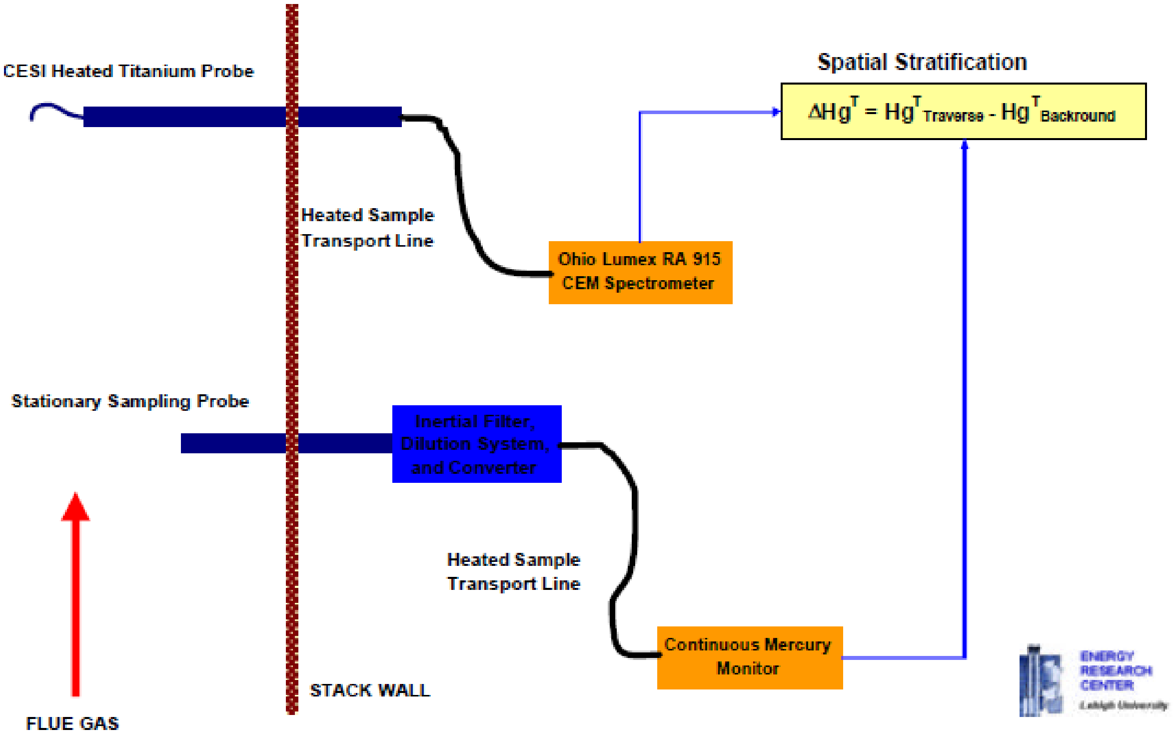


Figure 6-3: Schematic of the Background Correction Method

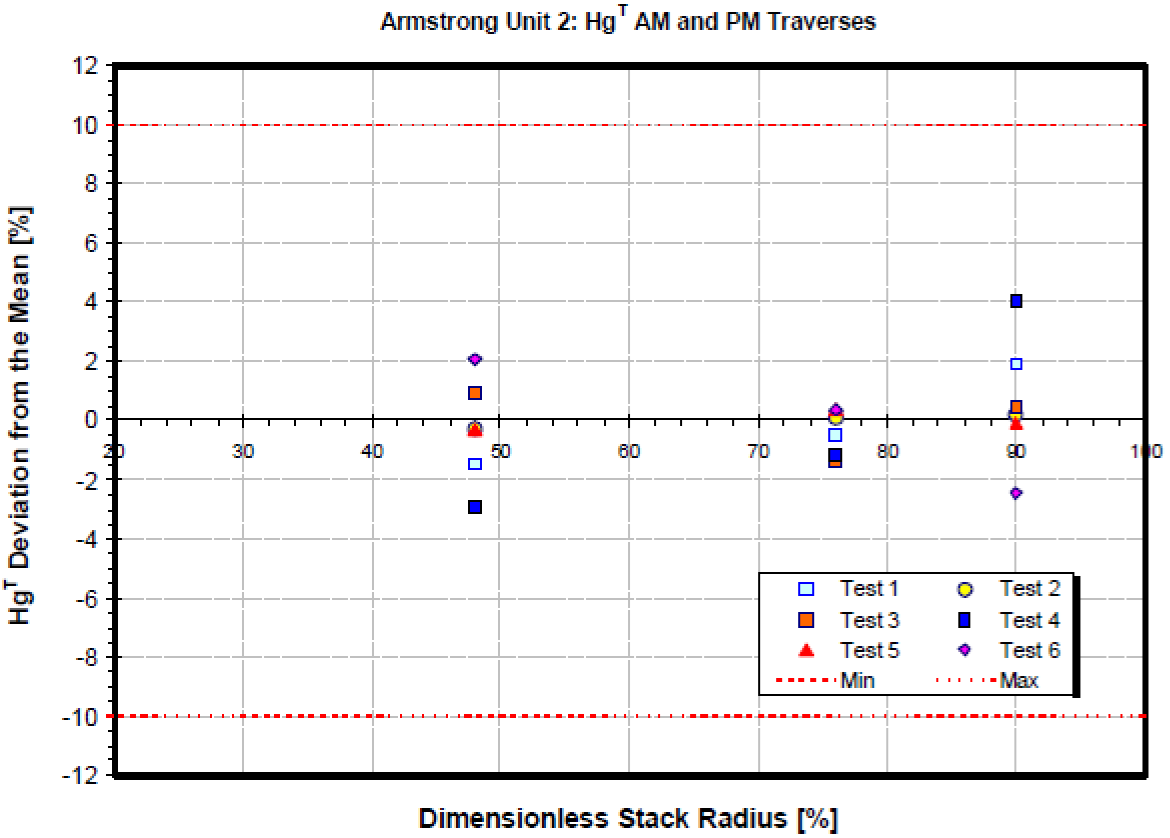


Figure 6-4: Spatial Stratification in HgT Measured at Armstrong

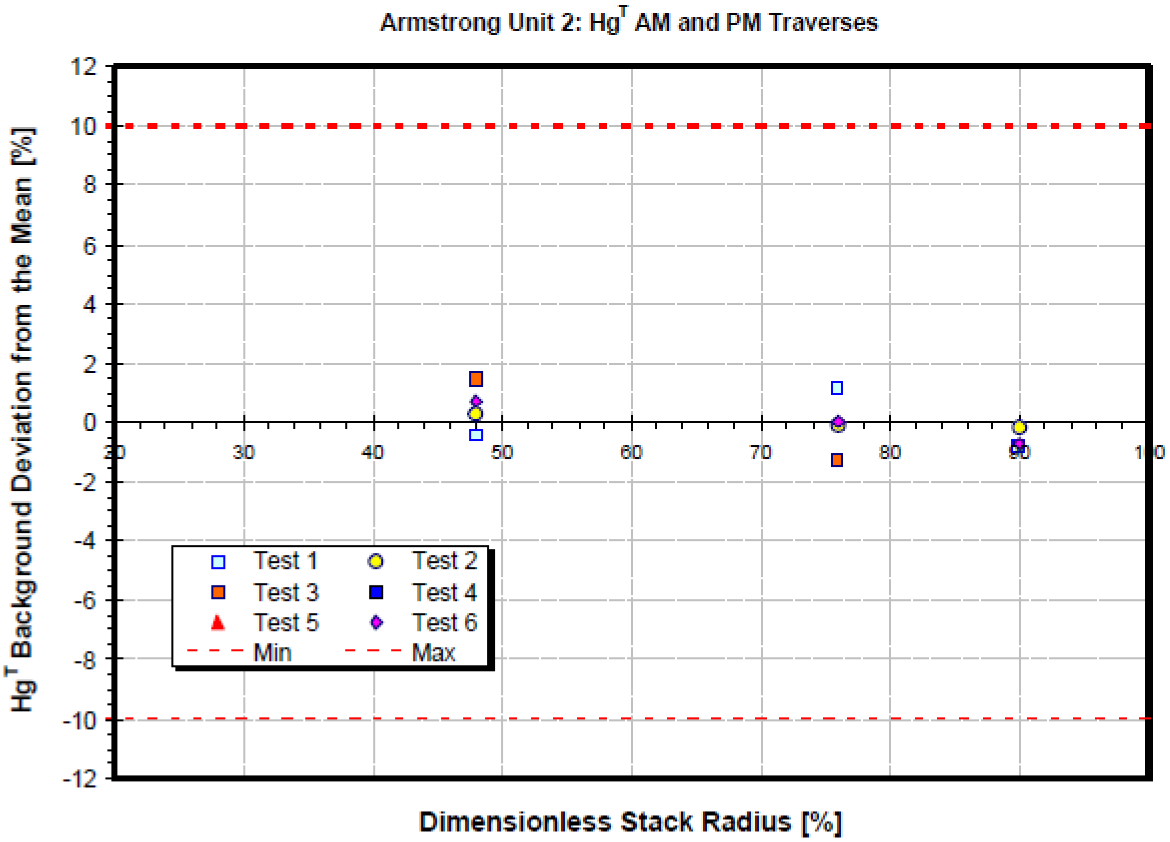


Figure 6-5: Temporal Variation in Background HgT Measured at Armstrong

Variations in the background HgT concentration, presented in Figure 6-5 as deviations from the mean value, show that temporal HgT variations measured at Armstrong during stratification tests were very small. The background concentration was measured by the Ohio Lumex semi-continuous Hg monitor.

The HgT stratification tests performed at Armstrong are the first mercury stratification tests ever conducted. Although the Armstrong results are very encouraging, more field testing is needed to test and further develop the Background Correction Method under conditions of large temporal variations in the background mercury concentration. Also, the sampling train for spatial mercury concentration measurements, used at Armstrong, would need to be modified for wet stacks. In addition, a minimum background HgT concentration level, below which determination of spatial stratification would not be required, needs to be established.

6.2. Sorbent Trap Array Method

The Sorbent Trap Array Method is based on simultaneous measurement of mercury concentration at a number of locations within the stack cross-sectional area by a fixed array of sorbent traps. The assumption is that temporal variation in Hg concentration affects all sorbent traps in the array equally. By comparing differences in the Hg concentration values measured by individual sorbent traps, the temporal variation part cancels out, and the resulting difference represents a true spatial stratification.

To facilitate stratification measurements, Frontier Geosciences Inc. was asked to design and manufacture two special sorbent trap probes, each consisting of four sorbent traps positioned at 1, 3, 5, and 7 ft distance from the stack wall, Figure 6-6. Stratification measurements were conducted in the North and South ports on the third CEM platform level using FSTM.

Figure 6-6: Fixed Array Sorbent Trap Probes Used at Armstrong

The mercury stratification measurements were performed at Armstrong on July 13 and 17, 2006. The measured values of HgT are presented in Figures 6-7 for the high-Hg coal and Figure 6-8 for the low-Hg coal. The HgT values measured at North and South ports agree quite well, except that for the North port the results for both coals show high Hg values near the stack centerline. The reason for this high reading is unknown. Also, for the low-Hg coal and South port, the near-wall HgT reading is lower compared to the rest of the data.

The maximum absolute difference in measured mercury concentration, measured for the high-Hg coal, is 2.6 mg/dm3, or 11 percent of the mean value. For the low-Hg coal, the maximum absolute difference in measured HgT concentration is 1.9 mg/dm3, or 20 percent of the mean value.

The deviation in HgT from the mean value measured by a fixed array of sorbent traps is presented in Figure 6-9 as a function of a dimensionless radial distance from the stack wall. The results show that spatial stratification in HgT measured at Armstrong, using a fixed array of sorbent traps, is within ± 6 percent from the mean value, except for two points: the near-centerline location for the and North port, and near-wall location for the South port, both measured for the low-Hg coal. The deviation of five percent or more from the mean value represents a minimally-stratified condition.

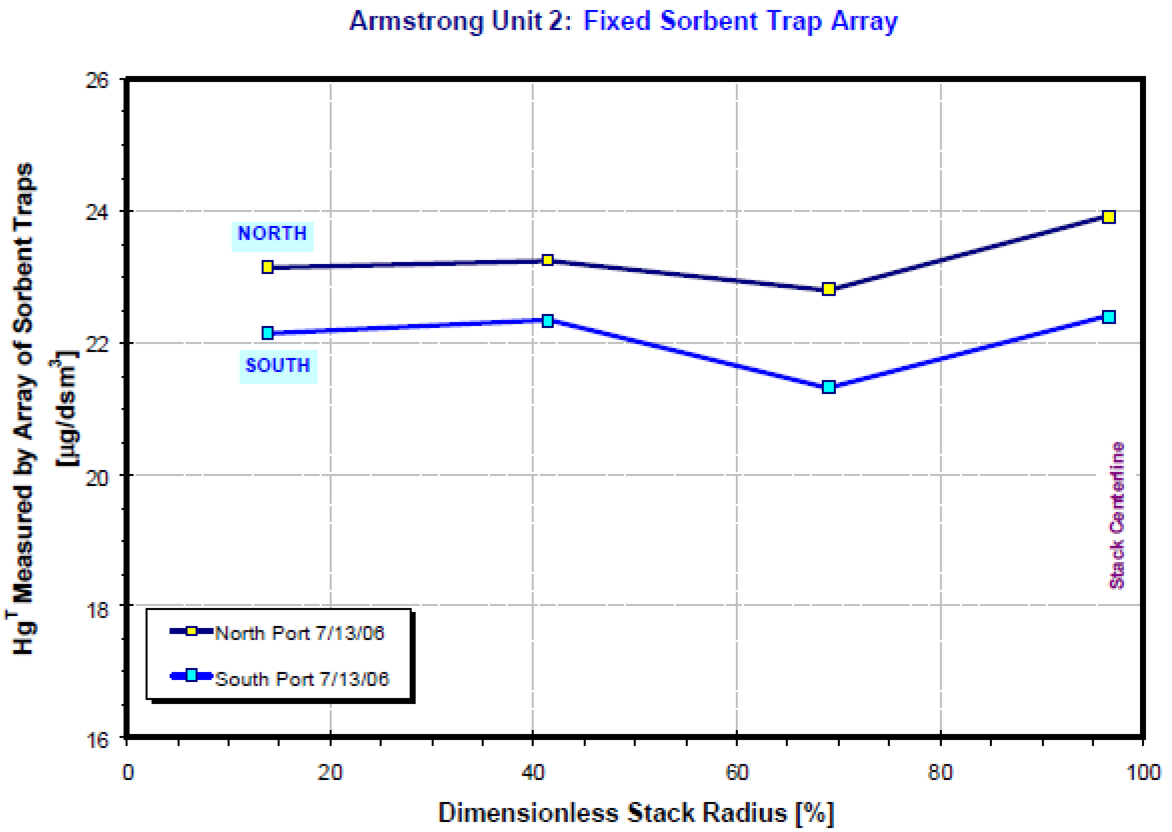


Figure 6-7: HgT Concentration as a Function of Distance From the Wall: FGS-FSTM, High-Hg Coal

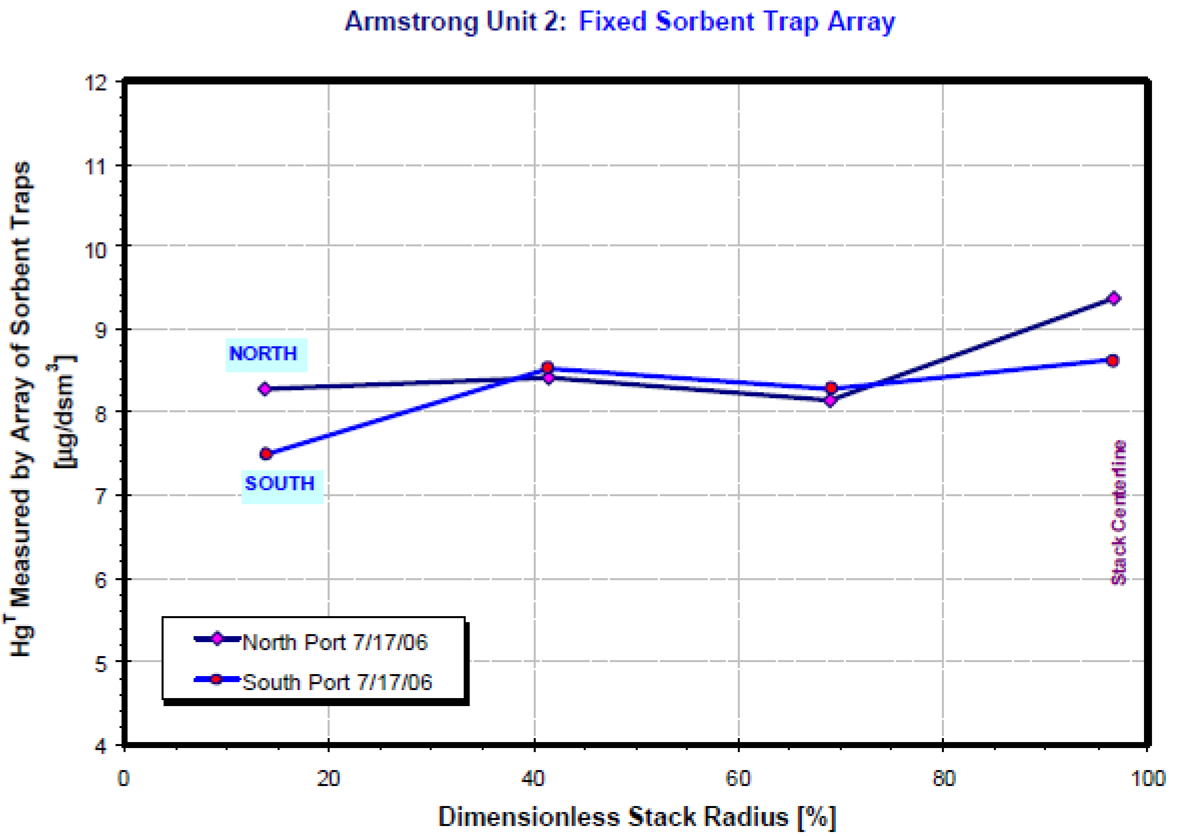


Figure 6-8: HgT Concentration as a Function of Distance From the Wall: FGS-FSTM, Low-Hg Coal

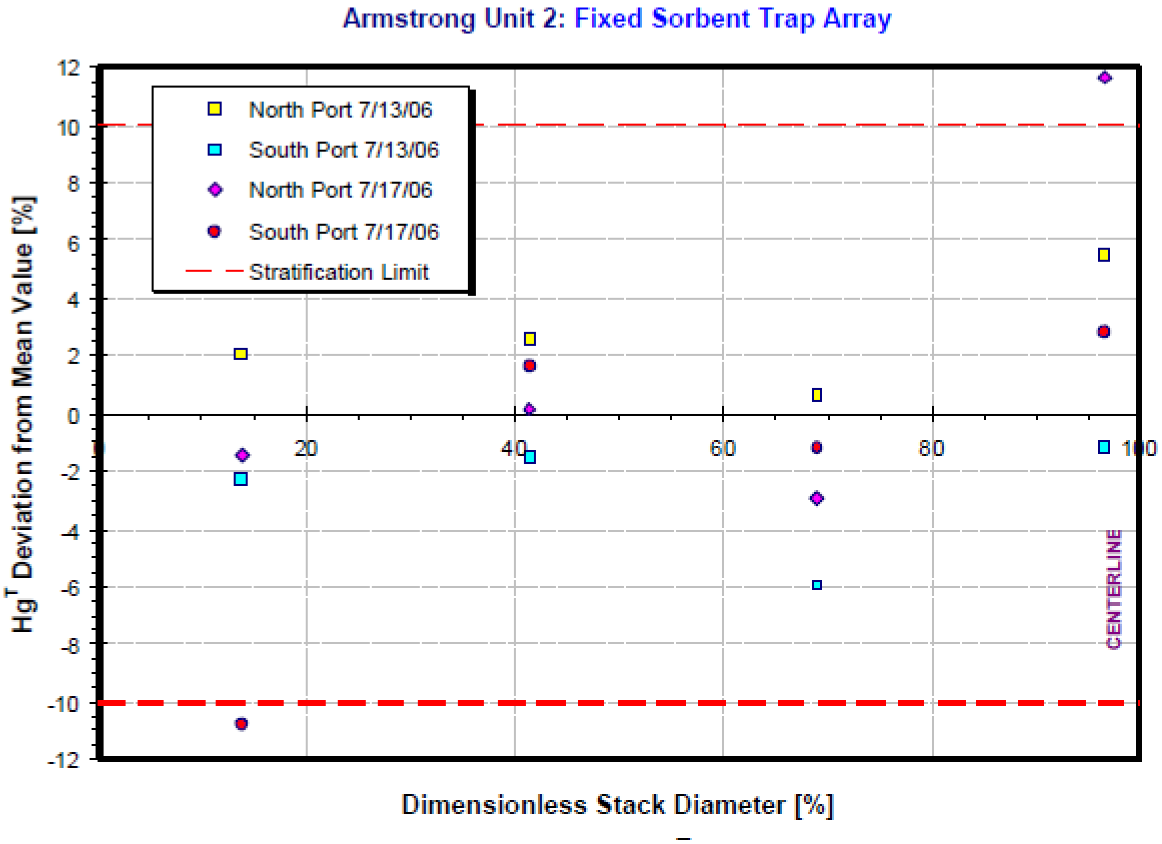


Figure 6-9: Spatial Stratification in HgT Measured by a Fixed Array of Sorbent Traps at Armstrong

The stratification results obtained by a Sorbent Trap Array method, obtained at Armstrong are encouraging. More testing is needed to determine repeatability of the measured stratification profile for cases where background Hg concentration varies in time.

6.3. Comparison of Stratification Test Results

A comparison of the stratification test results obtained by the Background Correction and Sorbent Trap Array Methods is presented in Figure 6-10. Except for the two points (near-centerline North port, and near-wall-south port), stratification profiles obtained by both methods are in very good agreement. Using EPA criteria for stratification, the spatial stratification in HgT measured at Armstrong would be considered non-stratified or minimally stratified. More testing of both methods is needed to determine measurement precision.

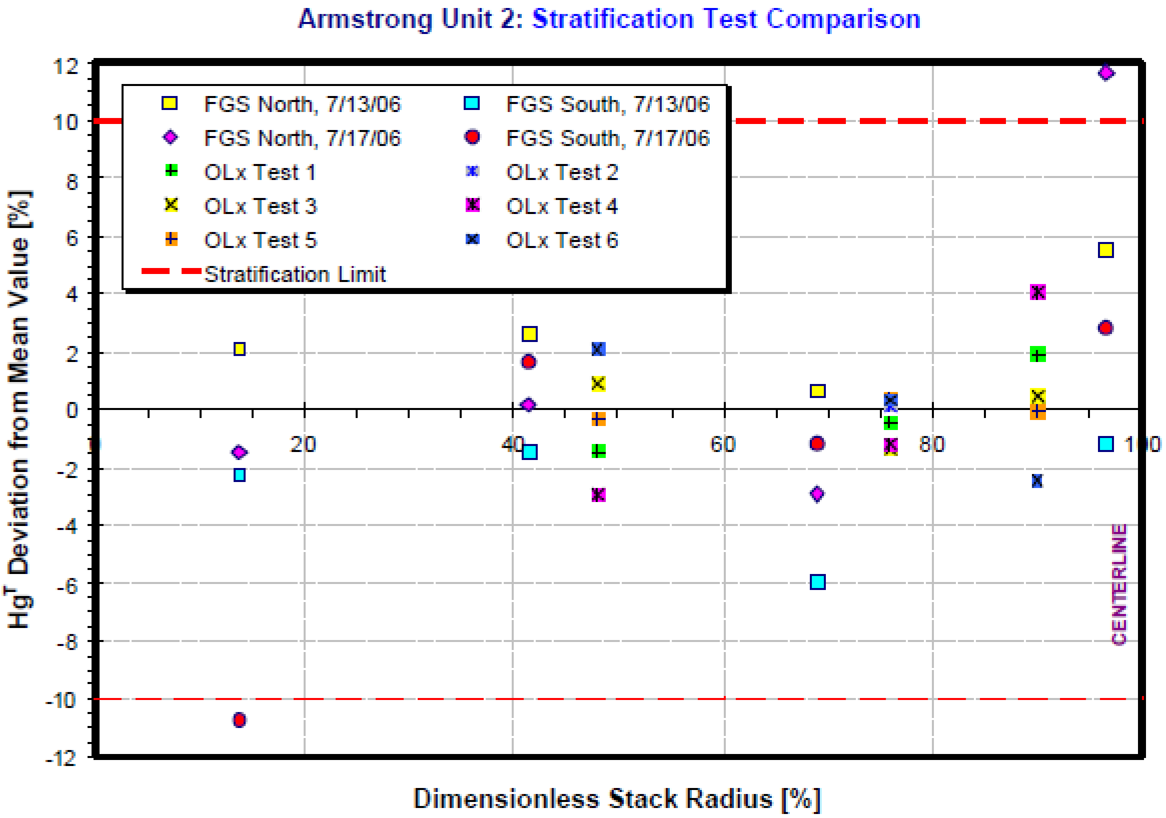


Figure 6-10: Comparison of Stratification Test Results

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. General

With the support from the U.S. EPA, EPRI, U.S. electrical utility companies, and the Italian Ministry of Economic Development, The Institute for Environment and Sustainability of the Joint Research Centre, and with great help from Allegheny Energy, the ERC organized a field test in which three continuous and two semi-continuous CMMs, currently commercially available in the U.S., were field-tested at Allegheny Energy's Armstrong Generating Station.

The Hg concentrations measured by the Hg CEMs were compared to the mercury concentrations measured by the Reference Method (OHM). The OHM was used as a reference for all Hg measurements. The on-site analysis of collected OHM samples was performed by Western Kentucky University.

Mercury emissions were also measured by the Sorbent Trap Method (Appendix K). Sorbent tubes and test equipment were provided by three manufacturers. The sorbent trap testing was conducted in parallel to the OHM tests. The start and end times for the OHM and sorbent trap tests were coordinated to allow direct comparison of the results.

Also, as part of the Armstrong project, the U.S. EPA, in association with Arcadis G&M, Inc., performed a first field test of the new Instrumental Reference Method (IRM).

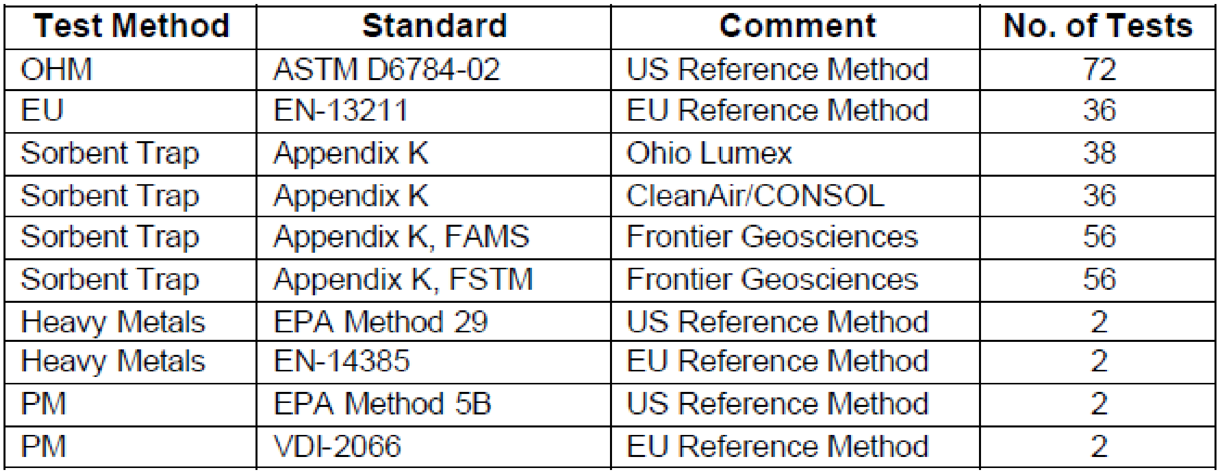
Field testing was performed in July 2006 by a joint U.S. and EU team at the Allegheny Energy Armstrong Generating Station, located northeast of Pittsburgh, Pennsylvania. For the first part of the test, the plant was firing locally mined bituminous coals having high and varying mercury content. For the second part of the test, a low- Hg coal from Virginia was fired.

The main objectives of the Armstrong project were the following:

- Test mercury CEMs under field conditions and compare against the reference method (OHM).
- Test the Appendix K (Part 75) sorbent trap method under field conditions and compare results against the reference method (OHM).
- Field-test the IRM. The IRM is designed as an alternative to OHM with the intent to provide an additional reference method for mercury RATAs.
- Compare reference methods for Hg measurement developed by the U.S. and EU. This allowed direct comparison of the emission levels measured in the U.S. and the EU.
- Determine whether there is a bias in pollutant emissions measured by the U.S. and EU reference methods.
- Compare all reference and other methods for mercury measurement under the same test conditions.
- Compare reference methods for heavy metals, and PM2.5, and PM10 developed in the U.S. and EU.

The total number of the OHM, EU, and sorbent trap tests performed at Armstrong is summarized in Table 7-1.

Table 7-1 Tests Performed at Armstrong



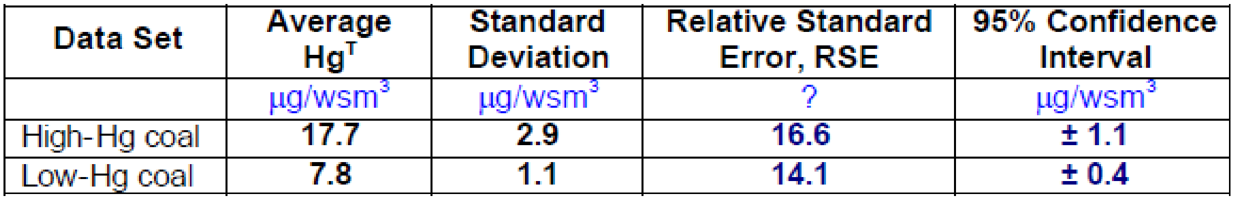
Test Method	Standard	Comment	No. of Tests
OHM	ASTM D6784-02	US Reference Method	72
EU	EN-13211	EU Reference Method	36
Sorbent Trap	Appendix K	Ohio Lumex	38
Sorbent Trap	Appendix K	CleanAir/CONSOL	36
Sorbent Trap	Appendix K, FAMS	Frontier Geosciences	56
Sorbent Trap	Appendix K, FSTM	Frontier Geosciences	56
Heavy Metals	EPA Method 29	US Reference Method	2
Heavy Metals	EN-14385	EU Reference Method	2
PM	EPA Method 5B	US Reference Method	2
PM	VDI-2066	EU Reference Method	2

7.2. Ontario Hydro Method (OHM)

The total gas-phase (Hg+2 and Hg0) and particulate-bound (HgP) mercury concentrations were measured by two paired OHM trains located in two mutually orthogonal sampling ports (Port 1 and Port 3) on the main CEM platform. The relative difference (RD) between the paired trains for Port 1 is 6.2 percent, while for the Port 3 the average value of RD is 4.2 percent. The RD value exceeded 10 percent for only one test. Elemental mercury (Hg0) represented approximately 20 percent of the total mercury HgT. The particulate -bound mercury (HgP) measured at Armstrong was very low (0.03 to 0.05 mg/dsm3), representing a very small fraction of the total mercury (approximately 0.1 to 0.2 percent).

Test statistics were calculated separately for the high-Hg and low-Hg coals. The results are summarized in Table 7-2. The relative standard deviation or error (RSD or RSE) values, obtained at Armstrong, are compared to the results from OHM tests performed at other sites in Figure 7-1.

Table 7-2 Test Statistics: OHM



Data Set	Average Hg^T	Standard Deviation	Relative Standard Error, RSE	95% Confidence Interval
	$\mu g/wsm^3$	$\mu g/wsm^3$	?	$\mu g/wsm^3$
High-Hg coal	**17.7**	**2.9**	**16.6**	**± 1.1**
Low-Hg coal	**7.8**	**1.1**	**14.1**	**± 0.4**

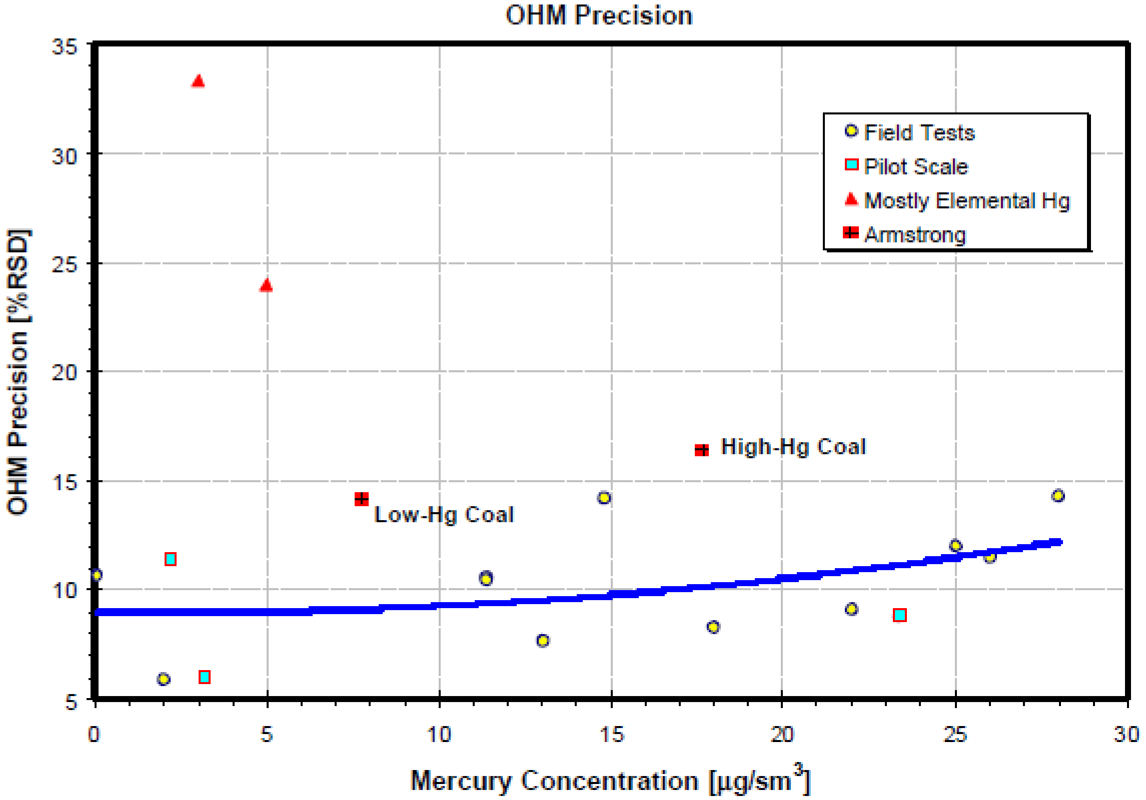


Figure 7-1: Precision of the OHM Tests

The results show that for the low-Hg coal, the RSE value for Armstrong was very close to the OHM tests performed at other units. For the high-Hg coal test, the RSE value for Armstrong was higher. This higher RSE value is caused by a large variability in mercury content in coals that were delivered from a number of local mines.

7.3. Mercury Monitors

The three continuous Hg CMMs, manufactured by Tekran, Thermo Electron, and GE-PSA, and two semi-continuous mercury monitors, manufactured by Ohio Lumex and Horiba were tested. The CMMs were located in the CEM shelters at the base of the stack and flue gas samples were delivered to the mercury analyzers by using 400 to 450 feet long heated umbilical cords. The portable semi-continuous mercury monitors were located at the CEM platform and used very short umbilical cords.

A comparison of the gas-phase mercury concentration measured by the Hg CEMs and OHM is presented in Figure 7-2. The results show a very good agreement between the Hg concentration values measured by the Hg CEMs and OHM. Also, the inter-comparison between Hg CEMs is very good, especially for the low-Hg coal.

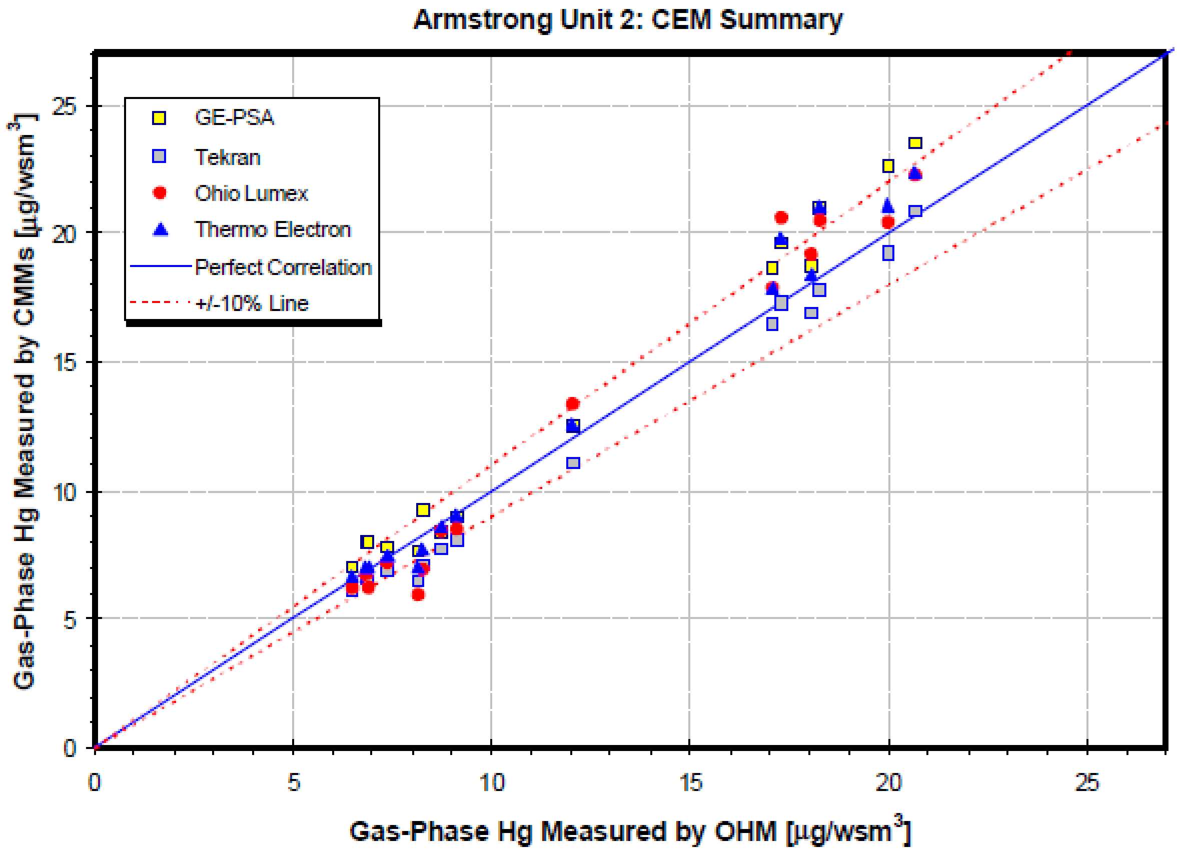


Figure 7-2: Comparison of Gas-Phase Hg Concentration Measured By Hg CEMs and OHM

The bias error between the Hg CEM and OHM results was calculated as:

B = (HgCEM/HgOHM – 1) x 100% Eqn. 7-1

The values of the bias error in the gas-phase Hg concentration measured by the Hg CEMs and OHM, calculated from Equation 7-1, are summarized in Table 7-3, and are also presented in graphical form in Figure 7-3.

Table 7-3 Hg CEM vs. OHM Bias

CEM Vendor	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
Tekran	- 4.2	- 3.1	- 10.4	± 44.2 Average ± 16.5 High-Hg Coal ± 14.1 Low-Hg Coal	± 11.4 Average ± 6.4 High-Hg Coal ± 5.0 Low-Hg Coal
Thermo Electron	+ 6.2	+ 7.8	- 2.3		
GE-PSA	+ 10.5	+ 10.5	+ 4.6		
Ohio Lumex	+ 6.2	+ 8.7	- 9.4		

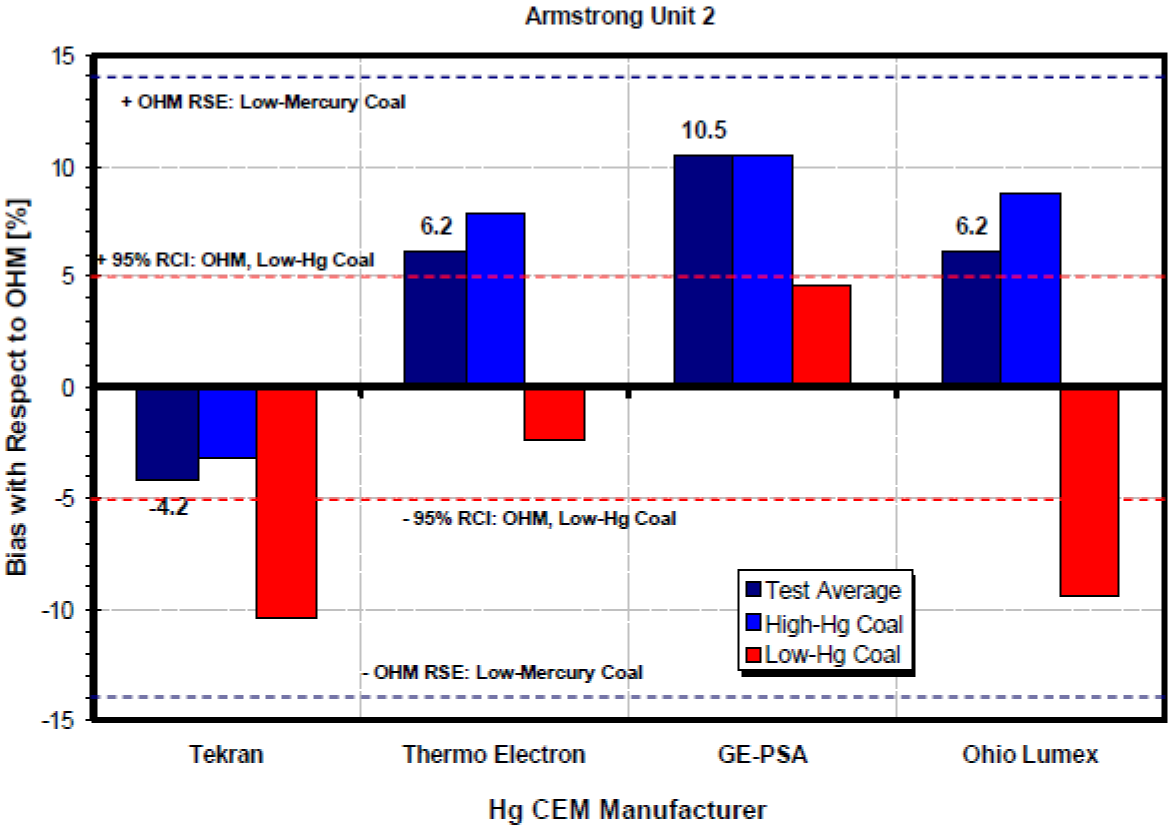


Figure 7-3: Hg CEM Bias Error With Respect to OHM

The average bias error B in the gas-phase Hg concentration measured at Armstrong by the Hg CEMs and OHM ranges from -4.2 to + 10.5 percent. The bias error for the high-Hg coal is in the -3.1 to 10.5 percent range, while for the low-Hg coal the value of B is in the -10.4 to 4.6 percent range.

A statistical analysis was performed to determine significance of the bias errors. The values of the relative standard deviation or error (RSD or RSE) and absolute and relative 95 percent confidence intervals (CI and RCI) were used in this analysis. The RSE value for OHM measurements, performed at Armstrong for the low-Hg coal, is ± 14.1 percent. The corresponding RCI value is ± 5.0 percent.

As shown in Figure 7-3, the bias errors for all mercury CEMs are contained within the ± RSE interval. Using the RSE value as a criterion, it can be concluded that bias errors for the Hg CEMs with respect to OHM, determined at Armstrong, are not statistically significant. If the ± RCI interval is used as a criterion, it may be concluded that bias errors for all mercury CEMs are statistically significant.

A more rigorous analysis involves comparison of the interval estimates, i.e., the Hgavg ± CI values measured by the OHM and Hg CEMs. This comparison is presented in Figures 7-4 and 7-5 for the high-Hg and low-Hg coals. The results for the high-Hg coals fired at Armstrong show that the bias between the OHM, GE-PSA CMM and Ohio Lumex Hg CEM could be statistically significant. For the low-Hg coals, the bias between the OHM, Tekran CMM and Ohio Lumex CEM are most likely statistically significant.

7.4. Sorbent Traps

The sorbent trap testing at Armstrong was conducted according to the Appendix K of 40 CFR Part 75 regulations in parallel to the OHM tests. The start and end times for the OHM and sorbent trap tests were coordinated to allow direct comparison of the results.

Sampling trains provided by Ohio Lumex-Apex Instruments, CleanAir Engineering-CONSOL, and Frontier Geosciences Inc. (FGS) were located on the second, third, and fourth CEM platforms at Armstrong. The Ohio Lumex/Apex Instruments probe and a sampler, and one of the FGS samplers were located on the 2nd CEM platform. The rest of the FGS equipment was located on the 3rd CEM Platform. The CleanAir-CONSOL equipment was located on the 4th CEM platform.

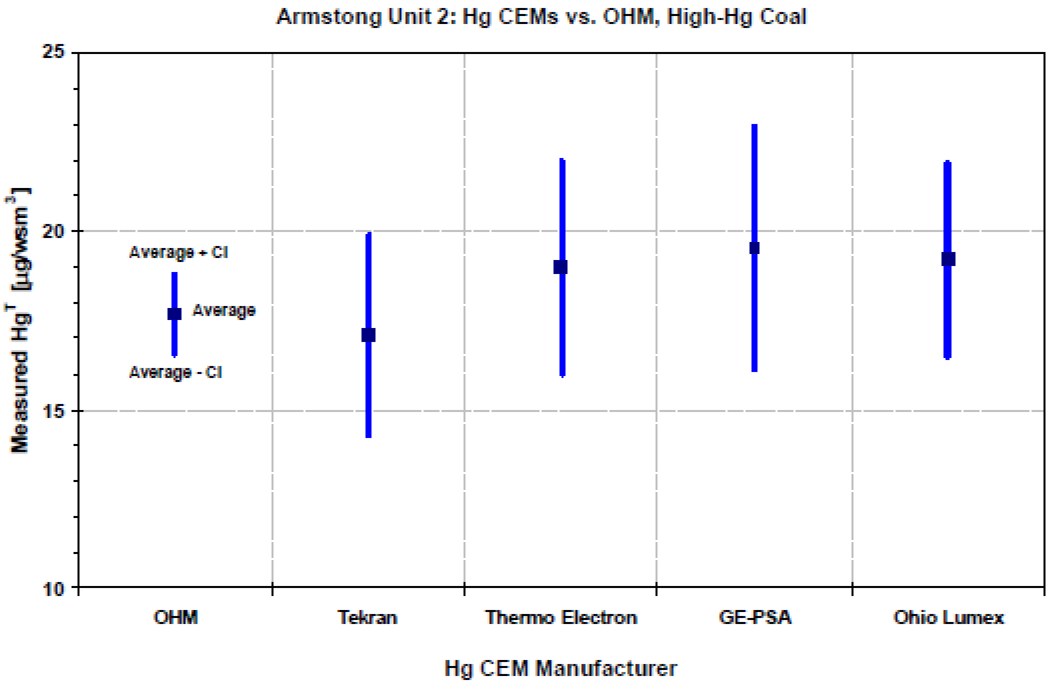


Figure 7-4: Comparison of the Interval Estimates for OHM and

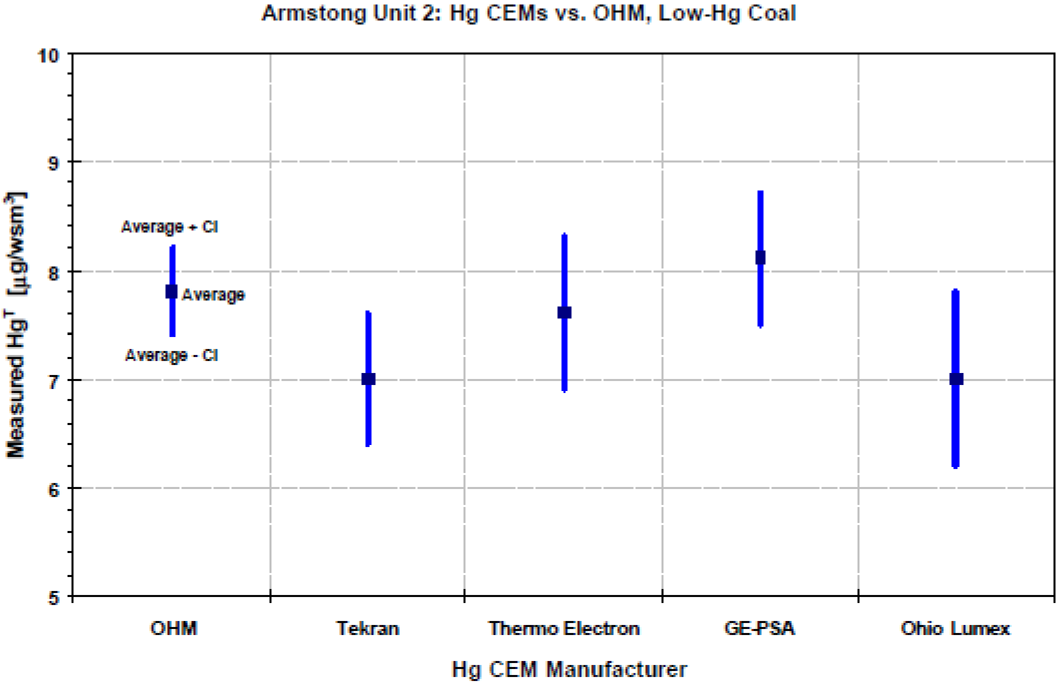


Figure 7-5: Comparison of the Interval Estimates for OHM and Hg

The Ohio Lumex sorbent traps were analyzed on site. The sorbent traps collected by CleanAir Engineering-CONSOL test team were analyzed in CONSOL's laboratory in Library, Pennsylvania. The FGS traps were shipped to California and analyzed in the FGS laboratory.

A comparison between the total mercury (HgT) concentration measured by the sorbent trap methods and OHM is presented in Figure 7-6. The results show a very good agreement between the mercury concentration measured by the sorbent trap methods and OHM. Also, the inter-comparison between different sorbent trap methods is very good, especially for the low-Hg coal.

The values of the bias error B in the HgT concentration values measured by the sorbent trap methods and OHM, calculated from Equation 7-1, are summarized in Table 7-4. The average bias error in HgT concentration, measured by the sorbent trap methods and OHM, ranges from –4.7 to 11.3 percent. The bias error for the high-Hg coal is within the -1 to 13.3 percent range, while for the low-Hg coal B is within the -12 to 7.9 percent range.

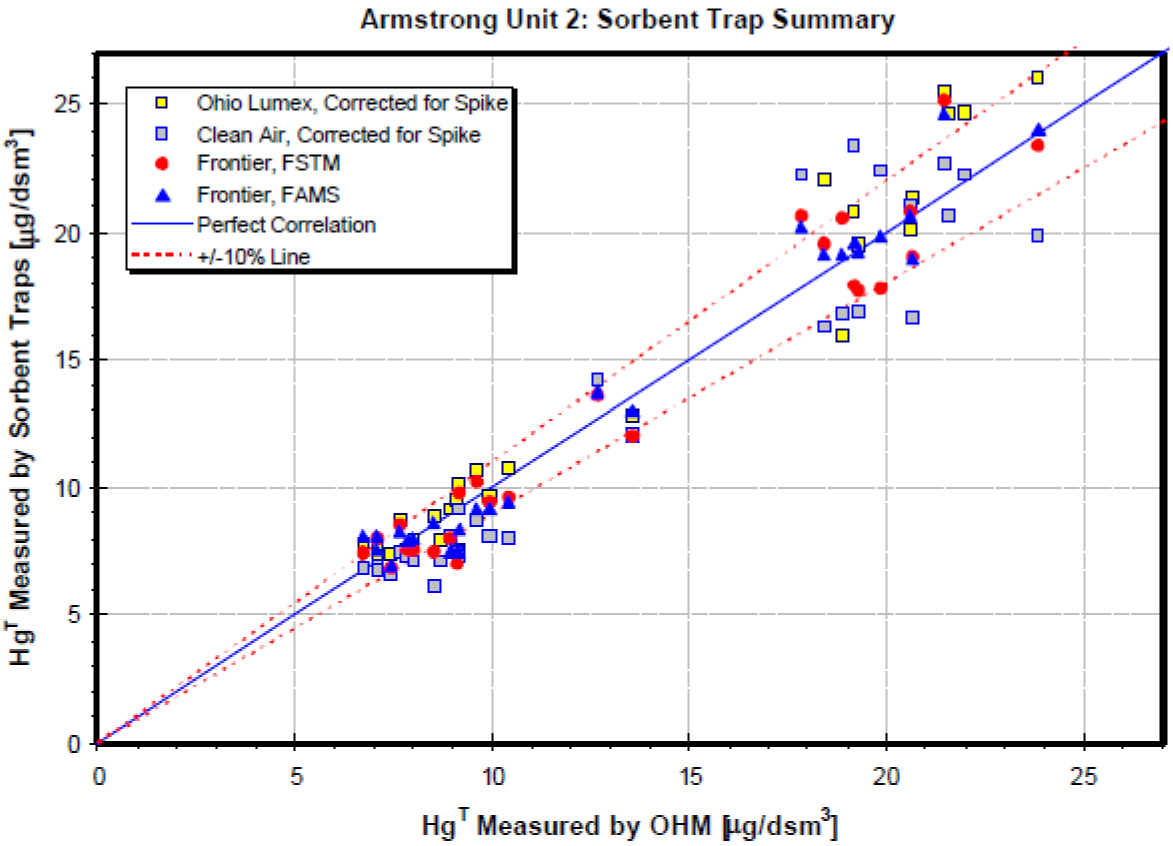
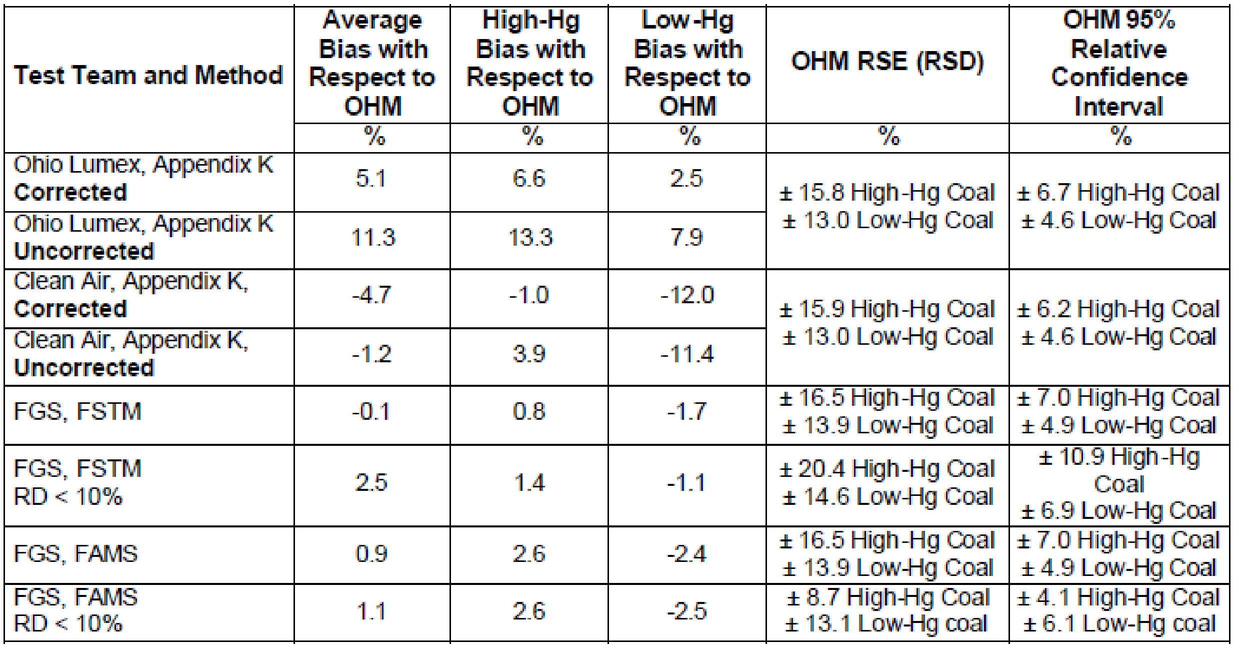


Figure 7-6: Comparison of HgT Concentration Measured By Sorbent Traps and OHM

Table 7-4 HgT Bias: Sorbent Traps vs. OHM



Test Team and Method	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
Ohio Lumex, Appendix K **Corrected**	5.1	6.6	2.5	± 15.8 High-Hg Coal ± 13.0 Low-Hg Coal	± 6.7 High-Hg Coal ± 4.6 Low-Hg Coal
Ohio Lumex, Appendix K **Uncorrected**	11.3	13.3	7.9		
Clean Air, Appendix K, **Corrected**	-4.7	-1.0	-12.0	± 15.9 High-Hg Coal ± 13.0 Low-Hg Coal	± 6.2 High-Hg Coal ± 4.6 Low-Hg Coal
Clean Air, Appendix K, **Uncorrected**	-1.2	3.9	-11.4		
FGS, FSTM	-0.1	0.8	-1.7	± 16.5 High-Hg Coal ± 13.9 Low-Hg Coal	± 7.0 High-Hg Coal ± 4.9 Low-Hg Coal
FGS, FSTM RD < 10%	2.5	1.4	-1.1	± 20.4 High-Hg Coal ± 14.6 Low-Hg Coal	± 10.9 High-Hg Coal ± 6.9 Low-Hg Coal
FGS, FAMS	0.9	2.6	-2.4	± 16.5 High-Hg Coal ± 13.9 Low-Hg Coal	± 7.0 High-Hg Coal ± 4.9 Low-Hg Coal
FGS, FAMS RD < 10%	1.1	2.6	-2.5	± 8.7 High-Hg Coal ± 13.1 Low-Hg coal	± 4.1 High-Hg Coal ± 6.1 Low-Hg coal

For the Armstrong data, not correcting measured HgT concentrations for spike resulted in higher reported HgT concentrations. The spike correction, therefore, affected the value of the bias error B.

The values of the bias error for the sorbent trap methods, tested at Armstrong, are presented in a graphical form in Figure 7-7. Not correcting the Ohio Lumex – Apex Instruments results for spike resulted in an increase in the bias error, while for the CleanAir Engineering - CONSOL results, the bias error for the uncorrected results has decreased. The lowest bias error was achieved by the Frontier Geosciences' FSTM and FAMS methods.

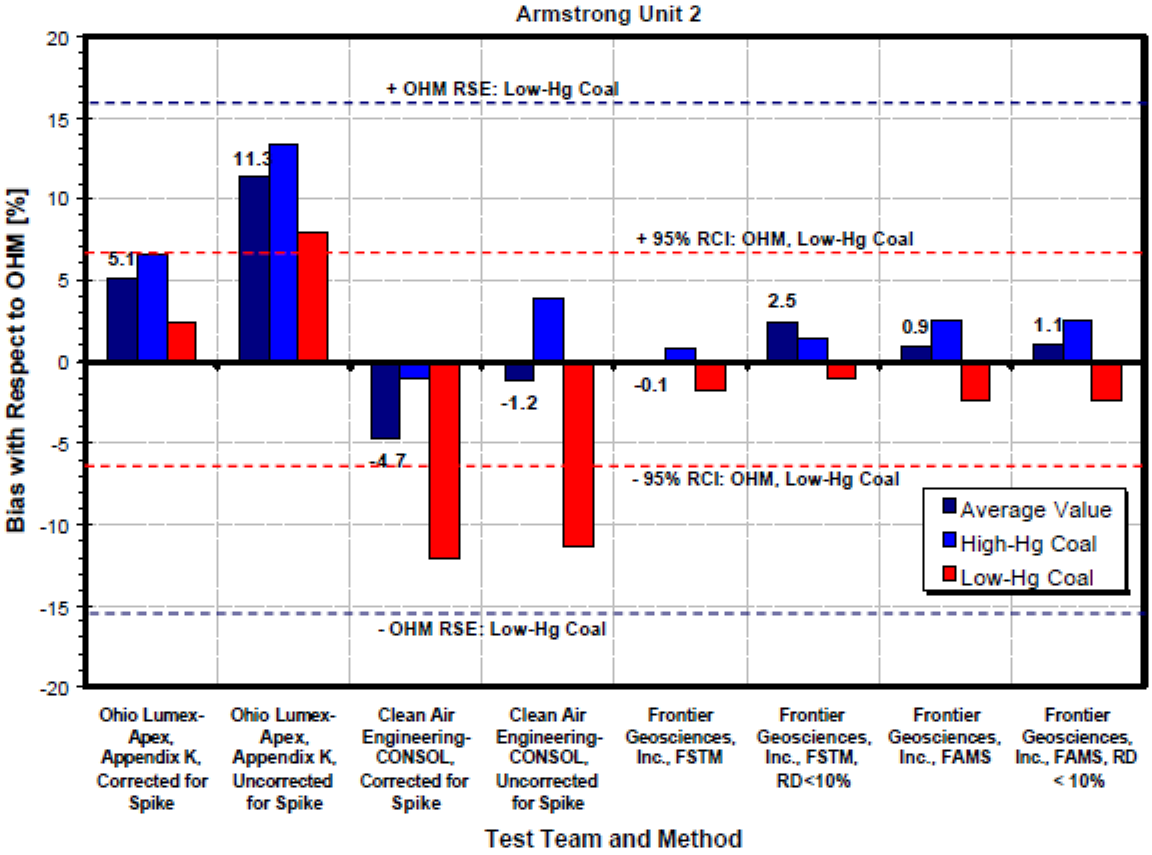


Figure 7-7: Sorbent Trap Bias Error With Respect To OHM

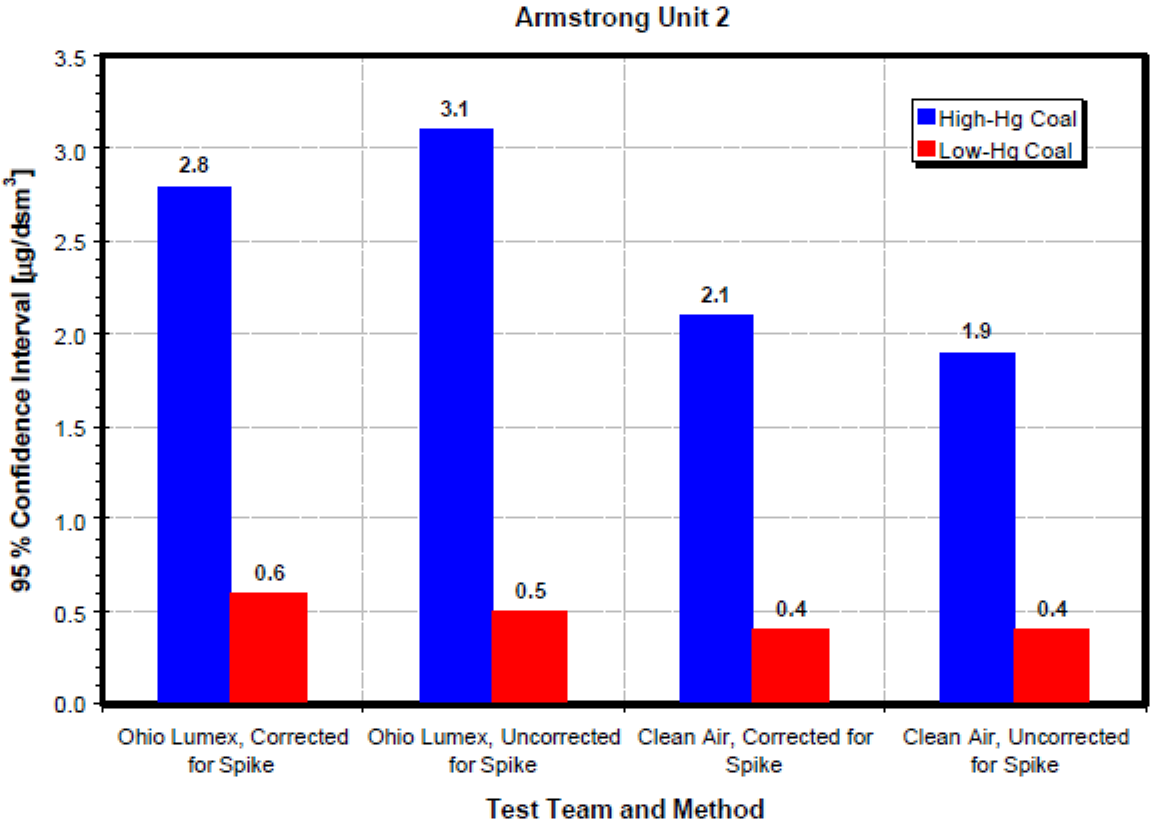


Figure 7-8: Precision of the Corrected and Uncorrected For Spike

Similar to the Hg CEMs, a statistical analysis was performed to determine significance of the bias errors determined for the sorbent trap methods. The values of the relative standard deviation or error (RSD or RSE) and absolute and relative 95 percent confidence intervals (CI and RCI) were used.

As shown in Figure 7-7, bias errors for all sorbent trap methods are contained within the ± RSE interval of the OHM. Therefore, if RSE is used as a criterion, it can be concluded that bias errors for the sorbent trap methods with respect to OHM, determined at Armstrong, are not statistically significant. If the ± RCI interval is used as a criterion, it may be concluded that bias errors for the uncorrected-for-spike Ohio Lumex results, and Clean Air Engineering – CONSOL results for the low-Hg coal are statistically significant.

A more rigorous analysis was performed by comparing interval estimates. The results of this comparison are presented in Figures 7-9 and 7-10 for the high-Hg and low-Hg coals. The results for the high-Hg coals fired at Armstrong, presented in Figure 7-9, show that the bias between the OHM, uncorrected Ohio Lumex, and Clean Air Engineering results is statistically significant.

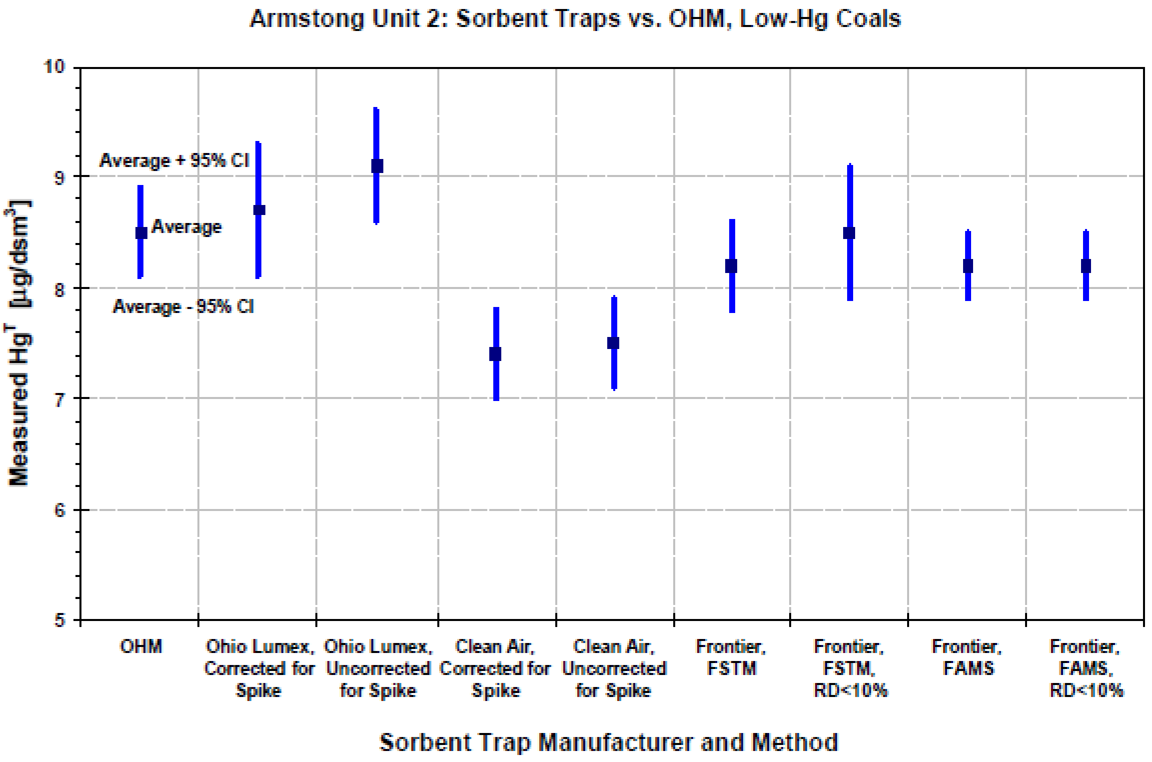


Figure 7-9: Comparison of Interval Estimates (Hgavg ± CI Values) for OHM and Sorbent Trap Methods: High-Hg Coal

For the low-Hg coals, the comparison of interval estimates, presented in Figure 7-10, shows that the bias between the OHM and uncorrected Ohio Lumex results is statistically significant.

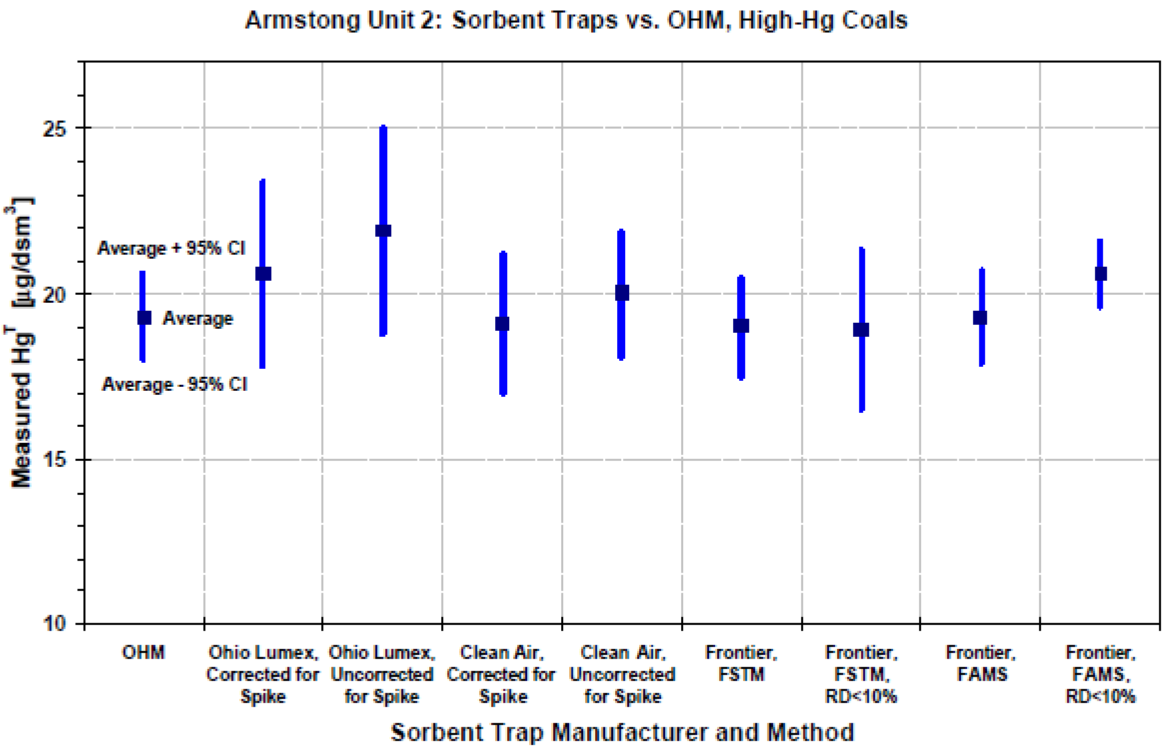


Figure 7 -10: Comparison of Interval Estimates (Hgavg ± CI Values) for OHM and Sorbent Trap Methods: Low-Hg Coal

7.5. EN-13211 Manual Method for Total Mercury

The EN-13211 manual method for measurement of total mercury was used by the EU test team. The total gas-phase (Hg+2 and Hg0) and particulate-bound (HgP) mercury concentrations were measured by two EU trains (Trains A and B) located in two mutually perpendicular test ports. A three-point traverse according to the EPA Equal Area Method (EAM) was used to obtain a composite mercury sample.

The relative difference (RD) in Hg T concentration measured by Trains A and B was calculated. It has to be noted that the obtained RD values represent a relative difference between two sampling trains located at two test ports. The average value of RD is 4.5 percent.

A comparison of the Hg T concentration values measured by EN-13211 and OHM, expressed on a wet basis, is presented in Figure 7-11. The data show a very good correlation between the two Reference Methods for HgT measurement.

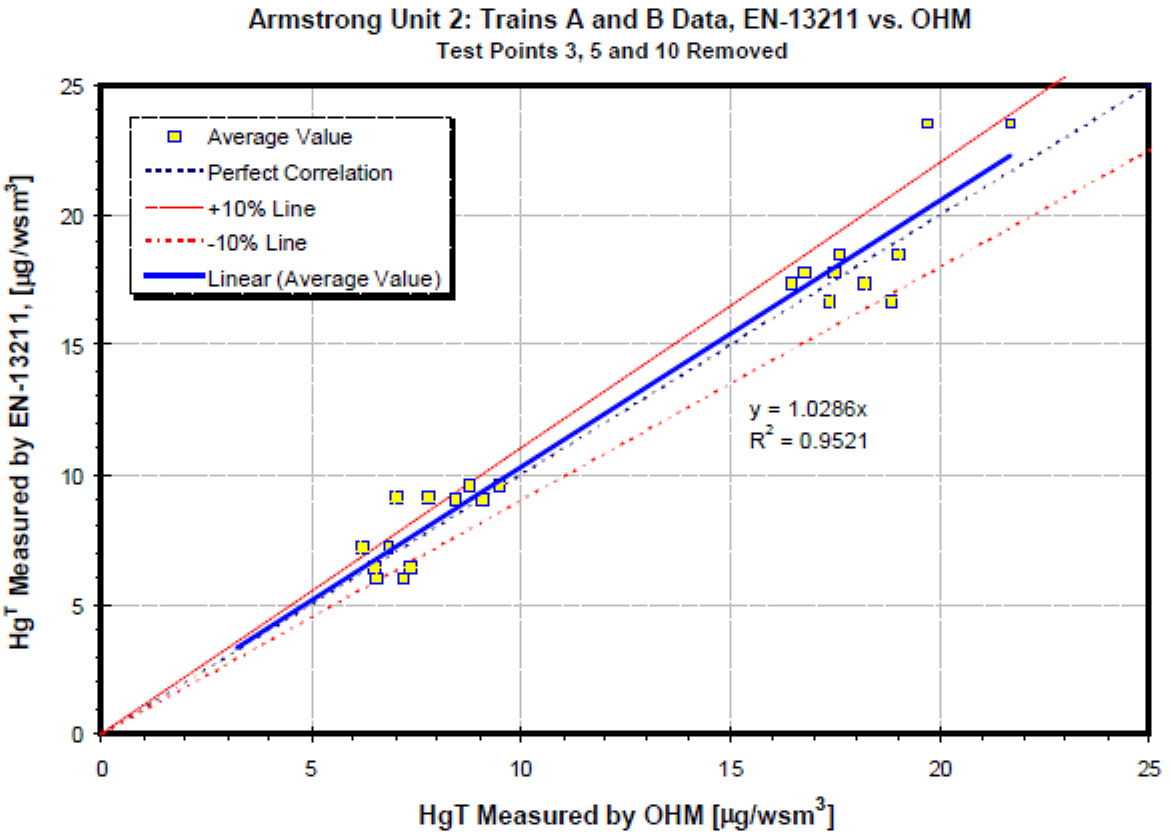


Figure 7-11: Comparison of Hg T Concentrations Measured By EN-13211 and OHM

The values of the bias error in HgT concentration measured by EN-13211 and OHM, calculated from Equation 7-1, are summarized in Table 7-5. The results show that bias error B is contained within the ± RSE and ± RCI intervals of the OHM, meaning that the calculated bias between EN-13211 and OHM is not statistically significant.

Table 7-5 Hg CEM vs. OHM Bias

Reference Method	Average Bias with Respect to OHM	High-Hg Bias with Respect to OHM	Low-Hg Bias with Respect to OHM	OHM RSE (RSD)	OHM 95% Relative Confidence Interval
	%	%	%	%	%
EN-13211	2.9	2.5	3.8	± 8.7 High-Hg Coal ± 14.8 Low-Hg Coal	± 4.1 High-Hg Coal ± 6.3 Low-Hg Coal

In summary, EN-13211 performed very well and, on average, produced almost identical values compared to OHM. This means that the Hg emission rates measured by the Reference Methods in the USA and

European Union are, from the practical point of view, identical and Global trading (if it ever becomes a reality), would be fair and unbiased, as far as measurement accuracy is concerned.

7.6. Heavy Metals and PMs

The heavy metal emissions were measured at Armstrong by employing EPA Method 29 and EN-14385 flux derived method. A separate sampling train was required to obtain flue gas samples according to the Method 29. Heavy metals sampling according to EN-14385 was conducted in parallel to the Hg sampling.

Unfortunately, the samples collected by EN-14385 were displaced and never found. Only the Method 29 samples were analyzed. Therefore, a direct comparison of the EU and U.S. methods for heavy metal emission measurement could not be performed.

EPA Method 5B and VDI Impaction Method were used to measure particulate matter (PM) emissions. A separate sampling train was required to obtain flue gas samples according to the EPA Method 5B (Section 4.1.3.). The PM sampling according to the VDI Impaction Method was conducted in parallel to the Hg sampling.

The PM2.5, PM10 and total PM concentrations, measured by the EPA Method 5B and VDI Impaction Method were compared. While the there is a good agreement between the PM2.5 and PM10 results, the total PM concentration measured by EPA Method 5B is significantly higher compared to the VDI method.

This discrepancy in the total measured PM could be explained by the filter breakthrough on the VDI probe; the VDI method is designed for one hour of sampling, while the EPA Method 5B requires two hours of sampling to collect a representative sample. To facilitate a direct comparison between the EU and U.S. methods, sampling was performed over a two hour period. This resulted in overloading of the paper filter in the VDI probe and the filter breakthrough.

7.7. Recommendations

The results from the Armstrong field test show there is a good agreement between the Reference Method (OHM), Hg CEMs, and sorbent trap methods. The maximum bias, calculated from the Armstrong data, with respect to the OHM is in the 10 percent range. Also, the precision of the OHM results obtained at Armstrong was comparable to the precision obtained at other sites.

Based on the results obtained and experience with the reference methods, test equipment, and Hg monitors, the following recommendations are given for the dry stacks:

- OHM is the oldest and most-proven Reference Method. However, it is manpower intensive and, therefore, time-consuming and expensive to use. Automating the OHM method to allow automatic isokinetic sample collection without manual intervention is recommended.
- For the Relative Accuracy Test Audit (RATA) testing purposes it would be of great help if the Hg T concentration in the impinger solutions collected by the OHM sampling train could be determined in the field by using a spectroscopy analysis, rather than by performing wet chemistry analyses. The Ohio Lumex RA-915+ analyzer could be used for this purpose. It is recommended that a comparison test be performed in which the HgT concentration obtained by performing the wet chemistry analysis of the collected samples is compared to the spectroscopic analysis results.
- Sorbent trap methods are simple to use and offer the same precision and accuracy compared to the Hg CEMs. However, they are not designed for continuous sampling. It also appears there are some spike recovery issues associated with the long-term sampling. However, sorbent traps are well suited for RATA testing. Appendix K will be approved as a Reference Method by the U.S. EPA later this year. Test personnel, using Appendix K, should be trained in the proper use of the sampling equipment. It is also recommended that the sorbent tubes be analyzed in a laboratory, unless well-trained and experienced personnel is available for field analysis.
- The Instrumental Reference Method (IRM) was tested by the EPA contractor, Arcadis G&M, Inc. The results and conclusions are presented in the Appendix. The IRM will be approved as a Reference Method by the U.S. EPA later this year. However, at this point, IRM is not tied to any specific hardware. Portable, affordable hardware needs to be developed. It is proposed that IRM hardware be developed by combining the already available U.S. and EU technology and components.
- Two methods were developed for mercury stratification testing. It is recommended that these methods be field-tested at several stacks, over a wide range of operating conditions, and for different fuels.
- Sootblowing interferes with Hg measurement. As sootblowing was initiated at Armstrong, the gas-phase mercury concentration measured by all Hg CEMs suddenly dropped. This sudden drop is believed to be caused by Hg adsorption/absorption on solid particles that were dislodged from tube surface by sootblowing and then entered the flue gas stream. For obtaining good quality repeatable Hg measurements that are required for RATAs, it is crucial that sootblowers are not used during the RATA test.

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Personnel:
Allegheny Energy: Mr. David Cannon
Ms. Marc Crimboli
Ms. Jeannine Hammer
Mr. Tom Hileman
Mr. Pete Kotsenas
Mr. Gerald Lang
Mr. Tom Pezze
Mr. Leo Rajter
Mr. Mark Seibel
Apex Instruments: Mr. Cody Cress
Mr. William H. Howe
Arcadis: Mr. Edward J. Brown
CESI RICERCA: Mr. Giordano Bocchiola
Dr. Cipriano Domenico
Mr. Antonio Negri
Mr. Claudio Vannini
CleanAir/CONSOL: Mr. Rob Doran
Mr. Volker Schmidt
Mr. Steve Winter
Mr. Jim Wright
Control Analytics: Mr. Pete Aiello
Mr. Greg Banchiei
Mr. Jim Carter
Frontier GeoScience: Mr. Robert Brunette
GE Infra Energy: Dr. Thomas A. Dunder
Mr. Mark Holt
Mr. Mike Murphy
Dr. Peter Stockwell
Horiba: Mr. Dean Masropian

Lehigh University: Mr. Jason Schatz
Ohio Lumex Company: Mr. Philip J. Dufresne
M.Sc. Joseph Siperstein
Tekran Instruments Corporation: Mr. John Cooper
Mr. Gabe Erias
Dr. Sergei Leikin
Mr. Chuck McDonald
Mr. Warren Postma
Thermo Electron Corporation: Mr. Adrian Cook
Mr. Michael Corvese
Mr. Tom Cosgrove
Mr. Jeff Socha
U.S. EPA: Dr. Ruben Deza
Mr. Frank Priciotta
Mr. Jeff Ryan
Mr. John Schakenbach
Western Kentucky University: Mr. Bobby I.T. Chen
Mr. Chein-Wei Chen
Mr. Tony Chen
Mr. Younes ElKhdari
Dr. Yun Meng
Mr. John Stucy
Mr. Nash Tseng
Dr. Jiashun Zhu

Implementation of Conceptual Instrumental Reference Method for Gaseous Mercury Emissions

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1. Introduction

1.1 Background

The United States Environmental Protection Agency's (USEPA) recently-promulgated Clean Air Mercury Rule (CAMR) includes provisions related to use of mercury (Hg) continuous emission monitoring systems (CEMS) to measure Hg emissions from coal- fired electric utility steam generating units. Among these are the Hg monitoring additions to 40 CFR Part 75 and a new Appendix B Performance Specification for 40 CFR Part 60 – "Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources" (PS-12A). Both of these provisions require a CEMS certification process that includes a Relative Accuracy Test Audit (RATA) using an approved EPA reference method (RM). At present, the only approved RM is ASTM Method D6784-02, colloquially referred to as the Ontario-Hydro Method (OHM), which is a wet chemistry method using impinger trains and post-test laboratory analyses. In order to make the certification process less burdensome, EPA is currently developing an Instrumental Reference Method (IRM) as a less costly and more timely option. The conceptual method draft was released on 22-February-2006 (listed among EPA's "preliminary methods" at http://www.epa.gov/ttnemc01/prelim/pre-009.pdf), and numerous researchers have been experimenting with the method's procedures since that time.

1.2 Project Description

This project was conducted as a parallel effort to a much larger field test organized by the Lehigh University Energy Research Center (ERC) and hosted by Allegheny Energy at its Armstrong generating station located northeast of Pittsburgh, PA. The objectives of the ERC project were (1) to compare RMs for heavy metals, PM2.5, and PM10 developed by the European Union (EU) and the United States (US), (2) to demonstrate and compare the performance of several Hg CEMS, and (3) to test several sorbent trap measurement methods, including EPA Appendix K (Part 75). EPA, as a study participant and sponsor of the study, performed additional testing to implement the conceptual IRM.

The central activity of the project was the comparative measurements phase, during which all of the participants collected simultaneous Hg measurements at the host site. The measurements taken during this portion of the test represent two different coal sources, with fundamentally different emissions characteristics. The tests began with the "local coal" (brought in by truck from various local mines), which produced higher Hg measurements that were also more variable than the "West Virginia coal" (brought in by train) which was used later in the test.

ARCADIS, under contract to EPA (EP-C-04-023) implemented the procedures contained in the conceptual Hg IRM on several candidate instrumental mercury measurement systems to gain insight to the efficacy of the draft method. This involved collecting quantitative data relative to the described procedures and performance criteria as well as evaluating the practical aspects of the draft method. Instrumental mercury measurement systems from five vendors participated in the

ERC study: three that were configured as stationary CEMS, and two that were configured specifically for IRM measurements. For the purposes of this test, all five systems were evaluated as potential IRM systems.

1.3 Project Objectives

The primary objectives of this project were (1) to implement the conceptual IRM procedures to the greatest extent possible, (2) to determine if the conceptual IRM procedures are feasible as written, (3) to estimate how long the procedures will take, (4) to gain valuable hands-on experience that can be shared with other researchers, and (5) to identify areas where the method may need to be clarified or changed to make it more accurate or more practical. The secondary objective was to evaluate the candidate measurement systems themselves from the standpoint of suitability for IRM use.

2. Conceptual IRM Procedures Overview and Approach

The test procedures used in this project were based on the "Emissions Test Procedure" contained in Section 8 of the Conceptual IRM, and were most strongly focused on procedures and checks that are most indicative of the quantitative performance of the IRM measurement systems. Specifically, we performed the Elemental Hg (Hg^0) System Calibration Error Test, Oxidized Hg (Hg^{+2}) System Calibration Error Test, Measurement System Response Time determination, System Integrity Checks, and Dynamic Spiking. For purposes of accounting for the differences between the different vendors' measurement systems and assuring data repeatability, a set of step-by-step procedures was developed for each system see. These procedures are included as Appendix A.

Due to the time constraints of the project, no corrective action was initiated with any of the measurements systems, and no IRM checks was repeated, even when performance criteria were not met. Also, because none of the measurement system probes were well-suited to being moved during sampling, neither the sample traverses nor the determination of stratification were performed as part of this IRM implementation.

2.1 Hg^0 System Calibration Error Test (IRM Section 8.2.3)

The method requires, as part of the process of preparing the measurement system for use, a three-point Hg^0 System Calibration Error Test. The purpose of this check is to verify the operation of the measurement system without regard to issues related to delivery and conversion of Hg^{+2}. No currently available Hg measurement system measures Hg^{+2} without first converting it to Hg^0, so the accuracy of the Hg^0 measurements is of primary importance to collecting accurate data.

In preparation for this and other IRM demonstrations, EPA has acquired a Tekran 3310 Hg^0 calibration gas generator and subjected it to some preliminary comparative testing at EPA and at NIST. It is anticipated that the "recognized traceability protocol" required by the method, once it is established, will involve the use of calibration gas generators as "transfer standards" for Hg^0

calibration gas. Our use of a Tekran 3310 does not establish that unit or any other 3310 as an independent calibration standard, and does not preclude the use of other gas generators (i.e., from other vendors) as transfer standards, once properly certified.

During the field tests, Hg^0 calibration gas was presented to each system at its "spike port" (i.e., the gas injection port closest to the tip of the probe). Table 1 shows the four concentrations that were injected, covering two overlapping measurement ranges. Although the measurement ranges are defined, based on applicable regulations, using a "standard cubic meter" at 20°C, the Tekran 3310 calculates concentrations based on a 0°C cubic meter, so it will display concentrations that are higher by a factor of $^{293.15}/_{273.15}$.

Table 1. Calibration Gas Levels

Calibration Gas Concentrations		**10 µg/m^3 (@20°C) Range**	**20 µg/m^3 (@ 20°C)Range**
µg/m^3 @ 0°C	**µg/m^3 @ 20°C**	**Calibration Level**	**Calibration Level**
2.68	2.50	Low	-------
5.37	5.00	Mid	Low
10.7	10.0	High	Mid
21.5	20.0	-------	High

2.2 Hg^{+2} System Calibration Error Test (IRM Section 8.2.4)

The method also requires a three-point Hg^{+2} ($HgCl_2$) System Calibration Error Test as part of the process of preparing the measurement system for use. The purpose of this check is to verify that there are no Hg^{+2} losses in the sample conditioning and delivery system, and that the system converter is operating at an acceptable efficiency. None of the measurement systems participating in this project have a Hg^{+2} calibration device integrated into their system, and none have an independent adjustment for Hg^{+2} response.

All Hg^{+2} calibration gases were generated by Hot Vapor Calibration (HoVaCal) devices that were set up at the platform level near the probes. Each injection system included a heated gas delivery line (set to 180°C) and a HoVaCal device with balance, evaporator, and computer. Like the Hg^0 gases, the Hg^{+2} gases were presented to each system's "spike port" by the heated delivery line. The HoVaCal systems were used interchangeably, sharing the same supply of injection solutions. The solutions were prepared from a NIST-traceable stock solution of 100 µg/l $HgCl_2$ in 1N HCl and HNO_3.

Table 2 shows the injection concentrations and the corresponding solution concentrations. All but the 40 µg/l solution were prepared in the laboratory and transported to the field, with plans to make all HoVaCal injections at ~2% moisture. During the test, when some of the systems showed low oxidized recoveries, some exploratory injections were done at ~8% moisture to see if it made a difference. There was no conclusive evidence that the moisture level made a significant difference in those instruments' responses to Hg^{+2}. The HoVaCal software calculates its delivered gas concentrations based on a 0°C cubic meter.

Table 2. HoVaCal Calibration Gases and Solutions

Calibration Gas Concentrations		Solution Concentrations, µg/liter	
$\mu g/m^3$ @ 0°C	$\mu g/m^3$ @ 20°C	For ~2% moisture delivery	For ~8% moisture delivery
2.68	2.50	170	40
5.37	5.00	340	80
10.7	10.0	670	170
21.5	20.0	1340	340
53.7	50.0	3340	-------

2.3 Measurement System Response Time (IRM Section 8.2.5)

All four-point calibration checks, for both Hg^0 and Hg^{+2}, were done in a 2.5-10-5-20 injection order, so that the data can be analyzed for determining response times. To simplify data analysis, all participating system clocks were surveyed periodically and discrepancies noted (and/or corrected). In general, measurement of the response time with Hg^0 is more straightforward, since the response of the 3310 generator is essentially immediate. For Hg^{+2}, since it takes a certain amount of time for a solution change to work its way through the HoVaCal system, the analysis is complicated by the need to determine the "time=0" point of reference (i.e., the time when the concentration delivered by the HoVaCal actually changed at the outlet end).

2.4 System Integrity Checks (IRM Section 8.2.6.1)

The method requires that individual runs or groups of runs (as many as four) be validated by system integrity checks before and after the run(s). The results of these integrity checks are used to calculate bias and drift (IRM Section 8.2.6.2). A failed bias check (outside of ±5% of the instrument span) invalidates all test runs since the last passed bias check. A failed drift check (outside of ±3% of the instrument span) does not invalidate any test runs, but does require corrective action before the IRM testing can continue.

For this project, integrity checks were performed at the beginning and end of each OH test day (two test runs on each day). Each check consisted of a single point injection of Hg^{+2} calibration gas, at 10 $\mu g/m^3$. There were no plans to perform any corrective action and, as it turned out, none was necessary.

2.5 Dynamic Spiking (IRM Section 8.5)

The method requires that a dynamic spiking test be performed before the first run and after the last run of a test series. This test involves the addition of a known quantity of Hg^{+2} to a probe that is sampling flue gas. The procedure requires that a calibration gas be injected at a flow which displaces 10% or less of the flue gas entering the probe, and that this gas increase the instrument response by 40-60% at one target level and 80-100% at the other. Spiking must be performed at each level in triplicate, with the recoveries at each level having a relative standard deviation (RSD) of 5% or less. The target recovery values are in the range of 100±5% for the pre-test spiking, and 100±10% for the post-test spiking.

For this project, the dynamic spiking test was performed on the three systems that were ready for this test before the first OH test day (July 10). The Pre-Test Dynamic Spiking Tests were done immediately after the Hg^{+2} System Calibration Error Tests on each system. Of the three spiking-capable systems, two underwent intermediate spiking between test days, as allowed in the method. Post-test dynamic spiking was performed on all three systems after the last OH test day.

The spiking procedures used in this project (see Appendix A) were patterned after the “Example Spiking Procedure” in section 8.5.3 of the conceptual IRM. During spiking, the HoVaCal device was used to generate the spike gas at precisely measured flow rates. Probe flow measurements were provided by the vendors’ systems, so the spike dilution factor (DF) was calculated from the ratio of these flows. Recovery calculations were performed after each spike injection, and the injections were repeated until there were three recoveries that met the method’s RSD requirement.

3. Results and Discussion

After a week of setup, procedure refinement, and preliminary checks on measurement systems, the IRM implementation began in earnest on 05-July. Appendix B shows a chronological summary of the IRM checks and the sampling test data that were collected. Although the calibration error checks were done for both a 0-10 $\mu g/m^3$ and a 0-20 $\mu g/m^3$ measurement range, the remaining checks were based on the range deemed most appropriate by the source concentration measurements: 0-20 $\mu g/m^3$.

Because implementation of the conceptual IRM was only a small part of a much larger comparative measurement study, the project team did not have complete control over the IRM-candidate measurement systems. As such, many of the adjustments that would normally be done before or during data collection were instead done numerically after the data collection. Put simply, none of the instruments were “calibrated” to the standards that were presented on site. Most of the system vendors, in pursuit of their goal of delivering good data to compare with the OH and other reference methods, performed their own calibrations using their own standards and on their own schedule. The initial goal of the IRM team was to collect enough calibration and measurement data to be able to apply an independent “calibration curve” to each system that would deliver data comparable to what would have resulted had the systems actually been adjusted to match the injected standards. In practice, the IRM team was able to calculate several of these curves for each system, based on the different calibration and integrity checks that were performed during the testing. Ultimately, because of the length of the project's measurements phase (8 days), the integrity check data proved to be the most useful tool for normalizing the data, and applying the "calibration error" adjustments of IRM section 12.3 (which are actually drift adjustments, based on integrity check data) generally improved the quality of the data. These adjustments were applied to the post-test dynamic spiking data (data sheets in Appendix C) and to the source measurement data that were compared to the other reference methods. The pre-test dynamic spiking data, because they were collected immediately after the Hg^{+2} System Calibration Error Test on each system, were adjusted using those results in place of system integrity check data.

Relative Accuracy Test Audit (RATA) calculations, based on all of the different normalizations and the two different emissions levels (from two different coals burned at the source site), are included as Appendix D. Each relative accuracy calculation also includes a bias test, which determines if the measurement system is biased low by a statistically significant amount. The bias factor included in the Appendix D tables is essentially a ratio of the average reference measurement to the CEMS measurement. According to 40 CFR Part 75, when a system fails the bias test, this bias factor is called a "Bias Adjustment Factor" (BAF), and is used to correct all subsequent monitoring data reported by that system. For purposes of this project, the bias factor is just a ratio indicating of how the system compares to the reference method.

3.1 GE Energy / PS Analytical Mercury CEMS

3.1.1 General Description

The GE/PSA system is shown in Figure 1. The probe box at the stack level has an inertial filter probe with dilution and a built in venturi for measuring the flow through the inertial filter loop. A heated 400-foot umbilical transports the diluted sample to the shelter at the base of the stack, where it feeds into a conditioning unit that includes a thermal converter and a chilled scrubber unit. From the conditioning unit, the sample flows through a "stream selector box" and on to the analyzer.

The PSA "Sir Galahad" analyzer uses a "trap and purge" technique, whereby the conditioned sample is passed through a "gold trap" that amalgamates and retains the mercury until the trap is heated to release it into an argon carrier that delivers it to an Atomic Fluorescence (AF) detector. A built-in programmable logic controller (PLC) manages all of the valves and heaters so that the mercury entering the detector does not contain any of the potentially interfering contaminants that may have existed in the original sample. The analyzer used for this project operates two of these trapping systems in series, where the first trap is "charged" from the sample stream, then subsequently "purged" into a carrier stream fed to the next trap, which is then "purged" into the carrier stream that feeds the AF detector. The system used during this project performed one analysis "cycle" every 4 minutes. As installed, the complete system had a response time of 12 minutes.

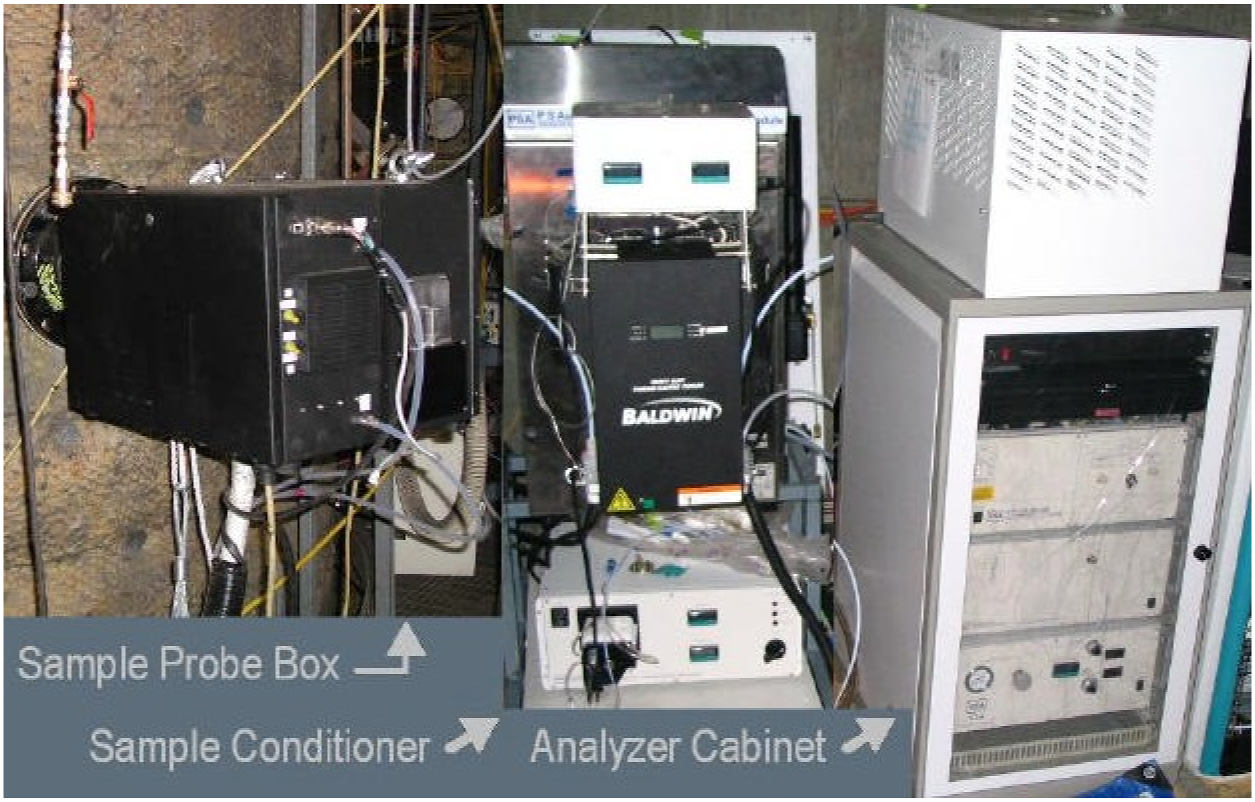


Figure 1. GE/PSA Measurement System

The GE/PSA system is equipped to independently measure the probe dilution ratio using pre- and post-dilution CO_2 measurements. It can also measure the probe flow using CO tracer injection, as a check to the venturi measurement or, in this case, as a substitute for that measurement. The system is highly automated, performing probe blowbacks and various calibrations without user intervention.

All calibration injections to the GE/PSA system were made to the spike port. ARCADIS personnel installed a ~15" PFA tubing jumper between the spike line and the access hole at the rear of the box, thus relying on the box heat (stated by the vendor to be set at 180°C) to maintain the temperature of the delivered calibration gas. Vendor personnel created a special "method" in their software to lower the loop flow for probe-flooding calibrations. ARCADIS personnel were provided sufficient training on site to perform calibration injections without vendor assistance.

3.1.2 Calibration Error Checks

The three-point Hg^{+2} System Calibration Error Test was performed on the morning of 06-July. The HoVaCal device was set to deliver the Hg^{+2} calibration standards at 2% moisture, using the appropriate solutions from Table 2. The three-point Hg^{0} System Calibration Error Test was performed on the afternoon of 09-July. The measurement system did perform some calibrations between these two IRM checks, but these activities were not intended to improve the system's performance on the IRM checks. Rather, many of the vendor's on-site activities were focused on collecting accurate measurement data during the overall project's comparative measurements phase which began on 10-July. Nonetheless, the data were processed according to the original plan of establishing a calibration curve based on the Hg^0 Calibration, and reporting the measured concentrations for Hg^0 and Hg^{+2} based on this curve. Table 3 shows the calibration error results for the data processed in this way.

Table 3. GE/PSA System Calibration Error Test Results

	Injected Gas Concentration µg/m^3 @ 20°C	**System Response µg/m^3 @ 20°C**	**Absolute Difference µg/m^3 @ 20°C**	**Calibration Error % of span**
Elemental	2.50	2.48	0.02	0.10%
	5.00	5.03	0.03	0.15%
	9.98	9.96	0.02	0.10%
	19.94	19.94	0.00	0.00%
Oxidized	2.41	2.40	0.01	0.05%
	4.83	4.94	0.11	0.55%
	9.63	9.24	0.39	1.95%
	19.26	18.74	0.52	2.60%

3.1.3 System Integrity Checks

System integrity checks began on the morning of 10-July, and were conducted twice daily through 17-July. Table 4 shows the results of these checks. This system did have some difficulty meeting the performance specifications for bias and drift, and the vendor conducted several calibrations during the comparative measurements phase of the project. Most of these calibrations (designated by a bold separator line in the table) were done after the post-run integrity checks and before the pre-run checks for the next day. The last one, however, was conducted mid-day on 17-July (i.e., between that day's integrity checks), which casts some doubt on the validity of the drift check for that day (a "passing" drift check following two consecutive days of drifts exceeding the performance specification). In general, it appears that this system needed daily calibrations in order to collect accurate measurement data.

Table 4. GE/PSA System Integrity Check Results

Date	Integrity Check	Injected Gas Concentration	Response	Calibration Error		Upscale Drift	
		(□ g/m^{3})	(□ g/m^{3})	(□ g/m^{3})	(% of span)	(□ g/m^{3})	(% of span)
10-July	Pre-run	9.53	9.29	- 0.24	-1.20%	0.50	2.50%
	Post-run	9.61	8.87	- 0.74	-3.70%		
11-July	Pre-run	9.81	10.52	0.71	3.55%	0.27	1.35%
	Post-run	9.78	10.22	0.44	2.20%		
12-July	Pre-run	9.89	11.05	1.16	5.80%	0.26	1.30%
	Post-run	9.76	11.18	1.42	7.10%		
13-July	Pre-run	10.22	10.69	0.47	2.35%	0.33	1.65%
	Post-run	10.14	10.94	0.80	4.00%		
14-July	Pre-run	10.14	10.08	- 0.06	-0.30%	0.31	1.55%
	Post-run	10.10	9.73	- 0.37	-1.85%		
15-July	Pre-run	10.39	10.84	0.45	2.25%	0.93	4.65%
	Post-run	10.79	10.31	- 0.48	-2.40%		
16-July	Pre-run	9.74	10.48	0.74	3.70%	1.02	5.10%
	Post-run	10.15	9.87	- 0.28	-1.40%		
17-July	Pre-run	9.77	9.84	0.07	0.35%		
	Post-run	10.07	9.91	- 0.16	-0.80%	0.23	1.15%

3.1.4 Dynamic Spiking

This system underwent pre-test dynamic spiking on 06-July (higher- level spiking) and 07-July (lower-level spiking). Post-test spiking was conducted on 19-July at both levels. Table 5 summarizes the results. All of the spiking calculations used a probe flow of 47.45 lpm. This value was established by the vendor based on tracer experiments performed before the pre-test spiking and verified after the post-test spiking.

For the pre-test spiking, the “% increase” targets were missed during the high- level spiking. This is always a possibility when a single spike gas delivery concentration, based on preliminary measurement data, is delivered for all injections. Neither level achieved the required recovery range (100 ± 5%), but were within the less stringent performance standard applied to post-test

Table 5. GE/PSA Dynamic Spiking Test Results

		Q_{probe} (lpm)	Q_{spike} (lpm)	DF	C_{native} (µg/m³)	C_{spike} (µg/m³)	C_{ss} (µg/m³)		% Increase	Difference (µg/m³)	% Spike Recovery	
							Expect	Measure				
Pre-Test Dynamic Spiking	High-level	47.45	4.61	10.3	5.96	41.78	9.44	8.96	50%	-0.48	88%	Avg. = 90.2%
		47.45	4.61	10.3	5.81	41.84	9.31	9.03	55%	-0.28	93%	
		47.45	4.61	10.3	5.98	41.82	9.46	9.02	51%	-0.44	89%	
	Low-level	47.45	4.61	10.3	5.70	32.38	8.29	8.07	42%	-0.22	93%	Avg. = 94.0%
		47.45	4.61	10.3	4.88	32.30	7.54	7.36	51%	-0.18	94%	
		47.45	4.61	10.3	5.91	32.36	8.48	8.33	41%	-0.15	95%	
Post-Test Dynamic Spiking	High-level	47.45	4.83	9.8	26.34	288.52	53.09	51.89	97%	-1.20	96%	Avg. = 96.8%
		47.45	4.85	9.8	26.59	290.62	53.53	52.59	98%	-0.94	97%	
		47.45	4.86	9.8	27.28	293.20	54.41	53.85	97%	-0.56	98%	
	Low-level	47.45	4.81	9.9	28.32	180.56	43.70	43.41	53%	-0.29	98%	Avg. = 97.2%
		47.45	4.82	9.8	29.39	182.36	45.00	44.22	50%	-0.78	96%	
		47.45	4.84	9.8	30.90	216.96	49.89	49.31	60%	-0.58	97%	

spiking (100 ± 10%). The post-test spiking met all performance standards except the requirement to have the spike flow displace =10% of the probe flow (i.e., DF = 10).

3.1.5 Sampling Data Comparisons

Figure 2 shows the GE/PSA results from the project's comparative measurements phase. This system collected data for all 8 days of that phase, and those data have been error-adjusted by each of the three calibration standard injections. The recorded averages represent the data collected by the measurement system based on its own calibration and data processing procedures, and represent this vendor's independent efforts to accurately measure the source concentration. The elemental and oxidized calibration error adjustments used the regression line for the IRM 3-point calibrations which were performed at the beginning of the test. The system integrity adjustments were performed on each day's measurements, based on the integrity checks for that day, using equation 3 from the IRM. The OHM results, as the current accepted Hg reference method, represent the "yardstick" to which all other measurements are compared. The very first OHM measurement, however, was disrupted by soot-blowing at the source, and will be discarded for purposes of determining relative accuracy.

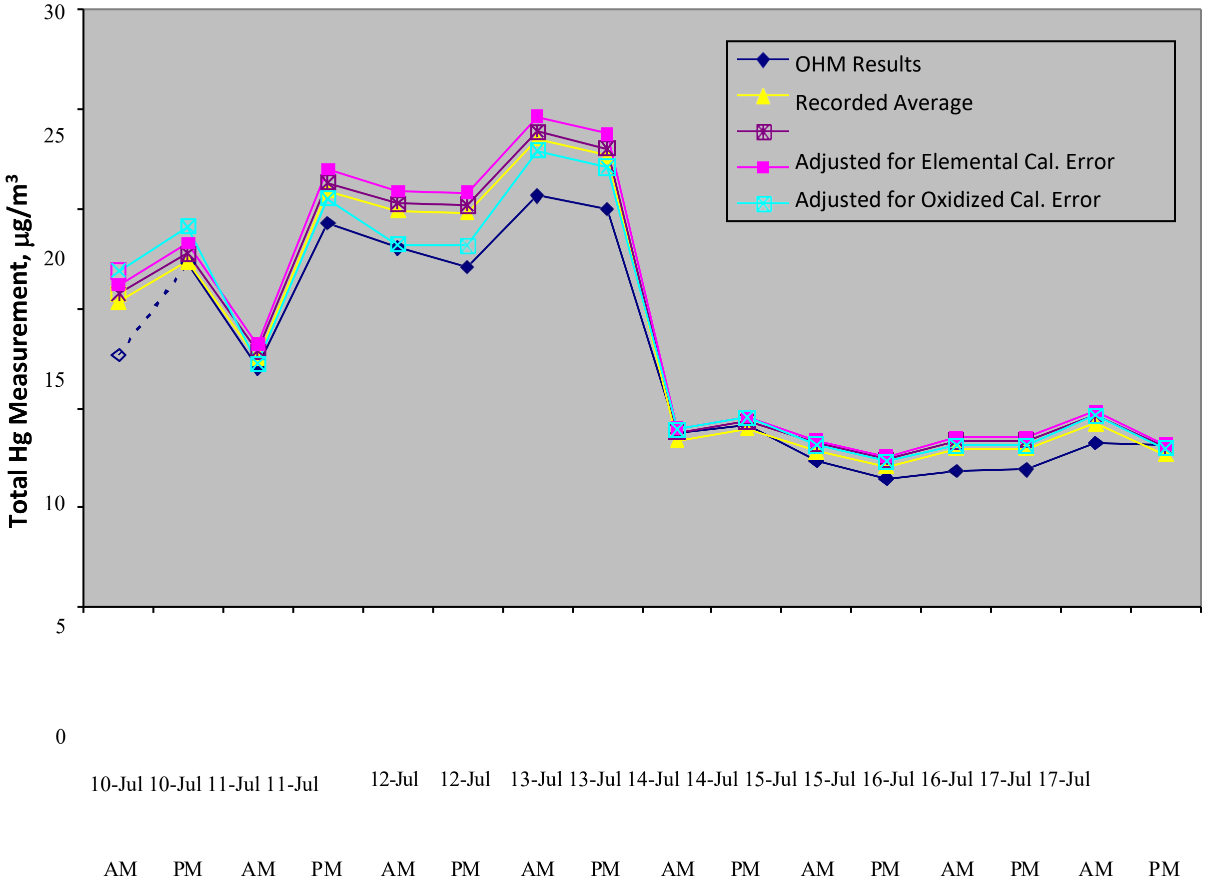


Figure 2. Comparison of GE/PSA Measurements with Ontario-Hydro

For most of the test days, the GE/PSA system had a positive bias relative to the OHM measurements. For the higher measurement levels seen 11-July through 13-July, the IRM adjustments brought the measurements closer together. Errors of lower magnitude, but similar proportion, were observed at the lower measurement levels, and the IRM adjustments made no improvement there. Table 6 summarizes the RATA results based on each trace of Figure 2. In general, the drifted-adjusted measurements gave the best RATA results, the exception being where the "as reported" measurements were closer to the OH measurements while the host site was burning West Virginia coal. The single-best RATA result was when everything was done "by the book" for both the conceptual IRM (including drift corrections) and the RATA calculations (arbitrarily excluding 3 runs).

Table 6. Summary of Various RATA Calculations for GE/PSA Measurement System

	All Valid Runs Included	Allowed 3 Runs Excluded	All WV Coal Runs Included	All Local Coal Runs Included
Number of Runs Included	15	12	8	7
Recorded Averages	13.31%	10.12%	12.28%	15.75%
Elemental Cal. Error Adjusted	16.45%	13.75%	17.26%	17.97%
Oxidized Cal. Error Adjusted	20.41%	17.30%	19.73%	21.99%
System Integrity (Drift) Adjusted	11.32%	9.90%	15.62%	11.71%

3.2 Horiba IRM System

The Horiba system used a straight-extractive probe with a flow rate in the 7.5-10 lpm range (adjustable). Probe flow is measured by a mass flow controller (for the analyzer flow) and a mass flow meter (for the excess flow). Calibration injections were initially made to the spike port, but it became apparent that the probe manufacturer sized the spike line for spike flow levels without consideration for using that same line for probe-flooding calibration injections. Afterward, the calibration line was connected to the “dirty” side of the probe filter housing. This system never produced any consistent results to the oxidized Hg calibration error check, and was eventually taken out of service by the vendor on July 12th after encountering numerous problems. No attempt was made to perform dynamic spiking on this system.

3.3 Ohio Lumex 915 MiniCEM-1x

3.3.1 General Description

The Ohio Lumex system (shown in Figure 3) uses a dilution probe with a flow rate of 6-8 lpm. Probe flow is measured by an inline volumetric flow meter. A 15 foot heated sample line transports the diluted sample to the analyzer case, which was located at the sampling platform level during these tests. The Ohio Lumex analyzer uses atomic absorption (AA) with Zeeman background correction, claiming a measurement range of 0.6 to 1,000 µg/dsm^3. The system had a response time of 7 minutes.

All calibration gases for this system were delivered to vendor’s heated umbilical, which he states is fed to the spike port. Since the probe does not use an inertial filter, probe flooding did not require any adjustment to the system. Only one attempt was made to perform dynamic spiking on this system, during which the vendor concluded that neither of the probe’s flow measurement systems (probe sample flow and spike flow) were accurate. The vendor requested, prior to the first OH test day, that integrity checks only be performed on this system in the evenings, as there was concern that residual mercury from morning integrity checks may bias the Lumex measurements high during the OH tests. On July 11th, the vendor asked us to discontinue all integrity checks until asked to resume by either himself or the probe vendor. A post-test integrity check was performed on July 18th, but the vendor was never able to recover the measurement data file for that injection.

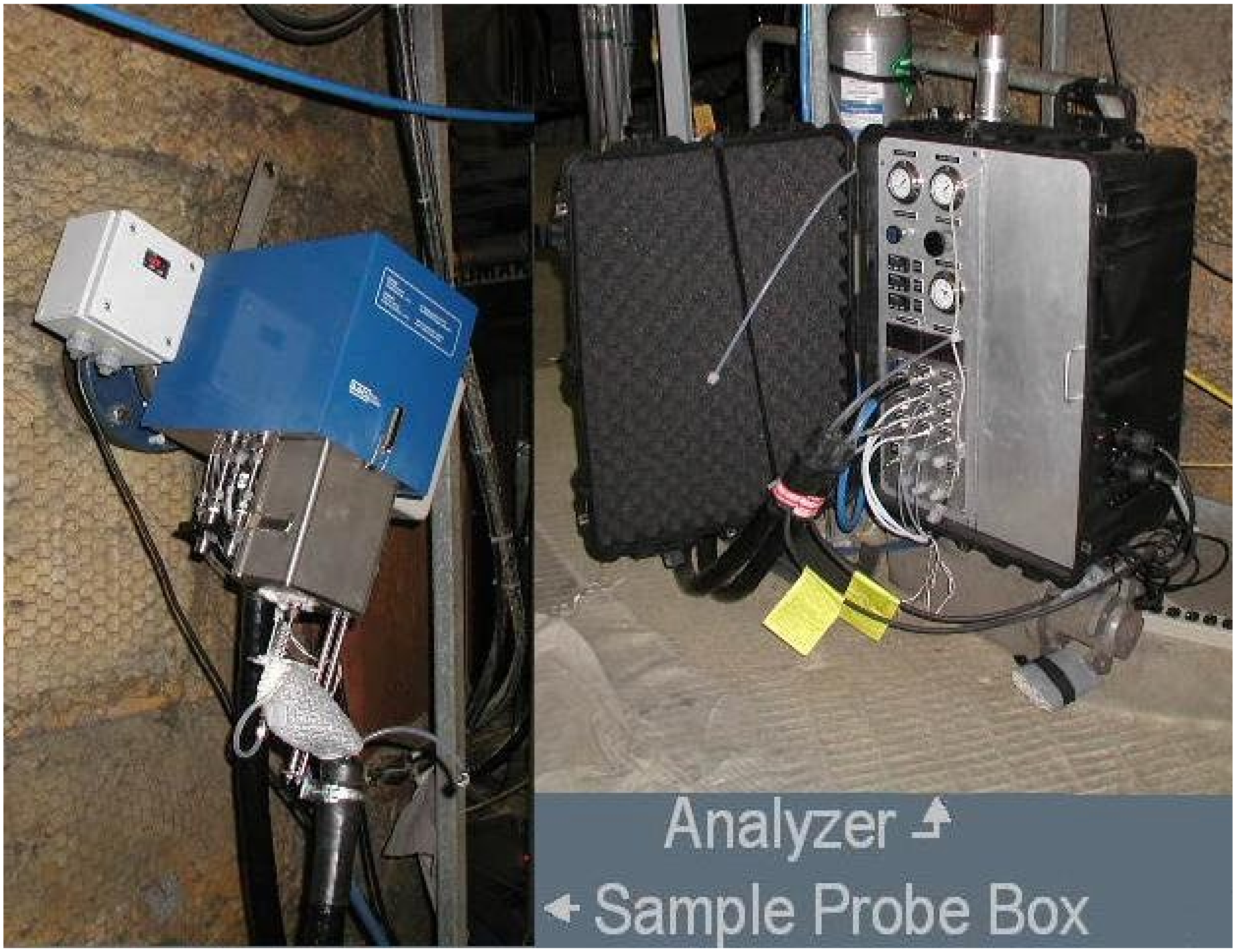


Figure 3. Ohio Lumex Measurement System

3.3.2 Calibration Error Checks

The three-point Hg^{+2} System Calibration Error Test was performed on the afternoon of 09-July. The HoVaCal device was set to deliver the Hg^{+2} calibration standards at 8% moisture, using the appropriate solutions from Table 2. The three-point Hg^0 System Calibration Error Test was performed that same evening (09-July). The measurement system performed its normal “baseline drift” correction routine, as designed into the software, during the measurement of all calibration gas responses. The system performs no automatic calibrations, and the measurement gain is a setting that can be altered directly in the software. The vendor altered this setting on site using the IRM calibration standards as a reference, and the setting was not altered for the remainder of the testing. Nonetheless, for consistency in data manipulation, the data were still processed by establishing a mathematical calibration curve based on the Hg^0 Calibration. Table 7 shows the calibration error results for the data processed in this way.

Table 7. Ohio Lumex System Calibration Error Test Results

	Injected Gas Concentration $\mu g/m^3$ @ 20°C	System Response $\mu g/m^3$ @ 20°C	Absolute Difference $\mu g/m^3$ @ 20°C	Calibration Error % of span
Elemental	2.50	2.52	0.02	0.10%
	5.00	5.12	0.12	0.60%
	9.98	9.78	0.20	1.00%
	19.94	20.01	0.07	0.35%
Oxidized	2.52	2.42	0.10	0.50%
	5.07	5.87	0.80	4.00%
	10.07	10.32	0.25	1.25%
	20.31	20.42	0.11	0.55%

3.3.3 Sampling Data Comparisons

Figure 4 shows the comparative test results from the Ohio Lumex during that phase of the project. This system did not collect comparative data during the last test day because it was being used to

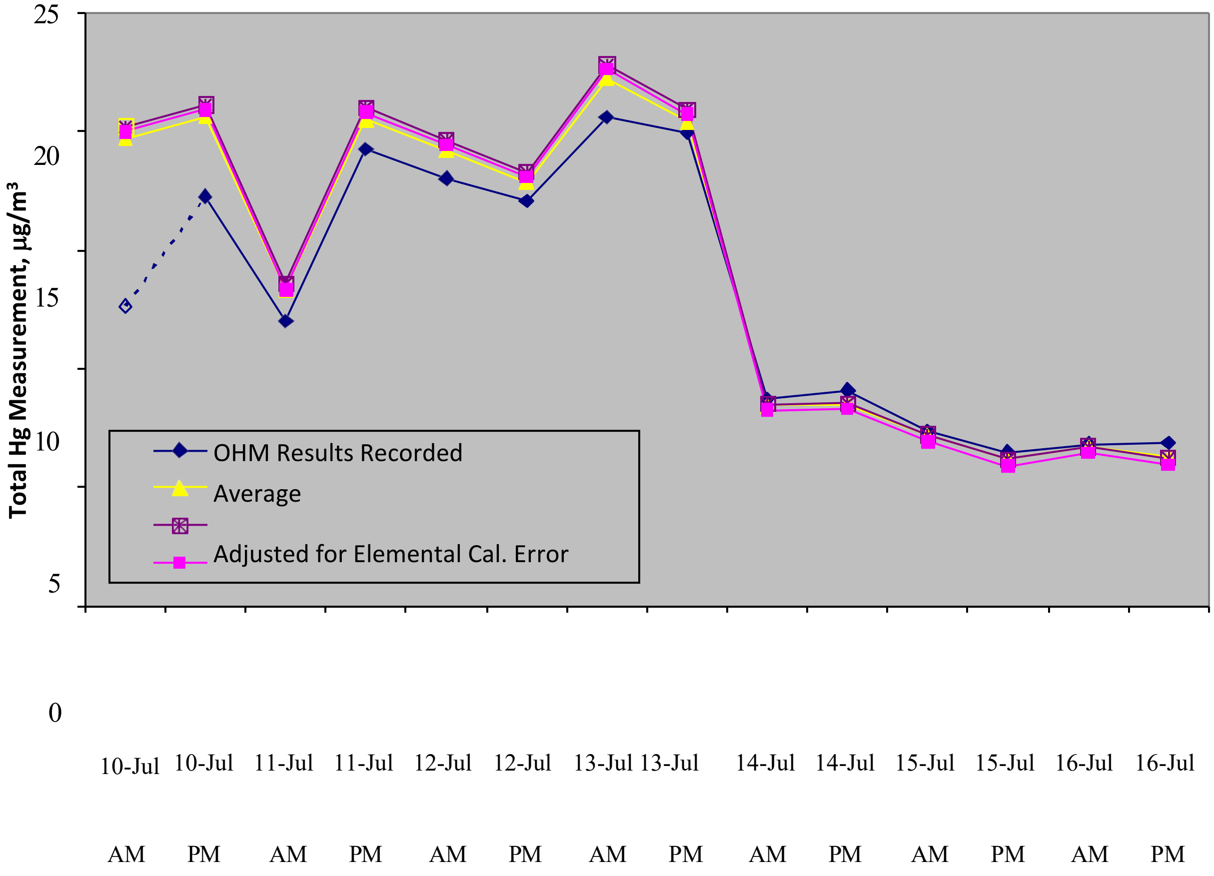


Figure 4. Comparison of Ohio Lumex Measurements with Ontario-Hydro

support stratification testing with a different probe. It appears that, even after the discarded first run, the system exhibited a positive bias relative to the OHM measurements. The vendor attributed this to some probe contamination from that morning's integrity checks (hence the request to discontinue those checks for the duration of the testing). This probe is believed to have been susceptible to such contamination due to the design of its prototype flow measurement apparatus.

After cessation of the integrity checks, the system continued to over-predict the OHM measurements by 5-10% until the source Hg level dropped to less than 10 μg/m^3 on 14-July, after which it under-predicted by 5-10%. Table 8 summarizes the RATA results, which clearly appear more favorable for the calculations that do not include the 10-July afternoon run. This illustrates the advantage of using the run exclusion process to remove gross outliers from the RATA calculation. Regardless, this system met the 20% performance standard, no matter how the data are calculated.

Table 8. Summary of Various RATA Calculations for Ohio Lumex Measurement System

	All Valid Runs Included	Allowed 3 Runs Excluded	All WV Coal Runs Included	All Local Coal Runs Included
Number of Runs Included	13	10	6	7
Recorded Averages	9.92%	5.55%	7.65%	12.83%
Elemental Cal. Error Adjusted	12.79%	8.51%	7.42%	15.55%
Oxidized Cal. Error Adjusted	11.13%	6.68%	11.09%	14.43%

3.4 Tekran Series 3300 Mercury CEM

3.4.1 General Description

The Tekran Series 3300 Hg CEM system (shown in Figure 5) has an inertial filter probe with a factory-calibrated venturi for measuring the flow through the inertial filter loop. The dilution orifice can be configured for ratios of 25:1 to 150:1. A heated 400 foot umbilical transports the diluted sample to the shelter at the base of the stack, where it feeds into a sample conditioner that includes a thermal converter and two chilled scrubber units. The second scrubber unit is part of a converter-bypass path for measuring Hg^0 only. So, by switching between total mercury (Hg^T) and Hg^0 only measurement, the system can provide speciation data. The system is highly automated, performing probe blowbacks, various calibrations, dilution ratio measurements, and elemental spiking with no user intervention required.

The mercury analyzer uses a "trap and purge" technique. It operates two trapping systems in parallel (one trapping while the other is being purged and analyzed) so that the stream from the sample conditioner is always being sampled onto one or the other of the traps (i.e., no continuity gaps in sample analysis). A full analyzer "cycle" takes 5 minutes to complete, but the dual-trap system delivers two analyses (one every 2.5 minutes) during that time. The installed system had a measured response time of one full cycle, or 5 minutes.

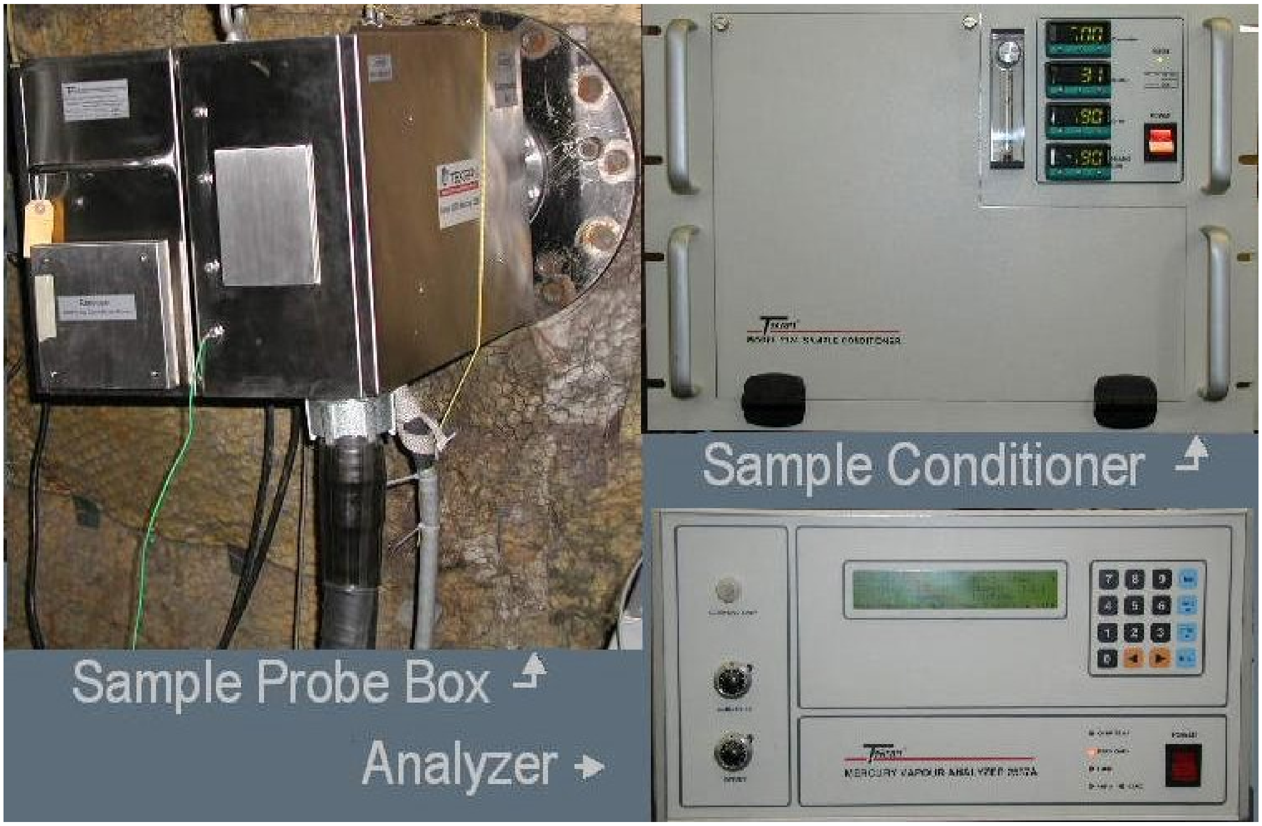


Figure 5. Tekran Series 3300 Measurement System

All calibration injections to the Tekran system were made at the spike port. The probe box includes a heated bulkhead that feeds directly to the spike line. ARCADIS personnel created, within the Tekran software, a sequence that lowered the loop flow for injection of calibration gases under “probe flooding” conditions. Another sequence, for dynamic spiking, makes no changes to the system operation other than to shut off speciation. Both spiking and probe-flooding calibrations were done in Hg^T-only mode. ARCADIS personnel were sufficiently familiar with the Tekran system to perform calibration injections and spiking without vendor assistance.

3.4.2 Calibration Error Checks

The three-point Hg^{+2} System Calibration Error Test was performed on the morning of 05-July. The HoVaCal device was set to deliver the Hg^{+2} calibration standards at 2% moisture, using the appropriate solutions from Table 2. The three-point Hg^0 System Calibration Error Test was performed on the morning of 09-July. The measurement system did perform an automated dilution ratio determination sequence between these two IRM checks, and there was a ~3% decrease in that parameter, as used by the vendor's software to calculate the measured stack concentration. This change was too subtle to make a noticeable change in the measurements, and was not even noticed until the data were being processed, so there was no chance to perform any repeat calibrations. If the parameter change were compensated out of the IRM data, it would increase the oxidized calibration error from the values shown in Table 9, but not enough to fail the ±5% performance specification. Regardless, there is no way to know if there was a real change in the dilution ratio related to some of the other adjustments that the vendor's onsite support team were performing. So, to be consistent, no adjustment was made to the IRM data to account for the dilution ratio change, and the data were processed using a calibration curve based on the Hg^0 calibration responses as recorded (just like the other systems).

Table 9. Tekran System Calibration Error Test Results

	Injected Gas Concentration **µg/m^3 @ 20°C**	**System Response** **µg/m^3 @ 20°C**	**Absolute Difference** **µg/m^3 @ 20°C**	**Calibration Error** **% of span**
Elemental	2.50	2.51	0.01	0.05%
	5.00	5.04	0.04	0.20%
	9.98	9.91	0.07	0.35%
	19.94	19.97	0.03	0.15%
Oxidized	2.47	2.12	0.35	1.75%
	5.08	4.95	0.13	0.65%
	9.94	9.23	0.71	3.55%
	19.88	19.53	0.35	1.75%

3.4.3 System Integrity Checks

System integrity checks began on the morning of 10-July, and were conducted twice daily through 17-July. Table 10 shows the results of these checks. No calibration adjustments were made to this measurement system for the duration of the comparative measurements phase of the project. The system had no difficulty meeting the performance specifications for bias, and only exceeded the drift specification once (on the last run, when no corrective action is necessary).

Table 10. Tekran System Integrity Check Results

Date	Integrity Check	Injected Gas Concentration	Response	Calibration Error		Upscale Drift	
		(□g/m^3)	(□g/m^3)	(□g/m^3)	(% of span)	(□g/m^3)	(% of span)
10-July	Pre-run	9.75	9.61	- 0.14	-0.70%	0.10	0.50%
	Post-run	9.72	9.48	- 0.24	-1.20%		
11-July	Pre-run	9.86	9.65	- 0.21	-1.05%	0.19	0.95%
	Post-run	9.78	9.38	- 0.40	-2.00%		
12-July	Pre-run	9.89	9.32	- 0.57	-2.85%	0.08	0.40%
	Post-run	9.77	9.28	- 0.49	-2.45%		
13-July	Pre-run	9.83	9.43	- 0.40	-2.00%	0.13	0.65%
	Post-run	9.82	9.29	- 0.53	-2.65%		
14-July	Pre-run	9.93	9.73	- 0.20	-1.00%	0.34	1.70%
	Post-run	9.93	9.39	- 0.54	-2.70%		
15-July	Pre-run	10.03	9.52	- 0.51	-2.55%	0.02	0.10%
	Post-run	9.92	9.43	- 0.49	-2.45%		
16-July	Pre-run	10.13	9.90	- 0.23	-1.15%	0.30	1.50%
	Post-run	9.93	9.40	- 0.53	-2.65%		
17-July	Pre-run	10.17	10.23	0.06	0.30%	0.66	3.30%
	Post-run	10.12	9.52	- 0.60	-3.00%		

3.4.4 Dynamic Spiking

This system underwent pre-test dynamic spiking on 06-July, and post-test spiking on 18-July. Also in order to explore another optional IRM component, the system underwent intermediate dynamic spiking on 11-July (higher-level spiking) and 12-July (lower- level spiking). Table 11 summarizes the results. The “% increase” targets were missed quite a bit during the spiking of this system, as most of the onsite calculations were based on data collected directly from the measurement system screen (no averaging, drift correctio n, etc.) . The onsite processing was, however, precise enough to assess the RSD of the accepted measurements, which were well within the performance specifications. The low-level pre-test spikes did not achieve the required recovery range (100 ± 5%), but those spikes and all subsequent spikes were within the less stringent performance standard applied to post-test spiking (100 ± 10%).

Table 11. Tekran Dynamic Spiking Test Results

		Q_{probe} (lpm)	Q_{spike} (lpm)	DF	C_{native} (µg/m^3)	C_{spike} (µg/m^3)	C_{ss} (µg/m^3)		% Increase	Difference (µg/m^3)	% Spike Recovery	
							Expect	Measure				
Pre-Test Dynamic Spiking	High-level	48.27	4.72	10.2	4.50	36.3	7.22	7.37	82%	0.15	93%	Avg. = 95.5%
		48.38	4.73	10.2	5.74	46.1	9.19	9.51	84%	0.32	96%	
		48.23	4.69	10.3	5.87	44.1	9.07	9.46	78%	0.39	97%	
	Low-level	48.40	4.72	10.3	7.74	39.2	10.79	10.53	36%	-0.26	93%	Avg. = 93.7%
		48.31	4.72	10.2	7.38	39.1	10.49	10.22	38%	-0.27	93%	
		48.27	4.72	10.2	5.78	36.5	8.79	8.62	49%	-0.17	95%	
Intermediate Dynamic Spiking	High-level	48.21	4.63	10.4	20.75	178.2	35.89	36.82	77%	0.93	105%	Avg. = 107.3%
		48.17	4.63	10.4	20.81	177.1	35.84	37.43	80%	1.59	109%	
		48.31	4.62	10.5	21.15	176.3	35.93	37.19	76%	1.26	108%	
	Low-level	48.43	4.63	10.5	20.23	109.5	28.73	28.61	41%	-0.12	99%	Avg. = 99.3%
		48.32	4.63	10.4	20.70	108.2	29.11	28.86	39%	-0.25	98%	
		48.23	4.63	10.4	20.76	109.7	29.31	29.47	42%	0.16	101%	
Post-Test Dynamic Spiking	High-level	48.29	4.66	10.4	7.62	61.1	12.76	12.97	70%	0.21	104%	Avg. = 103.3%
		48.31	4.67	10.3	8.03	68.7	13.92	14.09	75%	0.17	103%	
		48.42	4.67	10.4	8.39	68.8	14.20	14.48	73%	0.28	104%	
	Low-level	48.35	4.66	10.4	9.17	46.1	12.72	13.05	42%	0.33	107%	Avg. = 106.8%
		48.23	4.66	10.3	9.53	46.2	13.09	13.24	39%	0.15	103%	
		48.37	4.66	10.4	10.13	46.3	13.61	14.04	39%	0.43	110%	

3.4.5 Sampling Data Comparisons

Figure 6 shows the Tekran results from the project's comparative measurements phase. This system collected data for all 8 days of that phase, and those data have been error-adjusted by each of the three calibration standard injections. Of the four systems that completed the testing, this is the only one to report data that consistently under-predicts the OHM measurements. Corrected for drift, the system over-predicts, which is consistent with the dynamic spiking recoveries and with the other measurement systems.

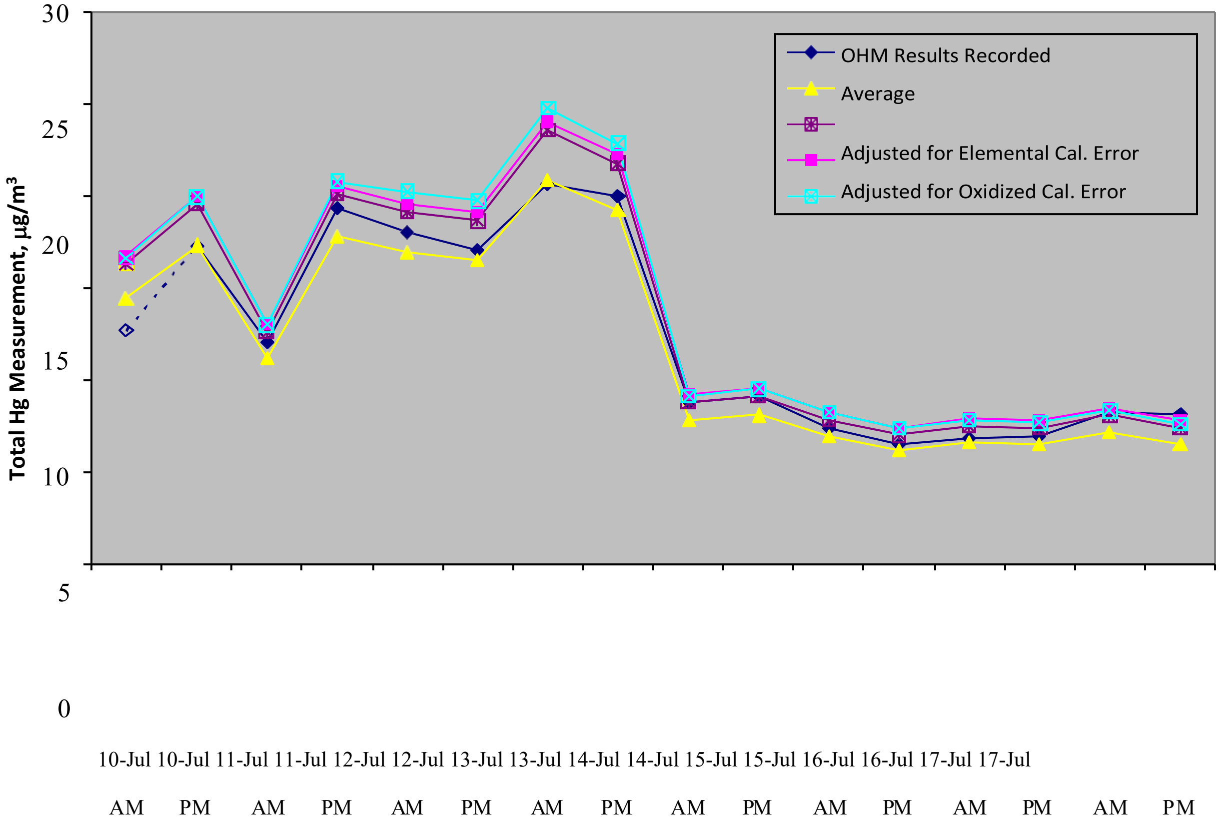


Figure 6. Comparison of Tekran Measurements with Ontario-Hydro

Table 12 summarizes the RATA results based on each trace of Figure 6. This system performed very well on the RATA, even without drift adjustment. In general, the drifted-adjusted measurements gave better RATA results while the host site was burning West Virginia coal, and the unadjusted measurements were closer to the OHM measurements while the local coal was burning. Regardless, all combinations of measurement adjustment and source coal yielded passing RATA results.

Table 12. Summary of Various RATA Calculations for Tekran Measurement System

	All Valid Runs Included	Allowed 3 Runs Excluded	All WV Coal Runs Included	All Local Coal Runs Included
Number of Runs Included	15	12	8	7
Recorded Averages	8.16%	6.49%	15.33%	6.85%
Elemental Cal. Error Adjusted	10.95%	7.74%	7.06%	13.25%
Oxidized Cal. Error Adjusted	14.37%	11.56%	11.93%	15.81%
System Integrity (Drift) Adjusted	16.76%	13.82%	11.63%	18.95%

3.5 Thermo Electron Mercury Freedom^{TM} System

3.5.1 General Description

Shown in Figure 7, the Thermo system has an inertial filter probe with dilution (100:1). Its Hg^{+2} to Hg^0 converter is also at the probe location, with a 400 foot heated umbilical transporting the sample down to a shelter at the base of the stack. The shelter contains the probe controller, analyzer, Hg^0 calibration gas generator, and a zero air system that delivers Hg-free air for the probe diluter and the calibrator. The analyzer uses continuous atomic fluorescence (AF) detection, and claims a detection limit of 1 ng/m^3. The system performed automatic probe blowbacks every 24 hours during these tests.

Figure 7. Thermo Electron "Mercury Freedom" System

All calibration gas injections to the Thermo system were made to the spike port. The probe box included an internal heated umbilical leading from the spike line at the probe end of the box to a connection point at the back of the box near a small access panel. The "low flow" mode (necessary for probe-flooding calibrations) was activated by navigating the system menus and lowering the pressure setting to the loop eductor. Vendor representatives provided both "high flow" and "low flow" values for the eductor pressure, and instructions for switching back and forth were incorporated into the detailed written test procedures that were used on-site (see Appendix A).

The probe flow was measured by a venturi which was calibrated on site, by vendor personnel, using a mass flow controller as a reference. The resulting calibration curve and equation were provided by the vendor for use during dynamic spiking. The venturi differential pressure, which was the dependent ("Y") variable in the calibration curve, is recorded continuously in the system data file.

3.5.2 Calibration Error Checks

The three-point Hg^{+2} System Calibration Error Test was performed on the morning of 05-July. The HoVaCal device was set to deliver the Hg^{+2} calibration standards at 2% moisture, using the appropriate solutions from Table 2. The vendor did make some adjustments to the system after this test was done, but (just as with the other systems) no attempt was made to repeat this test or otherwise quantify the impact of whatever changes were made.

A three-point Hg^0 System Calibration Error Test was attempted on 08-July, but the responses were extremely low and slow to stabilize. The other symptom, a large spike after the gas flow is stopped, is consistent with the Hg getting trapped in the probe. Nonetheless, the responses were recorded, and are shown in Table 13. Because of these unreasonable results, the calibration curve for this system was not calculated from the Hg^0 calibration results, as were the curves for all of the other systems. Instead, the curve was based on the Hg^{+2} calibration results, so the errors in the table are simply a measure of the linearity of the system. The system response time, also based on the Hg^{+2} injections, was determined to be 15 minutes.

Table 13. Thermo System Calibration Error Test Results

	Injected Gas Concentration µg/m³ @ 20°C	System Response µg/m³ @ 20°C	Absolute Difference µg/m³ @ 20°C	Calibration Error % of span
Elemental	2.50	2.41	0.09	0.45%
	5.00	2.87	2.13	10.65%
	9.99	3.67	6.32	31.60%
	19.94	6.48	13.46	67.30%
Oxidized	2.36	2.39	0.03	0.15%
	4.72	4.80	0.08	0.40%
	9.35	9.20	0.15	0.75%
	18.95	19.00	0.05	0.25%

3.5.3 System Integrity Checks

System integrity checks began on the morning of 10-July, and were conducted twice daily through 17-July. Table 14 shows the results of these checks. The system drifted downward during the comparative measurements phase of the project, and was failing the IRM bias checks by the third day, Nonetheless, no calibration adjustments were made to this measurement system, by either the vendor or the IRM implementation team, for the duration of the comparative measurements phase of the project.

Table 14. Thermo System Integrity Check Results

Date	Integrity Check	Injected Gas Concentration	Response	Calibration Error		Upscale Drift	
		(□g/m^3)	(□g/m^3)	(□g/m^3)	(% of span)	(□g/m^3)	(% of span)
10-July	Pre-run	9.58	9.02	- 0.56	-2.80%	0.16	0.80%
	Post-run	9.48	9.08	- 0.40	-2.00%		
11-July	Pre-run	9.87	9.09	- 0.78	-3.90%	0.42	2.10%
	Post-run	9.51	9.15	- 0.36	-1.80%		
12-July	Pre-run	10.05	9.48	- 0.57	-2.85%	0.70	3.50%
	Post-run	10.21	8.94	- 1.27	-6.35%		
13-July	Pre-run	9.96	9.05	- 0.91	-4.55%	0.17	0.85%
	Post-run	10.07	8.99	- 1.08	-5.40%		
14-July	Pre-run	10.49	8.89	- 1.60	-8.00%	0.05	0.25%
	Post-run	10.62	8.97	- 1.65	-8.25%		
15-July	Pre-run	10.58	9.17	- 1.41	-7.05%	0.13	0.65%
	Post-run	10.54	9.26	- 1.28	-6.40%		
16-July	Pre-run	10.44	9.60	- 0.84	-4.20%	0.58	2.90%
	Post-run	10.13	8.71	- 1.42	-7.10%		
17-July	Pre-run	9.98	8.64	- 1.34	-6.70%	0.10	0.50%
	Post-run	10.08	8.84	- 1.24	-6.20%		

3.5.4 Dynamic Spiking

This system underwent pre-test dynamic spiking on the afternoon of 05-July, and post-test spiking on the morning of 18-July. The system also underwent intermediate dynamic spiking on 13-July (higher- level spiking) and 14-July (lower-level spiking). Table 15 summarizes the results. The "% increase" targets were missed quite a bit during the spiking of this system, often when the recovery was also low. Low spike recovery was a recurring issue with this system, with no clear pattern for when it occurred. It is possible that the sample probe flow measurement was not reliable enough for use in the recovery calculations. The method used to calibrate the probe flow measurement – feeding air through a mass flow controller to the probe at room temperature – relied on some unverified assumptions that could not be fully investigated onsite.

Table 15. Thermo Dynamic Spiking Test Results

		Q_{probe} (lpm)	Q_{spike} (lpm)	DF	C_{native} ($\mu g/m^3$)	C_{spike} ($\mu g/m^3$)	C_{ss} ($\mu g/m^3$) Expect	Measure	% Increase	Difference ($\mu g/m^3$)	% Spike Recovery	
Pre-Test Dynamic Spiking	High-level	24.40	2.25	10.8	8.75	99.17	17.12	16.28	86%	-0.84	91%	Avg. = 90.5%
		24.49	2.25	10.9	8.45	98.95	16.75	15.87	88%	-0.88	90%	
		24.63	2.25	10.9	8.16	97.89	16.39	15.46	89%	-0.93	90%	
	Low-level	24.43	2.24	10.9	6.79	52.36	10.97	10.47	54%	-0.50	90%	Avg. = 97.2%
		24.49	2.24	10.9	6.66	52.35	10.85	10.88	63%	0.03	101%	
		24.60	2.24	11.0	6.04	52.11	10.23	10.30	71%	0.07	102%	
Intermediate DynamicSpiking	High-level	24.49	2.57	9.5	14.60	157.76	29.67	26.30	80%	-3.37	80%	Avg. = 80.4%
		24.55	2.57	9.6	12.12	146.20	26.09	23.06	90%	-3.03	80%	
		24.51	2.58	9.5	11.23	112.28	21.87	19.69	75%	-2.18	82%	
	Low-level	24.50	2.46	10.0	8.58	51.34	12.86	12.65	47%	-0.21	96%	Avg. = 97.4%
		24.67	2.47	10.0	8.61	52.27	12.98	12.90	50%	-0.08	99%	
		24.64	2.46	10.0	8.48	51.73	12.81	12.69	50%	-0.12	98%	
Post-Test Dynamic Spiking	High-level	24.45	2.47	9.9	5.71	62.00	11.40	10.43	83%	-0.97	85%	Avg. = 84.9%
		24.47	2.47	9.9	5.90	57.50	11.11	10.26	74%	-0.85	85%	
		24.49	2.48	9.9	6.32	57.57	11.50	10.62	68%	-0.88	85%	
	Low-level	24.47	2.44	10.0	7.05	42.07	10.55	10.11	43%	-0.44	89%	Avg. = 89.3%
		24.55	2.45	10.0	7.12	42.17	10.63	10.20	43%	-0.43	90%	
		24.49	2.47	9.9	6.95	42.50	10.54	10.03	44%	-0.51	88%	

3.5.5 Sampling Data Comparisons

Figure 8 shows the Thermo results from the project's comparative measurements phase. This system collected data for all 8 days of that phase, and those data have been error-adjusted for oxidized calibration error and system integrity (drift). All but the first and last runs were within ±10% unadjusted, and the drift-adjusted measurements were within ±5% for all but the last two runs.

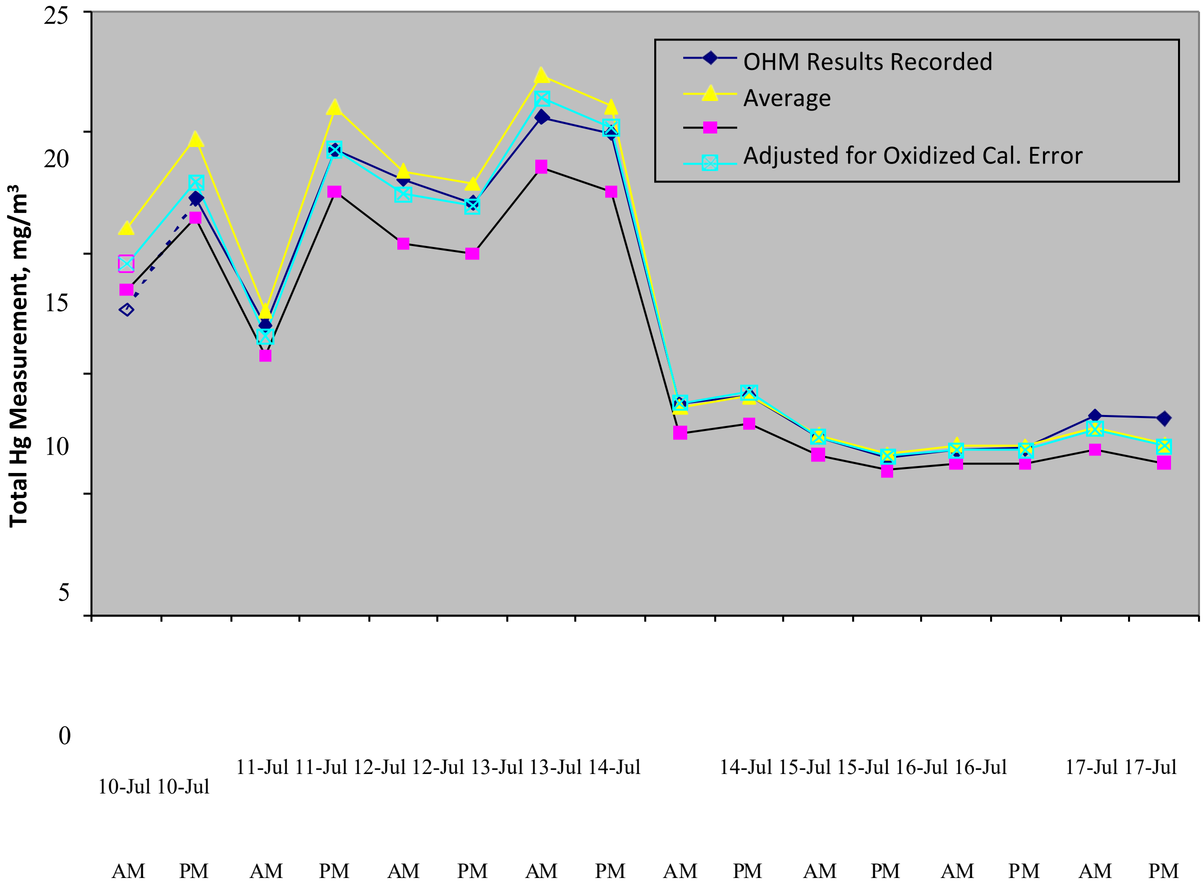


Figure 8. Comparison of Thermo Measurements with Ontario-Hydro

Table 16 summarizes the RATA results based on each trace of Figure 8. This system also performed very well on the RATA unadjusted, and the drift adjustment made substantial improvements in all but the "WV Coal" subset.

Table 16. Summary of Various RATA Calculations for Thermo Measurement System

	All Valid Runs Included	Allowed 3 Runs Excluded	All WV Coal Runs Included	All Local Coal Runs Included
Number of Runs Included	15	12	8	7
Recorded Averages	8.37%	4.78%	6.66%	11.14%
Oxidized Cal. Error Adjusted	14.49%	13.24%	18.21%	13.91%
System Integrity (Drift) Adjusted	2.67%	1.65%	7.20%	3.19%

4. Summary and Observations

The objective of this project was to implement the conceptual IRM at a field site in order to assess whether the procedures are feasible and the performance specifications are achievable. Both of these assessments were made based on the equipment which is currently available, even though little of the current technology was developed specifically for performing IRM measurements. Sampling probe designs, in particular, are currently more focused on continuous monitoring than on the requirements of an IRM system, which is why neither the sampling traverse nor the stratification test provisions of the conceptual IRM were implemented. All of the other field procedures were performed, and the results are documented in this report.

4.1 Feasibility

The conceptual IRM procedures were found to be feasible as written. Table 17 shows approximately how long each of the procedures took with each of the measurement systems. In general, all of the procedures took more time on the “trap and purge” systems (GE/PSA and Tekran) than the others, because of the additional time to record enough data points to assure a stable response. Because of the goals of this project, the IRM team often allowed conditions to stabilize longer than would be done by a commercial testing team during a shorter-term field test. Also, the choice of 2% moisture delivery of Hg^{+2} calibration gases (see discussion in section 4.3.3 of this report) added about an hour to the 3-point Hg^{+2} System Calibration Error tests for all but the Ohio Lumex (which received Hg^{+2} calibration gases at 8% moisture). With a little more refinement to the equipment and procedures, each of the System Calibration Error tests (Hg^0 and Hg^{+2}) should take about 2-3 hours, depending on the measurement system and the length of its sample line. System integrity checks generally took about an hour for each of the three systems that included those checks (which were the same three systems that sample through 400-foot sample lines).

Table 17. Time Summary of Conceptual IRM Procedures as Performed On-Site

	GE/PSA	Ohio Lumex	Tekran	Thermo
Hg^0 System Calibration Error Test	3 hours	2 hours	2 ½ hours	n/a
Hg^{+2} System Calibration Error Test	4 hours	2 hours	3 ½ hours	2 hours
Pre-Test Dynamic Spiking	16 hours [1]	n/a	6 hours	4 hours
System Integrity Checks (each)	1 hour	n/a	1 hour	1 hour
Intermediate Dynamic Spik ing	n/a	n/a	4 hours [1]	4 ½ hours [1]
Post-Test Dynamic Spiking	6.5 hours	n/a	5 ½ hours	4 hours

[1] This procedure was performed piecemeal over two consecutive days.

The time required to perform dynamic spiking was highly variable, mainly related to the stability of the stack concentration. One of the key observations of this test program, however, was that having the source hold its load constant was the single most important contributor to successfully performing the dynamic spiking procedures. Also, as with the 3-point calibration error tests, the continuous measurement system (Thermo) consistently required less time for spiking than the “trap and purge” systems did. For this system, dynamic spiking at two levels consistently required 4-5 hours to complete.

4.2 Performance Specification Achievability

The tables in Section 3 show that all of the IRM performance specifications were achievable, some more consistently than others. The Hg^0 System Calibration Error specification (±2%) was achieved by all but the Thermo system. The Hg^{+2} System Calibration Error specification (±5%) was achieved by all of the systems, but the Thermo's results are indicative only of the linearity of the system (as opposed to the Hg^{+2} response of a system calibrated on Hg^0). The System Integrity Check specification was achieved consistently with the Tekran, and on all but one day with the GE/PSA system. The Thermo system experienced some drift during the testing, and failed System Integrity for most of the latter half of the sampling phase. Most of this drift occurred during sampling on the third test day (12-July). Clearly, if the IRM team had been in control of this system, it would have been recalibrated to counteract this drift and would likely have passed the System Integrity specification for the remaining test days (for a total of 12 valid test runs, out of the 14 that were attempted).

The dynamic spiking results were mixed. Each of the three systems that underwent spiking was able to achieve the 100±5% pre-test spike recovery performance specification, but none of them achieved it at both levels during the pre-test spiking. The pre-test spiking did, however, meet the less stringent 100±10% recovery specification with all three systems, indicating that this may be a more reasonable performance specification for the IRM. The range of recoveries achieved during spiking is very similar to the range of bias factors calculated from the OHM comparisons (see RATA sheets in Appendix D), indicating that the dynamic spiking recoveries are a reliable indicator of IRM measurement accuracy. Another important observation is that there did not appear to be any systematic bias between the recoveries for the high-level and low-level spiking. This opens up the possibility that the IRM requirements might reasonably be reduced to single-level spiking (creating a time savings of 2-3 hours per test) without jeopardizing data quality.

4.3 Lessons Learned

4.3.1 Hg^0 Calibration Gas Generation

The concentration delivered by the 3310 is calculated based on three measurements: source temperature, source flow, and diluent flow. Of those three, the source temperature has the most precision over the full range of measurements. The flow measurements, on the other hand, are only calibrated at a dozen or so discreet settings. For intermediate settings, the Tekran software uses linear interpolation between those established calibration points. Depending on the nonlinearity of the flow meter, this could introduce a small error into the calculations. In all sequences that are provided by Tekran with new 3300 systems, all mass flow settings are made to correspond to the discreet calibration points of the flow devices, thereby minimizing the potential for error in those flow measurements.

As for the temperature measurements, RTDs have well-characterized response curves which preclude the need to perform linear interpolation between discreet calibration points. As such, the source temperature can be set to any value within the range of what the system can maintain. So, if a specific concentration is required, it may be better to use the flow settings as a “coarse adjustment” and the source temperature as a “fine adjustment” parameter. That said, it should be noted that temperature changes require some time for the system to stabilize, and temperatures very far from ambient (say 5°C in a 25°C room), can take a half- hour or more to attain. In general, when creating sequences to inject several calibration concentrations in sequence, it is best to choose one temperature for all the levels, and vary the flow (again, among the discreet calibration points) to create different concentrations.

4.3.2 Hg^{+2} Calibration Gas Generation

Generating Hg^{+2} calibration gas is a more intricate and time-consuming process than generating Hg^0 calibration gas. The process has been made somewhat easier by the new HoVaCal units that automatically calculate and adjust flow settings, and can save injection configurations for later retrieval. Nonetheless, there are some aspects of the HoVaCal operating principle that better software simply can’t improve. Most notable of these is the liquid delivery. For even the most compact physical layout, it takes a few feet of tubing to get the solution from the reservoir to the pump and then to the evaporator. Depending on the moisture content of the calibration gas, the solution could move through this tubing as slowly as a few inches per minute. At the 2% moisture condition used during most of the probe-flooding tests at Armstrong, it routinely took 5-10 minutes after a change in feed solution for that change to work its way through the system to the point of injection.

ARCADIS personnel experimented with speeding up the peristaltic pump to quickly purge the system after a solution replacement, but this resulted in a high-concentration pulse being fed to the system being calibrated. Some systems tolerate such pulses better than others, but it is still bad practice to dispose of unwanted calibration material through a measurement system. Avoiding this condition would involve diverting either the calibration gas feed or the liquid feed during the purge. Diverting the calibration gas feed is probably not feasible as part of a time-saving tactic, since all of the connections are wrapped up in some type of insulation. Disconnecting the liquid feed from the evaporator was considered, but PEEK fittings are not particularly well suited to providing leak-free connections after repeated disassembly. An alternative (which has yet to be explored) is to install a low-volume 3-way valve at the inlet to the evaporator. Turning the valve to divert the liquid feed into a waste container, the pump can then be sped up as much as necessary to quickly purge the system.

4.3.3 Hg^{+2} Calibration Gas Moisture Levels

Along with calibration gas concentration, moisture level is one of the two things that determine what solution concentrations are required for Hg^{+2} calibration gas injection. As a rule, a higher moisture level requires a lower solution concentration, and a lower moisture level requires a higher solution concentration to deliver the same calibration gas concentration. No “rule” exists, however, for what is the best moisture level to inject. Absent any injection or measurement issues, the “ideal” injection moisture level would probably be something similar to the stack level. In reality, however, moisture is a trade-off: the lower the level, the slower the solutions move through the HoVaCal system; the higher the level, the greater the impact on the calibration gas density. Gas density impacts the flow of sample (and calibration gas) through a critical orifice, which, in turn, affects the dilution ratio of a sampling probe.

Aside from temperature and pressure effects, gas density is a function of molecular weight (MW). The MW of coal flue gas is slightly more than the MW of air, where the MW of a HoVaCal-generated calibration gas will always be less than the MW of air, as long as air is used as the carrier. So, the only way to deliver calibration gas at moisture levels near stack levels is to use something other than pure air as the carrier. A mixture of, say, Argon or CO_2 in air can be made that will “balance” the effect of moisture on the final Hg^{+2} calibration gas MW. The newer HoVaCal devices, namely the 211 and 311 models, even have built in gas blending capabilities that can customize the carrier to achieve the optimum MW to best match the stack gas.

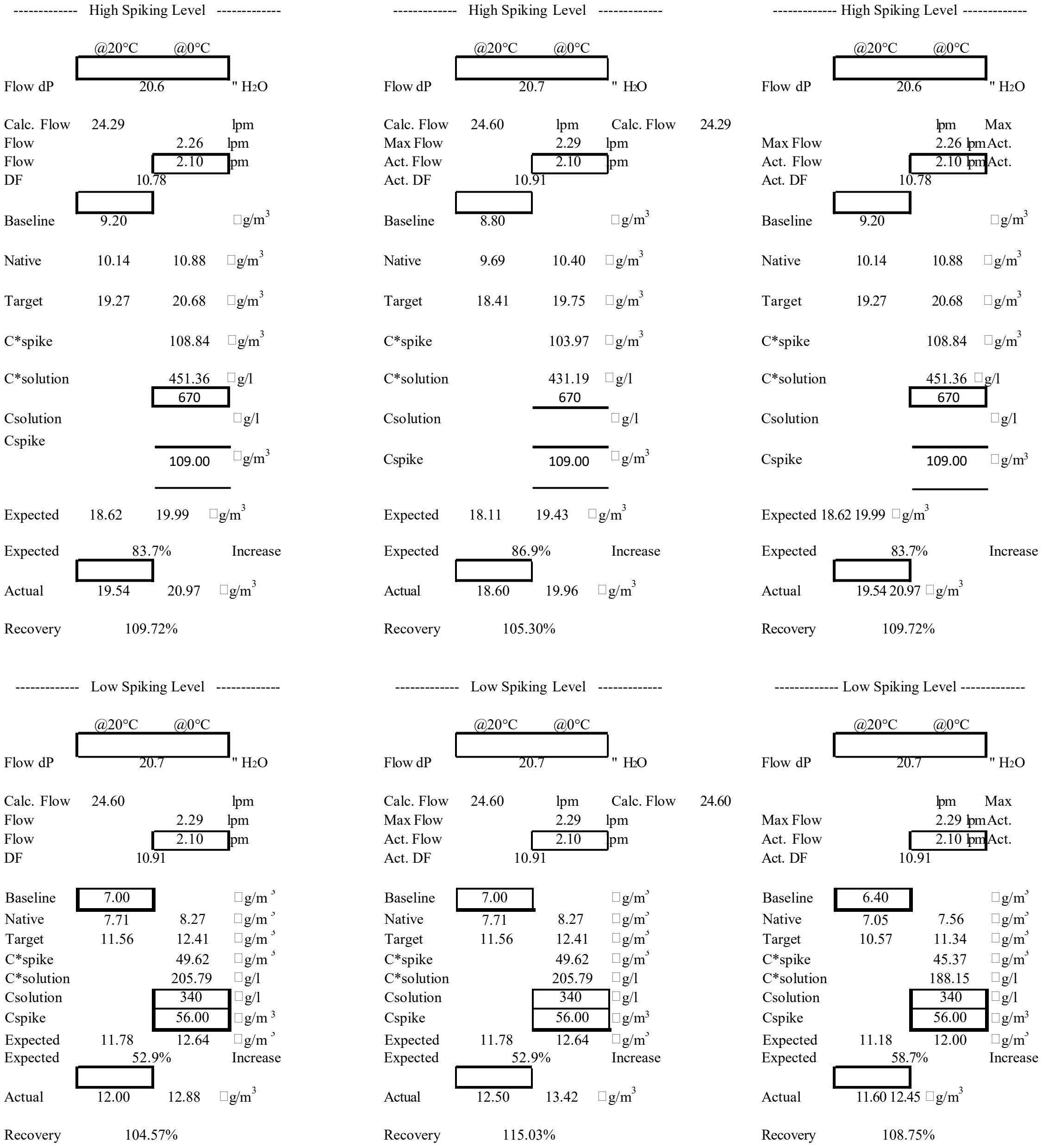
4.3.4 Dynamic Spiking

Dynamic spiking poses challenges for test personnel and equipment vendors alike. The vendors were challenged to provide sampling systems that drew a sample of at least 7.5 l/min, and could measure that flow accurately. Test personnel were challenged to make several on-site calculations to determine the spike injection parameters, monitor instrument responses continuously before, during, and after each spike injection, and perform on-the- fly preliminary recovery calculations to determine when enough injections have been done to have three at each level that satisfy the method’s RSD requirements.

Of the three systems that underwent dynamic spiking during these tests, one (Tekran) had a factory-calibrated flow measurement system that was already incorporated into spiking calculations performed by the system automatically using Hg^0 calibration gas. The GE/PSA system also had a “factory calibrated” flow measurement system (calibrated by the probe vendor), but the flow measurements were contradicted by tracer measurements performed by vendor personnel on-site. The Thermo system was calibrated on-site, but the calibration conditions may have been a bit unrealistic, and some “air dilution spiking” performed by ARCADIS has cast some doubt on the accuracy of those flow measurements. In short, “factory calibrated” means different things to different vendors, and the most directly verifiable means of measuring probe flow is with a tracer gas.

The dynamic spiking probe flow requirements, necessitated by the minimum flow limit of the HoVaCal system, have proven to be a complicating factor in designing smaller probes that can perform stack traverses. Of the two systems that were developed specifically for IRM applications, both of them have special “high flow” operating modes that are used only for spiking. The intent of dynamic spiking, however, is to have the system running in its normal sampling mode. It is clear now that, in order to have a reasonably sized IRM sampling probe, the probe flow requirements will need to be relaxed, which means a method must be developed to inject Hg^{+2} at substantially lower flow rates than are currently being used.

The field tester must have several things at his/her disposal to successfully perform dynamic spiking using the example procedure included in the conceptual IRM: (1) an assortment of injection solutions, with no concentration gap wider than a factor of two, (2) plenty of acid blank solution to inject continuously between spike injections, (3) continuous access to the measurement system data stream, and (4) a simple computerized spreadsheet to perform spiking calculations. Figure 9 shows an example spiking spreadsheet that accepts user inputs and calculates required injection parameters and recoveries. It is important to note that, for systems that measure flow and concentration using a 20°C “standard” cubic meter, the spiking calculations require quite a bit of conversion between that standard and the 0°C cubic meter used by the HoVaCal software.



------------- High Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.6		" H_2O
Calc. Flow	24.29		lpm
Flow		2.26	lpm
Flow		2.10	lpm
DF	10.78		
Baseline	9.20		µg/m^3
Native	10.14	10.88	µg/m^3
Target	19.27	20.68	µg/m^3
C*spike		108.84	µg/m^3
C*solution		451.36	µg/l
Csolution		670	µg/l
Cspike		109.00	µg/m^3
Expected	18.62	19.99	µg/m^3
Expected	83.7%		Increase
Actual	19.54	20.97	µg/m^3
Recovery	109.72%		

------------- High Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.7		" H_2O
Calc. Flow	24.60		lpm
Max Flow		2.29	lpm
Act. Flow		2.10	lpm
Act. DF	10.91		
Baseline	8.80		µg/m^3
Native	9.69	10.40	µg/m^3
Target	18.41	19.75	µg/m^3
C*spike		103.97	µg/m^3
C*solution		431.19	µg/l
Csolution		670	µg/l
Cspike		109.00	µg/m^3
Expected	18.11	19.43	µg/m^3
Expected	86.9%		Increase
Actual	18.60	19.96	µg/m^3
Recovery	105.30%		

------------- High Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.6		" H_2O
Calc. Flow	24.29		lpm
Max Flow		2.26	lpm
Act. Flow		2.10	lpm
Act. DF	10.78		
Baseline	9.20		µg/m^3
Native	10.14	10.88	µg/m^3
Target	19.27	20.68	µg/m^3
C*spike		108.84	µg/m^3
C*solution		451.36	µg/l
Csolution		670	µg/l
Cspike		109.00	µg/m^3
Expected	18.62	19.99	µg/m^3
Expected	83.7%		Increase
Actual	19.54	20.97	µg/m^3
Recovery	109.72%		

------------- Low Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.7		" H_2O
Calc. Flow	24.60		lpm
Flow		2.29	lpm
Flow		2.10	lpm
DF	10.91		
Baseline	7.00		µg/m^3
Native	7.71	8.27	µg/m^3
Target	11.56	12.41	µg/m^3
C*spike		49.62	µg/m^3
C*solution		205.79	µg/l
Csolution		340	µg/l
Cspike		56.00	µg/m^3
Expected	11.78	12.64	µg/m^3
Expected	52.9%		Increase
Actual	12.00	12.88	µg/m^3
Recovery	104.57%		

------------- Low Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.7		" H_2O
Calc. Flow	24.60		lpm
Max Flow		2.29	lpm
Act. Flow		2.10	lpm
Act. DF	10.91		
Baseline	7.00		µg/m^3
Native	7.71	8.27	µg/m^3
Target	11.56	12.41	µg/m^3
C*spike		49.62	µg/m^3
C*solution		205.79	µg/l
Csolution		340	µg/l
Cspike		56.00	µg/m^3
Expected	11.78	12.64	µg/m^3
Expected	52.9%		Increase
Actual	12.50	13.42	µg/m^3
Recovery	115.03%		

------------- Low Spiking Level -------------

	@20°C	@0°C	
Flow dP	20.7		" H_2O
Calc. Flow	24.60		lpm
Max Flow		2.29	lpm
Act. Flow		2.10	lpm
Act. DF	10.91		
Baseline	6.40		µg/m^3
Native	7.05	7.56	µg/m^3
Target	10.57	11.34	µg/m^3
C*spike		45.37	µg/m^3
C*solution		188.15	µg/l
Csolution		340	µg/l
Cspike		56.00	µg/m^3
Expected	11.18	12.00	µg/m^3
Expected	58.7%		Increase
Actual	11.60	12.45	µg/m^3
Recovery	108.75%		

Figure 9 : Example Spreadsheet for On-site Dynamic Spiking Calculations

The Appendix A operating procedures include two types of dynamic spiking procedures. The "continuous" spiking procedure allows the spiked concentration to stabilize at its elevated value before switching back to injecting acid blank. The "pulsed" spiking procedure, however, only injects solution long enough to get the expected rise in concentration, but not to stabilize at that level. This latter procedure takes less time to perform, and may be a bit more suitable to varying stack concentrations. One thing that none of the spiking procedures makes clear is that, for native stack concentrations that are steadily rising or falling, it may be necessary to adjust the spike concentration between replicates in order to stay within the target spiking range (i.e., 40-60% increase or 80-100% increase). In order to avoid inadvertently altering lagging data records, concentration adjustments should ONLY be made when the HoVaCal is feeding acid and the measured concentration is at the baseline or steadily falling to that level.

Hg^0 System Calibration Error Test on GE/PSA

1. Move the Tekran 3310 unit into position beside the GE/PSA probe and connect to electrical power and air.
2. On the 3310 Sequence screen, find the New_NIST_15Lpm sequence and click on the “+” box to expand the sequence description. Highlight the row below (the “Zero” step), and click “Execute Step Now” at the top of the screen.
3. At the GE/PSA probe box, open the rear access hatch and attach the delivery line to the ¼” PFA fitting tucked inside. Insulate the connection and all exposed tubing, and allow the hatch to close as much as possible.
4. On the GE/PSA computer, go to the “Instrument Sequence” screen and check that no sequence other than “Sample” in running. Click the “Edit” icon to activate the pull-down boxes in the “Run” column of the sequence table.
5. Use the pull-down boxes to change the “Yes” to a “No” in the “Sample” row, and the “No” to a “Yes” in the “Arc Low Flow Elemental” row. Click the “Update” icon to initiate these changes and deactivate the pull-down menus.
6. Returning to the 3310 software, go to the Overview screen and click on the Calibrator box to see details of the 3310. Check to make sure the “Hg source” temperature has reached 15°C.
7. On the Sequence screen, click on the C1 step (2.683 $\mu g/m^3$ injection) in the New_NIST_15Lpm sequence and click “Execute Step Now” at the top of the screen.
8. Monitor the GE/PSA response on the “Data” screen. Once the readings have stabilized, execute the sequence steps in the following order: C3 (10.73 $\mu g/m^3$), C2 (5.366 $\mu g/m^3$), and C4 (21.46 $\mu g/m^3$), allowing the GE/PSA response to stabilize for each injection.
9. After the last Hg^0 injection, return to the 3310 software Sequence screen and execute the Zero step to purge the system.
10. Return to the GE/PSA computer “Instrument Sequence” screen. Click the “Edit” icon, use the pull-down menus to reverse the changes made at step 5, and click the “Update” icon.
11. On the 3310 system Sequence screen, click “Stop Sequence” to shut down the injection.
12. Return to the probe box. Disconnect the delivery line, cap the ¼” PFA fitting (leaving it attached to the jumper inside the probe box), tuck the tube jumper back into the probe box, and close the rear access hatch.

Hg^{+2} System Calibration Error Test on GE/PSA

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the GE/PSA probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. At the GE/PSA probe box, open the rear access hatch and attach the delivery line to the ¼” PFA fitting tucked inside. Insulate the connection and all exposed tubing, and allow the hatch to close as much as possible.
4. Returning to the HoVaCAL instrument, make sure the balance is on and tared. Place a bottle of DI water on the balance, making sure the capacity of the balance is not exceeded.
5. Load the configuration file “blank10.cfg” and click on the “Start” icon to begin injecting. Make sure the peristaltic pump is turning and that the MFC is feeding air to the evaporator.
6. On the GE/PSA computer, go to the “Instrument Sequence” screen and check that no sequence other than “Sample” in running. Click the “Edit” icon to activate the pull-down boxes in the “Run” column of the sequence table.
7. Use the pull-down boxes to change the “Yes” to a “No” in the “Sample” row, and the “No” to a “Yes” in the “Arc Low Flow Ionic” row. Click the “Update” icon to initiate these changes and deactivate the pull-down menus.
8. In the HoVaCal software, click the “Store in file...” icon and select an appropriate filename.
9. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter ($A \square 100\% \square Meas.Flow / Speed\,\%$), make a log entry of the new parameter, and click the “Store configuration” icon to update the “blank10.cfg” file.
10. Check the levels on all $HgCl_2$ solution bottles. Agitate the 170 µg/l bottle and put it on the balance in place of the DI water. Click the “Load configuration” icon to load the “2_68at10.cfg” file. If the tube parameter was altered in step 8, immediately make that change in this configuration and click “Store configuration” to update the file.
11. Monitor the GE/PSA response on the “Data” screen. Once the readings have stabilized, inject the remaining solutions in the following order: 670 µg/l (file “10_7at10.cfg”), 340 µg/l (file “5_37at10.cfg”), and 1340 (file “21_5at10.cfg”), allowing the GE/PSA response to stabilize for each injection.
12. After the last Hg^{+2} injection, return the DI water bottle to the balance, and reload the “blank10.cfg” file. Return all solution bottles to their proper storage location.
13. As soon as the GE/PSA response begins to fall, return to the “Instrument Sequence” screen, click the “Edit” icon, use the pull-down menus to reverse the changes made at step 7, and click the “Update” icon.
14. In the Hovacal software, click off the “Start” icon to shut down the injection.

15. Return to the probe box. Disconnect the delivery line, cap the ¼” PFA fitting (leaving it attached to the jumper inside the probe box), tuck the tube jumper back into the probe box, and close the rear access hatch.
16. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^{+2} Dynamic Spiking on GE/PSA

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the GE/PSA probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. At the GE/PSA probe box, open the rear access hatch and attach the delivery line to the ¼” PFA fitting tucked inside. Insulate the connection and all exposed tubing, and allow the hatch to close as much as possible.
4. Returning to the HoVaCal unit, make sure the balance is on and tared. Place a bottle of acid blank solution on the balance, making sure the capacity of the balance is not exceeded.
5. Check with the GE/PSA personnel on-site to get the probe flow value, as determined by their latest tracer and dilution ratio determination procedures.
6. Check the status of the GE/PSA “Instrument Status” screen. If a blowback event is in progress or eminent, allow it to complete before proceeding. Click the “Edit” icon to activate the pull-down boxes in the “Run” column of the sequence table.
7. Use the pull-down boxes to change the “Yes” to a “No” in the “Sample” row, and the “No” to a “Yes” in the “Arc High Flow Ionic” row. Click the “Update” icon to initiate these changes and deactivate the pull-down menus.
8. Go to the “Data” screen and note the measured native stack concentration (C_{native}).
9. Calculate the required spike gas concentrations for the mid-point target readings of $1.5 \square C_{native}$ and $1.9 \square C_{native}$ based on the minimum spike dilution factor ($DF \square Q_{probe} | Q_{spike}$) of 10. Use the formula $C^*_{spike} \square DF \square C_{target} - C_{native} \square \square C_{native}$.
10. Calculate the solution concentrations ($C^*_{Solution}$) required to deliver these C_{spike} gas concentrations with 30% moisture ($Y_{H_2O} \square 0.3$) using the formula shown here

$$C^*_{Solution} \square \frac{C^*_{spike} \square .08206 \square 273.15}{18.016 \square Y_{H_2O}}$$

Note: Each of the calculated $C^*_{Solution}$ *values will likely fall between a pair of available solution concentrations; always use the higher of the two available concentrations.*

11. Check the levels in both $HgCl_2$ solution bottles. Enter the molarity corresponding to the higher concentration into the HoVaCal software, and enter the desired injection concentration (□g/m^3 from step 10) into the “Setpoint” columnof the concentration

table.

12. Click the “Store in file…” icon and select an appropriate filename. Enter a total flow setpoint (SP) of 4300 ml/min, and click the “Start” icon to begin injecting air and water vapor.

13. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (A ⍰ 100% ⍰ $\mathit{Meas.Flow} / \mathit{Speed}$ %), and make a log entry of the new parameter.
14. Once the liquid flow has stabilized, move the acid blank bottle to a flat surface near the HoVaCal. Also move the hood from the HoVaCal scale and set it over the acid blank bottle, so the dip tube remains in the bottle.
15. Agitate the higher concentration solution bottle, remove the cap, and put it on the balance. Allow it to sit undisturbed long enough for the HoVaCal software to register its weight.
16. Monitor the GE/PSA response on the “Data” screen. Once the readings have stabilized, move the balance hood into position over the solution bottle, ensuring that the dip tube enters the bottle.
17. Look for an increase in the mercury measurements. Allow the readings to stabilize at this elevated value, and ensure that the data are properly recorded.
18. Move the hood back to the acid blank solution, and continue observing the measurements as they settle back to the “baseline” level. Allow the instrument to record at least 4 stable data points before making any changes.
19. Repeat from step 15 above until at least 3 peaks of similar area are recorded.
20. Enter the molarity of the second mercury solution and the desired injection concentration (⍰g/m^3 from step 10) into the HoVaCal software.
21. Repeat steps 14 through 18 with this lower concentration solution.
22. After the last solution injection, replace the solution on the balance with DI water.
23. When the final stable background response is recorded, move the balance hood into place over the DI water bottle, and return both solutions and the acid blank bottle to storage.
24. After 5 minutes, click off the “Start” icon in the HoVaCal software to shut down the injection.
25. Return to the probe box. Disconnect the delivery line, cap the ¼” PFA fitting (leaving it attached to the jumper inside the probe box), tuck the tube jumper back into the probe box, and close the rear access hatch.
26. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.
27. Return to the GE/PSA computer “Instrument Sequence” screen. Click the “Edit” icon, use the pull-down menus to reverse the changes made at step 7, and click the “Update” icon.

Hg^0 System Calibration Error Test on Ohio Lumex

1. Move the Tekran 3310 unit into position beside the Ohio Lumex probe and connect to electrical power and air.
2. Have the vendor initiate a data collection event, ensuring that the duration is set for a period long enough to complete this procedure.
3. On the 3310 Sequence screen, find the New_NIST_15Lp m sequence and click on the "+" box to expand the sequence description. Highlight the row below (the "Zero" step), and click "Execute Step Now" at the top of the screen.
4. Using an appropriate adapter fitting, attach the delivery line to the end of the calib ration gas line provided by the vendor for this purpose.
5. Returning to the 3310 software, go to the Overview screen and click on the Calibrator box to see details of the 3310. Check to make sure the "Hg source" temperature has reached 15°C.
6. On the Sequence screen, click on the C1 step (2.683 µg/m³ injection) in the New_NIST_15Lpm sequence and click "Execute Step Now" at the top of the screen.
7. Monitor the Ohio Lumex response. Once the readings have stabilized, execute the sequence steps in the following order: C3 (10.73 µg/m³), C2 (5.366 µg/m³), and C4 (21.46 µg/m³), allowing the Ohio Lumex response to stabilize for each injection.
8. After the last Hg^0 injection, return to the 3310 software Sequence screen and execute the Zero step to purge the system.
9. As soon as the Ohio Lumex response begins to fall, have the vendor terminate the sampling event and ensure that the responses are properly recorded.
10. On the 3310 system Sequence screen, click "Stop Sequence" to shut down the injection.
11. Disconnect the delivery line from the vendor's calibration line.

Hg^{+2} System Calibration Error Test on Ohio Lumex

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Ohio Lumex probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. Have the vendor initiate a data collection event, ensuring that the duration is set for a period long enough to complete this procedure.
4. Using an appropriate adapter fitting, attach the delivery line to the end of the calibration gas line provided by the vendor for this purpose. Wrap the junction between the two lines with webbing.
5. Returning to the HoVaCAL instrument, make sure the balance is on and tared. Place a bottle of DI water on the balance, making sure the capacity of the balance is not exceeded.
6. Load the configuration file “blank10.cfg” and click on the “Start” icon to begin injecting. Make sure the peristaltic pump is turning and that the MFC is feeding air to the evaporator.
7. Click the “Store in file…” icon and select an appropriate filename.
8. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (*A* ⍰ 100% ⍰ *Meas.Flow* / *Speed* %), make a log entry of the new parameter, and click the “Store configuration” icon to update the “blank10.cfg” file.
9. Check the levels on all $HgCl_2$ solution bottles. Agitate the 170 µg/l bottle and put it on the balance in place of the DI water. Click the “Load configuration” icon to load the “2_68at10.cfg” file. If the tube parameter was altered in step 8, immediately make that change in this configuration and click “Store configuration” to update the file.
10. Monitor the Ohio Lumex response. Once the readings have stabilized, inject the remaining solutions in the following order: 670 µg/l (file “10_7at10.cfg”), 340 µg/l (file “5_37at10.cfg”), and 1340 (file “21_5at10.cfg”), allowing the Ohio Lumex response to stabilize for each injection.
11. After the last Hg^{+2} injectio n, return the DI water bottle to the balance, and reload the “blank10.cfg” file. Return all solution bottles to their proper storage location.
12. As soon as the Ohio Lumex response begins to fall, have the vendor terminate the sampling event and ensure that the responses are properly recorded.
13. In the Hovacal software, click off the “Start” icon to shut down the injection.
14. Disconnect the delivery line from the vendor’s calibration line.
15. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^0 System Calibration Error Test on Tekran

1. Move the Tekran 3310 unit into position beside the Tekran probe and connect to electrical power and air (use an extension to reach the air supply connection near the Lumex probe).

Note: To avoid confusion between the Tekran measurement system and the Tekran 3310 calibrator, the latter unit will hereafter be referred to only by its "3310" model number.

2. On the 3310 Sequence screen, find the New_NIST_15Lpm sequence and click on the "+" box to expand the sequence description. Highlight the row below (the "Zero" step), and click "Execute Step Now" at the top of the screen.
3. Using an appropriate adapter fitting, attach the delivery line to the 3/8" port on the bottom of the Tekran probe box. Carefully store the (HOT) port plug for re-installation in step 16.
4. On the Tekran computer, check the status of the scheduler. If a blowback event is in progress or eminent, allow it to complete before proceeding.
5. On the Sequence screen, find the ARCADIS_Low_Flow sequence and click on the "+" box to expand the sequence description. Highlight the row below (the single step which is also called ARCADIS_Low_Flow), and click "Execute Step Now" at the top of the screen.
6. Returning to the 3310 software, go to the Overview screen and click on the Calibrator box to see details of the 3310. Check to make sure the "Hg source" temperature has reached 15°C.
7. On the Sequence screen, click on the C1 step (2.683 µg/m³ injection) in the New_NIST_15Lpm sequence and click "Execute Step Now" at the top of the screen.
8. Monitor the Tekran response on the "Hg Data" screen. Once the readings have stabilized, execute the sequence steps in the following order: C3 (10.73 µg/m³), C2 (5.366 µg/m³), and C4 (21.46 µg/m³), allowing the Tekran response to stabilize for each injection.
9. After the last Hg^0 injection, return to the 3310 software Sequence screen and execute the Zero step to purge the system.
10. Return to the Tekran measurement system Hg Data screen. As soon as the measurement response begins to fall, go to the Sequence screen and click "Stop Sequence" to restore the probe to full flow operation.
11. On the 3310 system Sequence screen, click "Stop Sequence" to shut down the injection.
12. Return to the probe box. Disconnect the delivery line and replace the port plug.

Hg^{+2} System Calibration Error Test on Tekran

1. Outfit one of the HoVaCal units with a "black" peristaltic pump tube and a "normal" (high flow) evaporator. Move this unit into position beside the Tekran probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. Using an appropriate adapter fitting, attach the delivery line to the 3/8" port on the bottom of the Tekran probe box. Carefully store the (HOT) port plug for re-installation in step 16.
4. Wrap the junction between the delivery line and the port with webbing.
5. Returning to the HoVaCAL instrument, make sure the balance is on and tared. Place a bottle of DI water on the balance, making sure the capacity of the balance is not exceeded.
6. Load the configuration file "blank10.cfg" and click on the "Start" icon to begin injecting. Make sure the peristaltic pump is turning and that the MFC is feeding air to the evaporator.
7. On the Tekran computer, check the status of the scheduler. If a blowback event is in progress or eminent, allow it to complete before proceeding.
8. On the Sequence screen, find the ARCADIS_Low_Flow seque nce and click on the "+" box to expand the sequence description. Highlight the row below (the single step which is also called ARCADIS_Low_Flow), and click "Execute Step Now" at the top of the screen.
9. In the HoVaCal software, click the "Store in file…" icon and select an appropriate filename.
10. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (*A* ⍰ 100% ⍰ *Meas.Flow* / *Speed* %), make a log entry of the new parameter, and click the "Store configuration" icon to update the "blank10.cfg" file.
11. Check the levels on all $HgCl_2$ solution bottles. Agitate the 170 µg/l bottle and put it on the balance in place of the DI water. Click the "Load configuration" icon to load the "2_68at10.cfg" file. If the tube parameter was altered in step 10, immediately make that change in this configuration and click "Store configuration" to update the file.
12. Monitor the Tekran response on the "Hg Data" screen. Once the readings have stabilized, inject the remaining solutions in the following order: 670 µg/l (file "10_7at10.cfg"), 340 µg/l (file "5_37at10.cfg"), and 1340 (file "21_5at10.cfg"), allowing the Tekran response to stabilize for each injection.
13. After the last Hg^{+2} injection, return the DI water bottle to the balance, and reload the "blank10.cfg" file. Return all solution bottles to their proper storage location.
14. As soon as the Tekran response begins to fall, click "Stop Sequence" on the Sequence screen.
15. In the Hovacal software, click off the "Start" icon to shut down the injection.
16. Return to the probe box. Disconnect the delivery line and replace the port plug.

17. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^{+2} Dynamic Spiking on Tekran (Pulsed Spiking Procedure)

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Tekran probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. Using an appropriate adapter fitting, attach the delivery line to the 3/8” port on the bottom of the Tekran probe box. Carefully store the (HOT) port plug for re-installation in step 16.
4. Wrap the junction between the delivery line and the port with webbing.
5. Returning to the HoVaCal unit, make sure the balance is on and tared. Place a bottle of acid blank solution on the balance, making sure the capacity of the balance is not exceeded.
6. Go to the Tekran “Overview” screen and check the probe flow to make sure it is stable at a flow near 45 lpm.
7. Check the status of the “Scheduler” screen. If a blowback event is in progress or eminent, allow it to complete before proceeding.
8. On the Sequence screen, find the ARCADIS_Spiking sequence and click on the “+” box to expand the sequence description. Highlight the row below (the single step which is also called ARCADIS_Spiking), and click “Execute Step Now” at the top of the screen.
9. Go to the “Hg Data” screen and note the measured native stack concentration (C_{native}).
10. Calculate the required spike gas concentrations for the mid-point target readings of $1.5 \times C_{native}$ and $1.9 \times C_{native}$ based on the minimum spike dilution factor ($DF = Q_{probe} / Q_{spike}$) of 10. Use the formula $C^*_{spike} = DF\left(C_{target} - C_{native}\right) + C_{native}$.
11. Calculate the solution concentrations ($C^*_{Solution}$) required to deliver these C^*_{spike} gas concentrations with 30% moisture ($Y_{H_2O} = 0.3$) using the formula shown here

$$C^*_{Solution} = \frac{C^*_{spike} \times .08206 \times 273.15}{18.016 \times Y_{H_2O}}$$

Note: Each of the calculated $C^*_{Solution}$ *values will likely fall between a pair of available solution concentrations; always use the higher of the two available concentrations.*

12. Check the levels in both $HgCl_2$ solution bottles. Enter the molarity corresponding to the higher concentration into the HoVaCal software, and enter the desired injection concentration (µg/m³ from step 10) into the “Setpoint” column of the concentration

table.

13. Click the “Store in file…” icon and select an appropriate filename. Enter a total flow setpoint (SP) of 4300 ml/min, and click the “Start” icon to begin injecting air and water vapor.

14. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (*A* ⍰ 100% ⍰ *Meas.Flow* / *Speed* %), and make a log entry of the new parameter.
15. Once the liquid flow has stabilized, move the acid blank bottle to a flat surface near the HoVaCal. Also move the hood from the HoVaCal scale and set it over the acid blank bottle, so the dip tube remains in the bottle.
16. Agitate the higher concentration solution bottle, remove the cap, and put it on the balance. Allow it to sit undisturbed long enough for the HoVaCal software to register its weight.
17. Monitor the Tekran response on the “Hg Data” screen. Once the readings have stabilized, move the balance hood into position over the solution bottle, ensuring that the dip tube enters the bottle.
18. After 10 minutes, move the hood back to the acid blank solution.
19. Observe the Tekran measurements as the spike pulse works its way through the system
20. As the response settles back to its “baseline” level, repeat from step 17 above until at least 3 peaks of similar area are recorded.
21. Enter the molarity of the second mercury solution and the desired injection concentration (⍰g/m^3 from step 10) into the HoVaCal software.
22. Repeat steps 16 through 20 with this lower concentration solution.
23. After the last solution injection, replace the solution on the balance with DI water.
24. When the final stable background response is recorded, move the balance hood into place over the DI water bottle, and return both solutions and the acid blank bottle to storage.
25. Click “Stop Sequence” on the Tekran Sequence screen.
26. After 5 minutes, click off the “Start” icon in the HoVaCal software to shut down the injection.
27. Return to the probe box. Disconnect the delivery line and replace the port plug.
28. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^{+2} Dynamic Spiking on Tekran (Continuous Spiking Procedure)

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Tekran probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. Using an appropriate adapter fitting, attach the delivery line to the 3/8” port on the bottom of the Tekran probe box. Carefully store the (HOT) port plug for re-installation in step 16.
4. Wrap the junction between the delivery line and the port with webbing.
5. Returning to the HoVaCal unit, make sure the balance is on and tared. Place a bottle of acid blank solution on the balance, making sure the capacity of the balance is not exceeded.
6. Go to the Tekran “Overview” screen and check the probe flow to make sure it is stable at a flow near 45 lpm.
7. Check the status of the “Scheduler” screen. If a blowback event is in progress or eminent, allow it to complete before proceeding.
8. On the Sequence screen, find the ARCADIS_Spiking sequence and click on the “+” box to expand the sequence description. Highlight the row below (the single step which is also called ARCADIS_Spiking), and click “Execute Step Now” at the top of the screen.
9. Go to the “Hg Data” screen and note the measured native stack concentration (C_{native}).
10. Calculate the required spike gas concentrations for the mid-point target readings of $1.5 \square C_{native}$ and $1.9 \square C_{native}$ based on the minimum spike dilution factor ($DF \square Q_{probe} \,|\, Q_{spike}$) of 10. Use the formula $C^{*}_{spike} \square DF \left(C_{target} - C_{native} \right) + C_{native}$.
11. Calculate the solution concentrations ($C^{*}_{Solution}$) required to deliver these C^{*}_{spike} gas concentrations with 30% moisture ($Y_{H_2O} \square 0.3$) using the formula shown here

$$C^{*}_{Solution} \square \frac{C^{*}_{spike} \square .08206 \square 273.15}{18.016 \square Y_{H_2O}}$$

Note: Each of the calculated $C^{*}_{Solution}$ values will likely fall between a pair of available solution concentrations; always use the higher of the two available concentrations.

12. Check the levels in both $HgCl_2$ solution bottles. Enter the molarity corresponding to the higher concentration into the HoVaCal software, and enter the desired injection concentration (□g/m^3 from step 10) into the “Setpoint” column of the concentration

table.

13. Click the “Store in file…” icon and select an appropriate filename. Enter a total flow setpoint (SP) of 4300 ml/min, and click the “Start” icon to begin injecting air and water vapor.

14. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (A ⍰ 100% ⍰ $Meas.Flow$ / $Speed$ %), and make a log entry of the new parameter.
15. Once the liquid flow has stabilized, move the acid blank bottle to a flat surface near the HoVaCal. Also move the hood from the HoVaCal scale and set it over the acid blank bottle, so the dip tube remains in the bottle.
16. Agitate the higher concentration solution bottle, remove the cap, and put it on the balance. Allow it to sit undisturbed long enough for the HoVaCal software to register its weight.
17. Monitor the Tekran response on the “Hg Data” screen. Once the readings have stabilized, move the balance hood into position over the solution bottle, ensuring that the dip tube enters the bottle.
18. Look for an increase in the mercury measurements. Allow the readings to stabilize at this elevated value, and ensure that the data are properly recorded.
19. Move the hood back to the acid blank solution, and continue observing the measurements as they settle back to the “baseline” level. Allow the instrument to record at least 4 stable data points before making any changes.
20. Repeat from step 17 above until at least 3 peaks of similar area are recorded.
21. Enter the molarity of the second mercury solution and the desired injection concentration (⍰g/m^3 from step 10) into the HoVaCal software.
22. Repeat steps 16 through 20 with this lower concentration solution.
23. After the last solution injection, replace the solution on the balance with DI water.
24. When the final stable background response is recorded, move the balance hood into place over the DI water bottle, and return both solutions and the acid blank bottle to storage.
25. Click “Stop Sequence” on the Tekran Sequence screen.
26. After 5 minutes, click off the “Start” icon in the HoVaCal software to shut down the injection.
27. Return to the probe box. Disconnect the delivery line and replace the port plug.
28. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^0 System Calibration Error Test on Thermo

1. Move the Tekran 3310 unit into position beside the Thermo probe and connect to electrical power and air.
2. On the 3310 Sequence screen, find the New_NIST_15Lpm sequence and click on the "+" box to expand the sequence description. Highlight the row below (the "Zero" step), and click "Execute Step Now" at the top of the screen.
3. At the Thermo probe box, remove the rear access cover and the large cover on the left side of the probe box (when facing the box from the rear).
4. Inside the probe box, locate the end of the spike line (a heated umbilical along the bottom edge of the side opening). Disconnect this line from the Thermo supply line and connect it to the 3310 delivery line.
5. Re-install the left side cover on the box and stuff a hot glove into the rear access opening.
6. In the Thermo "I-Port" software, go to the "Eductor Air Pressure" screen under the "Service" and "Set Pressures" menu layers. Lower the setting to 270 "counts" using the same onscreen up/down buttons that navigate the menus. Click the on screen "Enter" button to save setting.

Note: This process can be a bit tedious when done through the I-Port software, as it was designed for the faster interface built into the instrument. It is important to note that pressing either the up or down button more than 9 times in rapid succession will cause larger than expected changes in the displayed value. To get to 270 more quickly (from 3760), try pressing the down button 29 times in rapid succession; then, after a pause, press again 22 times in rapid succession; after another pause, press the up button 8 times. Use the opposite of this technique (up 29, up 22, down 8) in step 11.

7. Returning to the 3310 software, go to the Overview screen and click on the Calibrator box to see details of the 3310. Check to make sure the "Hg source" temperature has reached 15°C.
8. On the Sequence screen, click on the C1 step (2.683 $\mu g/m^3$ injection) in the New_NIST_15Lpm sequence and click "Execute Step Now" at the top of the screen.
9. Monitor the Thermo response on the I-Port screen. Once the readings have stabilized, execute the sequence steps in the following order: C3 (10.73 $\mu g/m^3$), C2 (5.366 $\mu g/m^3$), and C4 (21.46 $\mu g/m^3$), allowing the Thermo response to stabilize for each injection.
10. After the last Hg^0 injection, execute the Zero step to purge the system.
11. As soon as the Thermo response begins to fall, return to the "I-Port" software's "Eductor Air Pressure" screen and raise the setting back up to 3760 counts, clicking "Enter" to save.
12. On the 3310 Sequence screen, click "Stop Sequence" to shut down the injection.
13. Return to the probe box. Disconnect the delivery line and reconnect the Thermo supply line. Replace all probe box covers.

Hg^{+2} System Calibration Error Test on Thermo

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Thermo probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. At the Thermo probe box, remove the rear access cover and the large cover on the left side of the probe box (when facing the box from the rear).
4. Inside the probe box, locate the end of the spike line (a heated umbilical along the bottom edge of the side opening). Disconnect this line from the Thermo supply line and connect it to the HoVaCal delivery line.
5. Wrap the junction between the two heated lines with webbing. Re- install the left side cover on the box and stuff a hot glove into the rear access opening.
6. Returning to the HoVaCAL instrument, make sure the balance is on and tared. Place a bottle of DI water on the balance, making sure the capacity of the balance is not exceeded.
7. Load the configuration file “blank10.cfg” and click on the “Start” icon to begin injecting. Make sure the peristaltic pump is turning and that the MFC is feeding air to the evaporator.
8. In the Thermo “I-Port” software, go to the “Eductor Air Pressure” screen under the “Service” and “Set Pressures” menu layers. Lower the setting to 270 “counts” using the same onscreen up/down buttons that navigate the menus. Click the on screen “Enter” button to save setting.

Note: This process can be a bit tedious when done through the I-Port software, as it was designed for the faster interface built into the instrument. It is important to note that pressing either the up or down button more than 9 times in rapid succession will cause larger than expected changes in the displayed value. To get to 270 more quickly (from 3760), try pressing the down button 29 times in rapid succession; then, after a pause, press again 22 times in rapid succession; after another pause, press the up button 8 times. Use the opposite of this technique (up 29, up 22, down 8) in step 14.

9. In the HoVaCal software, click the “Store in file…” icon and select an appropriate filename.
10. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (*A* ▯ 100% ▯ *Meas.Flow* / *Speed* %), make a log entry of the new parameter, and

    click the “Store configuration” icon to update the “blank10.cfg” file.
11. Check the levels on all $HgCl_2$ solution bottles. Agitate the 170 µg/l bottle and put it on the balance in place of the DI water. Click the “Load configuration” icon to load the “2_68at10.cfg” file. If the tube parameter was altered in step 10, immediately make that change in this configuration and click “Store configuration” to update the file.

12. Monitor the Thermo response on the I-Port screen. Once the readings have stabilized, inject the remaining solutions in the following order: 670 µg/l (file “10_7at10.cfg”), 340 µg/l (file“5_37at10.cfg”), and 1340 (file “21_5at10.cfg”), allowing the Thermo response to stabilize for each injection.
13. After the last Hg^{+2} injection, return the DI water bottle to the balance, and reload the “blank10.cfg” file. Return all solution bottles to their proper storage location.
14. As soon as the Thermo response begins to fall, return to the “I-Port” software’s “Eductor Air Pressure” screen and raise the setting back up to 3760 counts, clicking “Enter” to save.
15. In the Hovacal software, click off the “Start” icon to shut down the injection.
16. Return to the probe box. Disconnect the delivery line and reconnect the Thermo supply line. Replace all probe box covers.
17. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^{+2} Dynamic Spiking on Thermo (Pulsed Spiking Procedure)

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Thermo probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. At the Thermo probe box, remove the rear access cover and the large cover on the left side of the probe box (when facing the box from the rear).
4. Inside the probe box, locate the end of the spike line (a heated umbilical along the bottom edge of the side opening). Disconnect this line from the Thermo supply line and connect it to the HoVaCal delivery line.
5. Wrap the junction between the two heated lines with webbing. Re- install the left side cover on the box and stuff a hot glove into the rear access opening.
6. Returning to the HoVaCal unit, make sure the balance is on and tared. Place a bottle of acid blank solution on the balance, making sure the capacity of the balance is not exceeded.
7. In the Thermo “I-Port” software, go to the “Pressures” screen under the “Diagnostics” menu. Note the “Venturi dP” reading and look up the flow on the chart provided by Thermo. It should be about 25 lpm.
8. Also note from the I-Port software the measured native stack concentration (C_{native}).

   Note: For systems that measure flow and concentrations at “standard” conditions of 20°C, it will be necessary to make corrections to 0°C for all spiking calculations.
9. Calculate the required spike gas concentrations for the mid-point target readings of 1.5 □ C_{native} and 1.9 □ C_{native} based on the minimum spike dilution factor ($DF \square Q_{probe} | Q_{spike}$) of 10. Use the formula

   $$C^*_{spike} \square DF \square C_{target} - C_{native} \square \square C_{native}.$$
10. Calculate the solution concentrations ($C^*_{Solution}$) required to deliver these C_{spike} gas concentrations with 30% moisture ($Y_{H_2O} \square 0.3$) using the formula shown here

    $$C^*_{Solution} \square \frac{C^*_{spike} \square .08206 \square 273.15}{18.016 \square Y_{H_2O}}$$

Note: Each of the calculated $C^*_{Solution}$ *values will likely fall between a pair of available solution concentrations; always use the higher of the two available concentrations.*

11. Check the levels in both $HgCl_2$ solution bottles. Enter the molarity corresponding to the higher concentration into the HoVaCal software, and enter the desired injection concentration (μg/m^3 from step 10) into the “Setpoint” column of the concentration table.

12. Click the “Store in file…” icon and select an appropriate filename. Enter a total flow setpoint (SP) of 4300 ml/min, and click the “Start” icon to begin injecting air and water vapor.
13. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (A ⍰ 100% ⍰ $Meas.Flow\,/\,Speed$ %), and make a log entry of the new parameter.
14. Once the liquid flow has stabilized, move the acid blank bottle to a flat surface near the HoVaCal. Also move the hood from the HoVaCal scale and set it over the acid blank bottle, so the dip tube remains in the bottle.
15. Agitate the higher concentration solution bottle, remove the cap, and put it on the balance. Allow it to sit undisturbed long enough for the HoVaCal software to register its weight.
16. Monitor the Thermo measurement response from the I-port software. Once the readings have stabilized, move the balance hood into position over the solution bottle, ensuring that the dip tube enters the bottle.
17. After 5 minutes, move the hood back to the acid blank solution.
18. Observe the Thermo measurements as the spike pulse works its way through the system
19. As the response settles back to its “baseline” level, repeat from step 16 above until at least 3 peaks of similar area are recorded.
20. Enter the molarity of the second mercury solution and the desired injection concentration (μg/m^3 from step 10) into the HoVaCal software.
21. Repeat steps 15 through 19 with this lower concentration solution.
22. After the last solution injection, replace the solution on the balance with DI water.
23. When the final stable background response is recorded, move the balance hood into place over the DI water bottle, and return both solutions and the acid blank bottle to storage.
24. After 5 minutes, click off the “Start” icon in the HoVaCal software to shut down the injection.
25. Return to the probe box. Disconnect the delivery line and reconnect the Thermo supply line. Replace all probe box covers.
26. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Hg^{+2} Dynamic Spiking on Thermo (Pulsed Spiking Procedure)

1. Outfit one of the HoVaCal units with a “black” peristaltic pump tube and a “normal” (high flow) evaporator. Move this unit into position beside the Thermo probe and connect to electrical power and air.
2. Turn on the evaporator heater and make sure that it and the delivery line are heating up.
3. At the Thermo probe box, remove the rear access cover and the large cover on the left side of the probe box (when facing the box from the rear).
4. Inside the probe box, locate the end of the spike line (a heated umbilical along the bottom edge of the side opening). Disconnect this line from the Thermo supply line and connect it to the HoVaCal delivery line.
5. Wrap the junction between the two heated lines with webbing. Re- install the left side cover on the box and stuff a hot glove into the rear access opening.
6. Returning to the HoVaCal unit, make sure the balance is on and tared. Place a bottle of acid blank solution on the balance, making sure the capacity of the balance is not exceeded.
7. In the Thermo “I-Port” software, go to the “Pressures” screen under the “Diagnostics” menu. Note the “Venturi dP” reading and look up the flow on the chart provided by Thermo. It should be about 25 lpm.
8. Also note from the I-Port software the measured native stack concentration (C_{native}).

   Note: For systems that measure flow and concentrations at “standard” conditions of

   20°C, it will be necessary to make corrections to 0°C for all spiking calculations.
9. Calculate the required spike gas concentrations for the mid-point target readings of $1.5 \square C_{native}$ and $1.9 \square C_{native}$ based on the minimum spike dilution factor ($DF \square Q_{probe} | Q_{spike}$) of 10. Use the formula $C^*_{spike} \square DF \square C_{target} - C_{native} \square C_{native}$.
10. Calculate the solution concentrations ($C^*_{Solution}$) required to deliver these C_{spike} gas concentrations with 30% moisture ($Y_{H_2O} \square 0.3$) using the formula shown here

$$C^*_{Solution} \square \frac{C^*_{spike} \square .08206 \square 273.15}{18.016 \square Y_{H_2O}}$$

Note: Each of the calculated $C^*_{Solution}$ *values will likely fall between a pair of available solution concentrations; always use the higher of the two available concentrations.*

11. Check the levels in both $HgCl_2$ solution bottles. Enter the molarity corresponding to the higher concentration into the HoVaCal software, and enter the desired injection concentration (μg/m^3 from step 10) into the “Setpoint” column of the concentration table.

12. Click the “Store in file…” icon and select an appropriate filename. Enter a total flow setpoint (SP) of 4300 ml/min, and click the “Start” icon to begin injecting air and water vapor.
13. Check that the unit is delivering the target moisture levels. If necessary, adjust the tube parameter (*A* ⍰ 100% ⍰ *Meas.Flow* / *Speed* %), and make a log entry of the new parameter.
14. Once the liquid flow has stabilized, move the acid blank bottle to a flat surface near the HoVaCal. Also move the hood from the HoVaCal scale and set it over the acid blank bottle, so the dip tube remains in the bottle.
15. Agitate the higher concentration solution bottle, remove the cap, and put it on the balance. Allow it to sit undisturbed long enough for the HoVaCal software to register its weight.
16. Monitor the Thermo measurement response from the I-port software. Once the readings have stabilized, move the balance hood into position over the solution bottle, ensuring that the dip tube enters the bottle.
17. Look for an increase in the mercury measurements. Allow the readings to stabilize at this elevated value, and ensure that the data are properly recorded.
18. Move the hood back to the acid blank solution, and continue observing the measurements as they settle back to the “baseline” level. Allow the instrument to record at least 4 stable data points before making any changes.
19. Repeat from step 16 above until at least 3 peaks of similar area are recorded.
20. Enter the molarity of the second mercury solution and the desired injection concentration (⍰g/m^3 from step 10) into the HoVaCal software.
21. Repeat steps 15 through 19 with this lower concentration solution.
22. After the last solution injection, replace the solution on the balance with DI water.
23. When the final stable background response is recorded, move the balance hood into place over the DI water bottle, and return both solutions and the acid blank bottle to storage.
24. After 5 minutes, click off the “Start” icon in the HoVaCal software to shut down the injection.
25. Return to the probe box. Disconnect the delivery line and reconnect the Thermo supply line. Replace all probe box covers.
26. Shut down the air supply to the HoVaCal unit, and shut off the evaporator heater.

Appendix B. CHRONOLOGICAL SUMMARY OF IRM TEST DATA

GE/PSA Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	□g/m^3 @ 20°C	
			slpm	(g/min)	c (□g/l)		Expected	Recorded
7/6/2006 9:09	Oxidized Calibration Error	HovaQuick	10.025	0.152	170	1.89%	2.41	2.02
7/6/2006 10:31	Oxidized Calibration Error	HovaQuick	10.027	0.155	670	1.92%	9.63	8.85
7/6/2006 11:28	Oxidized Calibration Error	HovaQuick	10.029	0.153	340	1.90%	4.83	4.55
7/6/2006 12:29	Oxidized Calibration Error	HovaQuick	10.029	0.155	1340	1.92%	19.26	18.35
7/6/2006 17:12	Dynamic Spiking, High	HovaQuick					8.98	8.38
7/6/2006 19:13	Dynamic Spiking, High	HovaQuick					8.86	8.44
7/6/2006 20:10	Dynamic Spiking, High	HovaQuick					9.00	8.44
7/7/2006 11:19	Dynamic Spiking, Low	HovaQuick					7.84	7.51
7/7/2006 13:16	Dynamic Spiking, Low	HovaQuick					7.12	6.83
7/7/2006 19:05	Dynamic Spiking, Low	HovaQuick					8.03	7.76
7/8/2006 0:33	-------------	System performs a "DO:10" Calibration Method				------------		
7/9/2006 13:39	Elemental Calibration Error	3310					2.50	2.10
7/9/2006 14:45	Elemental Calibration Error	3310					9.98	9.58
7/9/2006 15:50	Elemental Calibration Error	3310					5.00	4.65
7/9/2006 16:35	Elemental Calibration Error	3310					19.94	19.55
7/10/2006 8:15	System Integrity Check	HovaDigi	9.285	0.142	670	1.90%	9.53	8.91
7/10/2006 11:14	Sampling Test Number 3	Stack					12.66	15.34
7/10/2006 15:36	Sampling Test Number 4	Stack					17.29	17.36
7/10/2006 19:44	System Integrity Check	HovaDigi	9.281	0.143	670	1.92%	9.61	8.49
7/10/2006 22:59	-------------	System performs a "DO:10" Calibration Method				------------		
7/11/2006 6:36	System Integrity Check	HovaDigi	9.287	0.146	670	1.96%	9.81	10.13
7/11/2006 10:33	Sampling Test Number 5	Stack					12.02	12.46
7/11/2006 15:28	Sampling Test Number 6	Stack					19.28	20.93
7/11/2006 16:57	System Integrity Check	HovaDigi	9.294	0.146	670	1.95%	9.78	9.84
7/12/2006 8:00	System Integrity Check	HovaDigi	9.291	0.147	670	1.97%	9.89	10.67
7/12/2006 10:43	Sampling Test Number 7	Stack					18.04	19.90
7/12/2006 15:34	Sampling Test Number 8	Stack					17.08	19.81
7/12/2006 18:15	System Integrity Check	HovaDigi	9.290	0.145	670	1.95%	9.76	10.80
7/12/2006 22:54	-------------	System performs a "DO:10" Calibration Method				------------		
7/13/2006 7:50	System Integrity Check	HovaDigi	9.298	0.152	670	2.04%	10.22	10.31
7/13/2006 10:44	Sampling Test						20.65	23.51
7/13/2006 15:27	Sampling Test						19.98	22.66
7/13/2006 17:52	System Integrity Check	HovaDigi	9.294	0.151	670	2.02%	10.14	10.55
7/14/2006 0:00	-------------	System performs a "DO:10" Calibration Method				------------		

GE/PSA Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow slpm	Feed Rate (g/min)	Solution c (µg/l)	% H2O	µg/m³ @ 20°C Expected	Recorded
7/14/2006 7:43	System Integrity Check	HovaDigi	9.298	0.151	670	2.02%	10.14	9.70
7/14/2006 11:02	Sampling Test						8.73	8.39
7/14/2006 15:44	Sampling Test						9.11	8.94
7/14/2006 18:21	System Integrity Check	HovaDigi	9.294	0.150	670	2.01%	10.10	9.34
7/15/2006 1:20	-------------	System performs a "DO:10" Calibration Method				-------------		
7/15/2006 8:23	System Integrity Check	HovaDigi	9.301	0.155	670	2.07%	10.39	10.45
7/15/2006 11:05	Sampling Test						7.38	7.82
7/15/2006 15:32	Sampling Test						6.49	7.03
7/15/2006 17:41	System Integrity Check	HovaDigi	9.308	0.161	670	2.15%	10.79	9.93
7/16/2006 1:36	-------------	System performs a "DO:10" Calibration Method				-------------		
7/16/2006 7:40	System Integrity Check	HovaDigi	9.288	0.145	670	1.94%	9.74	10.10
7/16/2006 11:18	Sampling Test						6.83	7.97
7/16/2006 14:48	Sampling Test						6.90	7.98
7/16/2006 16:53	System Integrity Check	HovaDigi	9.294	0.151	670	2.02%	10.15	9.49
7/17/2006 8:11	System Integrity Check	HovaDigi	9.290	0.145	670	1.95%	9.77	9.45
7/17/2006 10:49	Sampling Test						8.25	9.22
7/17/2006 12:42	-------------	System performs a "DO:10" Calibration Method				-------------		
7/17/2006 15:46	Sampling Test						8.14	7.64
7/17/2006 17:55	System Integrity Check	HovaDigi	9.295	0.150	670	2.01%	10.07	9.52
7/18/2006 0:25	-------------	System performs a "DO:10" Calibration Method				-------------		
7/18/2006 12:12	-------------	System performs a "DO:10" Calibration Method				-------------		
7/19/2006 9:43	Dynamic Spiking, High	HovaDigi					56.14	58.43
7/19/2006 10:32	Dynamic Spiking, High	HovaDigi					56.70	59.22
7/19/2006 11:20	Dynamic Spiking, High	HovaDigi					57.75	60.64
7/19/2006 12:09	Dynamic Spiking, Low	HovaDigi					47.08	48.92
7/19/2006 12:58	Dynamic Spiking, Low	HovaDigi					48.36	49.82
7/19/2006 13:46	Dynamic Spiking, Low	HovaDigi					53.47	55.54
7/19/2006 16:09	Oxidized Calibration Error	HovaDigi	9.310	0.160	170	2.13%	2.71	3.90
7/19/2006 17:02	Oxidized Calibration Error	HovaDigi	9.295	0.152	670	2.03%	10.20	10.92
7/19/2006 17:38	Oxidized Calibration Error	HovaDigi	9.290	0.152	3340	2.04%	50.95	57.48

Lumex Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	□g/m^3 @ 20°C	
			slpm	(g/min)	c (□g/l)		Expected	Recorded
7/09/2006 12:58	Oxidized Calibration Error	HovaDIgi	6.152	0.416	40	8.42%	2.52	2.57
7/09/2006 13:15	Oxidized Calibration Error	HovaDIgi	6.156	0.391	170	7.91%	10.07	10.19
7/09/2006 13:38	Oxidized Calibration Error	HovaDIgi	6.154	0.418	80	8.45%	5.07	5.90
7/09/2006 14:04	Oxidized Calibration Error	HovaDIgi	6.159	0.395	340	7.98%	20.31	19.94
7/09/2006 17:23	Elemental Calibration Error	3310					2.50	2.67
7/09/2006 17:32	Elemental Calibration Error	3310					9.98	9.68
7/09/2006 17:48	Elemental Calibration Error	3310					5.00	5.18
7/09/2006 18:21	Elemental Calibration Error	3310					19.94	19.54
7/10/2006 11:15	Sampling Test Number 3						12.66	19.74
7/10/2006 15:38	Sampling Test Number 4						17.29	20.63
7/11/2006 10:35	Sampling Test Number 5						12.02	13.35
7/11/2006 15:30	Sampling Test Number 6						19.28	20.52
7/12/2006 10:45	Sampling Test Number 7						18.04	19.20
7/12/2006 15:37	Sampling Test Number 8						17.08	17.89
7/13/2006 10:47	Sampling Test Number 9						20.65	22.27
7/13/2006 15:30	Sampling Test Number 10						19.98	20.45
7/14/2006 11:02	Sampling Test Number 11						8.73	8.47
7/14/2006 15:45	Sampling Test Number 12						9.11	8.51
7/15/2006 11:05	Sampling Test Number 13						7.38	7.21
7/15/2006 15:35	Sampling Test Number 14						6.49	6.21
7/16/2006 11:20	Sampling Test Number 15						6.83	6.73
7/16/2006 14:48	Sampling Test Number 16						6.90	6.26

Tekran Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	□g/m^3 @ 20°C	
			slpm	(g/min)	c (□g/l)		Expected	Recorded
7/05/2006 20:35	Oxidized Calibration Error	HovaDIgi	9.147	0.143	170	1.94%	2.47	1.87
7/05/2006 21:27	Oxidized Calibration Error	HovaDIgi	9.164	0.146	670	1.98%	9.94	8.16
7/05/2006 22:07	Oxidized Calibration Error	HovaDIgi	9.037	0.145	340	2.00%	5.08	4.37
7/05/2006 23:17	Oxidized Calibration Error	HovaDIgi	9.110	0.145	1340	1.98%	19.88	17.27
7/06/2006 10:59	Dynamic Spiking, Low	HovaDigi					9.67	8.96
7/06/2006 11:27	Dynamic Spiking, Low	HovaDigi					9.38	8.69
7/06/2006 14:44	Dynamic Spiking, High	HovaDigi					6.82	6.19
7/06/2006 16:04	Dynamic Spiking, Low	HovaDigi					7.86	7.28
7/06/2006 16:34	Dynamic Spiking, High	HovaDigi					8.77	8.07
7/06/2006 17:34	Dynamic Spiking, High	HovaDigi					8.65	8.02
7/06/2006 20:12	Oxidized Orifice Check	HovaDigi	6.144	0.095	670	1.93%	9.70	7.70
7/07/2006 10:05	-------------	John Cooper runs	DilRatio sequence		-------------			
7/07/2006 18:57	Oxidized Orifice Check	HovaDigi	6.142	0.094	670	1.90%	9.53	8.22
7/07/2006 21:00	Oxidized Orifice Check	HovaQuick	6.019	0.094	670	1.94%	9.74	8.16
7/09/2006 10:08	Elemental Calibration Error	3310					2.50	2.21
7/09/2006 10:36	Elemental Calibration Error	3310					9.98	8.76
7/09/2006 11:11	Elemental Calibration Error	3310					5.00	4.45
7/09/2006 11:46	Elemental Calibration Error	3310					19.94	17.65
7/10/2006 06:47	System Integrity Check	HovaQuick	10.028	0.157	670	1.94%	9.75	8.50
7/10/2006 11:15	Sampling Test Number 3						12.66	14.40
7/10/2006 15:35	Sampling Test Number 4						17.29	17.30
7/10/2006 18:07	System Integrity Check	HovaQuick	10.035	0.156	670	1.94%	9.72	8.38
7/11/2006 05:35	System Integrity Check	HovaQuick	10.032	0.159	670	1.97%	9.86	8.53
7/11/2006 10:35	Sampling Test Number 5						12.02	11.12
7/11/2006 15:25	Sampling Test Number 6						19.28	17.79
7/11/2006 18:30	System Integrity Check	HovaQuick	10.036	0.157	670	1.95%	9.78	8.29
7/11/2006 20:17	Dynamic Spiking, High	HovaQuick					32.88	30.92
7/11/2006 20:44	Dynamic Spiking, High	HovaQuick					32.81	31.44
7/11/2006 21:34	Dynamic Spiking, High	HovaQuick					33.28	31.23
7/12/2006 07:02	System Integrity Check	HovaQuick	10.038	0.159	670	1.97%	9.89	8.23
7/12/2006 08:02	Dynamic Spiking, Low	HovaQuick					25.76	23.91
7/12/2006 08:24	Dynamic Spiking, Low	HovaQuick					26.03	24.12
7/12/2006 08:44	Dynamic Spiking, Low	HovaQuick					26.23	24.64
7/12/2006 10:40	Sampling Test Number 7						18.04	16.92
7/12/2006 15:32	Sampling Test Number 8						17.08	16.49
7/12/2006 18:40	System Integrity Check	HovaQuick	10.040	0.157	670	1.95%	9.77	8.20

Tekran Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	□g/m^3 @ 20°C	
			slpm	(g/min)	c (□g/l)		Expected	Recorded
7/13/2006 05:42	System Integrity Check	HovaQuick	10.036	0.158	670	1.96%	9.83	8.33
7/13/2006 10:47	Sampling Test Number 9						20.65	20.85
7/13/2006 15:30	Sampling Test Number 10						19.98	19.24
7/13/2006 18:07	System Integrity Check	HovaQuick	10.044	0.158	670	1.96%	9.82	8.21
7/14/2006 06:52	System Integrity Check	HovaQuick	10.039	0.160	670	1.98%	9.93	8.60
7/14/2006 10:57	Sampling Test Number 11						8.73	7.76
7/14/2006 15:45	Sampling Test Number 12						9.11	8.08
7/14/2006 17:52	System Integrity Check	HovaQuick	10.047	0.160	670	1.98%	9.93	8.30
7/15/2006 06:30	System Integrity Check	HovaQuick	10.041	0.161	670	2.00%	10.03	8.41
7/15/2006 11:05	Sampling Test Number 13						7.38	6.90
7/15/2006 15:35	Sampling Test Number 14						6.49	6.17
7/15/2006 18:10	System Integrity Check	HovaQuick	10.047	0.160	670	1.98%	9.92	8.34
7/16/2006 07:05	System Integrity Check	HovaQuick	10.042	0.163	670	2.02%	10.13	8.75
7/16/2006 11:20	Sampling Test Number 15						6.83	6.62
7/16/2006 14:47	Sampling Test Number 16						6.90	6.52
7/16/2006 17:35	System Integrity Check	HovaQuick	10.047	0.160	670	1.98%	9.93	8.30
7/17/2006 06:20	System Integrity Check	HovaQuick	10.043	0.164	670	2.03%	10.17	9.04
7/17/2006 10:50	Sampling Test Number 17						8.25	7.13
7/17/2006 15:40	Sampling Test Number 18						8.14	6.51
7/17/2006 18:12	System Integrity Check	HovaQuick	10.054	0.163	670	2.02%	10.12	8.42
7/18/2006 10:22	Dynamic Spiking, High	HovaQuick					11.62	10.78
7/18/2006 10:49	Dynamic Spiking, High	HovaQuick					12.67	11.71
7/18/2006 11:09	Dynamic Spiking, High	HovaQuick					12.95	12.04
7/18/2006 12:59	Dynamic Spiking, Low	HovaQuick					11.34	10.85
7/18/2006 13:44	Dynamic Spiking, Low	HovaQuick					11.62	11.01
7/18/2006 14:24	Dynamic Spiking, Low	HovaQuick					12.07	11.67

Thermo Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	µg/m³ @ 20°C	
			slpm	(g/min)	c (µg/l)		Expected	Recorded
7/05/2006	-------------	Dilution factor ("dilf") was changed ~40% over the holiday weekend					-------------	
7/05/2006	Oxidized Calibration Error	HovaQuick	10.03	0.1496	170	1.86%	2.36	2.17
7/05/2006	Oxidized Calibration Error	HovaQuick	10.02	0.1501	670	1.86%	9.35	10.68
7/05/2006	Oxidized Calibration Error	HovaQuick	10.02	0.1493	340	1.85%	4.72	5.18
7/05/2006	Oxidized Calibration Error	HovaQuick	10.02	0.1522	1340	1.89%	18.95	22.92
7/05/2006	Dynamic Spiking, High	HovaQuick					18.26	19.51
7/05/2006	Dynamic Spiking, High	HovaQuick					17.86	19.01
7/05/2006	Dynamic Spiking, High	HovaQuick					17.38	18.49
7/05/2006	Dynamic Spiking, Low	HovaQuick					11.71	12.26
7/05/2006	Dynamic Spiking, Low	HovaQuick					11.55	12.78
7/05/2006	Dynamic Spiking, Low	HovaQuick					10.79	12.05
7/07/2006	-------------	Numerous Thermo personnel on site, making various adjustments					-------------	
7/08/2006	Elemental Calibration	3310					9.99	3.78
7/08/2006	Elemental Calibration	3310					2.50	2.21
7/08/2006	Elemental Calibration	3310					5.00	2.77
7/08/2006	Elemental Calibration	3310					19.94	7.28
7/10/2006	System Integrity Check	HavaDigi	9.286	0.142	670	1.91%	9.58	10.46
7/10/2006	Sampling Test Number 3						12.66	16.05
7/10/2006	Sampling Test Number 4						17.29	19.78
7/10/2006	System Integrity Check	HavaDigi	9.282	0.141	670	1.89%	9.48	10.53
7/11/2006	System Integrity Check	HavaDigi	9.290	0.147	670	1.97%	9.87	10.54
7/11/2006	Sampling Test Number 5						12.02	12.61
7/11/2006	Sampling Test Number 6						19.28	21.08
7/11/2006	System Integrity Check	HavaDigi	9.284	0.141	670	1.90%	9.51	10.61
7/12/2006	System Integrity Check	HavaDigi	9.292	0.150	670	2.00%	10.05	11.04
7/12/2006	Sampling Test Number 7						18.04	18.41
7/12/2006	Sampling Test Number 8						17.08	17.89
7/12/2006	System Integrity Check	HavaDigi	9.300	0.152	670	2.03%	10.21	10.35
7/13/2006	System Integrity Check	HavaDigi	9.295	0.148	670	1.98%	9.96	10.50
7/13/2006	Sampling Test Number 9						20.65	22.38
7/13/2006	Sampling Test Number10						19.98	21.10
7/13/2006	System Integrity Check	HavaDigi	9.296	0.150	670	2.01%	10.07	10.41
7/13/2006	Dynamic Spiking, High	HavaDigi					30.36	28.31
7/13/2006	Dynamic Spiking, High	HavaDigi					26.67	24.76
7/13/2006	Dynamic Spiking, High	HavaDigi					22.31	21.06
7/14/2006	System Integrity Check	HavaDigi	9.306	0.156	670	2.09%	10.49	10.29

Thermo Test Results

			-------	HovaCAL Parameters		-------	Hg^T Values	
Date & Time	IRM Check	Source	Flow	Feed Rate	Solution	% H2O	□g/m^3 @ 20°C	
			slpm	(g/min)	c (□g/l)		Expected	Recorded
7/14/2006	Sampling Test Number 11						8.73	8.61
7/14/2006	Sampling Test Number 12						9.11	9.07
7/14/2006	System Integrity Check	HavaDigi	9.305	0.158	670	2.12%	10.62	10.39
7/14/2006	Dynamic Spiking, Low	HavaDigi					12.58	12.49
7/14/2006	Dynamic Spiking, Low	HavaDigi					12.69	12.74
7/14/2006	Dynamic Spiking, Low	HavaDigi					12.51	12.53
7/15/2006	System Integrity Check	HavaDigi	9.305	0.158	670	2.11%	10.58	10.64
7/15/2006	Sampling Test Number 13						7.38	7.47
7/15/2006	Sampling Test Number 14						6.49	6.67
7/15/2006	System Integrity Check	HavaDigi	9.303	0.157	670	2.10%	10.54	10.76
7/16/2006	System Integrity Check	HavaDigi	9.302	0.156	670	2.08%	10.44	11.18
7/16/2006	Sampling Test Number 15						6.83	7.04
7/16/2006	Sampling Test Number 16						6.90	7.03
7/16/2006	System Integrity Check	HavaDigi	9.293	0.151	670	2.02%	10.13	10.06
7/17/2006	System Integrity Check	HavaDigi	9.291	0.149	670	1.99%	9.98	9.98
7/17/2006	Sampling Test Number 17						8.25	7.75
7/17/2006	Sampling Test Number 18						8.14	7.05
7/17/2006	System Integrity Check	HavaDigi	9.295	0.150	670	2.01%	10.08	10.23
7/18/2006	Dynamic Spiking, High	HavaDigi					11.16	10.60
7/18/2006	Dynamic Spiking, High	HavaDigi					10.87	10.43
7/18/2006	Dynamic Spiking, High	HavaDigi					11.29	10.82
7/18/2006	Dynamic Spiking, Low	HavaDigi					10.38	10.27
7/18/2006	Dynamic Spiking, Low	HavaDigi					10.47	10.36
7/18/2006	Dynamic Spiking, Low	HavaDigi					10.36	10.17

Appendix C. DYNAMIC SPIKING DATA SHEETS

Dynamic Spiking Data Sheet (Oxydized Cal Error Corrected)

Facility name: Armstrong Date: 6-Jul-06 Time 14:51

Unit(s) tested: Unit 2Test personnel: JEB, NFR Analyzer make & model: GE/PSA

Estimated native Hg concentration: 4.7 □g/m^3

Serial number: Estimated unspiked sample flow rate 47.45 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.6 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	Lower	Upper	Lower		
High	9.3	8.4	53	43	42	8.3
Low	7.4	6.5	33	24		

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	Post	Avg.	
High	47.45	4.60	9.29	4.65	5.91	5.28	X 111.8% X
	47.45	4.61	9.33	5.91	5.96	5.93	X 98.0% X
	47.45	4.61	8.96	5.96	5.96	5.96	88.30%
	47.45	4.61	8.74	5.96	5.61	5.78	X 86.9% X
	47.45	4.61	9.03	5.61	6.01	5.81	93.16%
	47.45	4.61	9.02	6.01	5.94	5.98	89.27%
						Avg.	90.2%
						RSD	2.8%
Low							
						Avg.	
						RSD	

Dynamic Spiking Data Sheet (Oxydized Cal Error Corrected)

Facility name: Armstrong Date: 7-Jul-06 Time 8:17

Unit(s) tested: Unit 2Test personnel: JEB, NFR Analyzer make & model: GE/PSA

Estimated native Hg concentration: 5.0 □g/m^3

Serial number: Estimated unspiked sample flow rate 47.45 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.6 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	10.1	9.1	57	47		
Low	8.1	7.1	36	26	32	7.7

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High							
						Avg.	
						RSD	
Low	47.45	4.61	7.44	5.04	5.73	5.39	X 82.0% X
	47.45	4.61	7.63	5.73	5.46	5.59	X 81.8% X
	47.45	4.61	8.07	4.99	6.41	5.70	92.8%
	47.45	4.61	7.36	4.56	5.20	4.88	94.1%
	47.45	4.61	7.00	4.69	5.39	5.04	X 77.7% X
	47.45	4.61	7.40	3.82	5.31	4.57	X 104.3% X
	47.45	4.61	8.33	5.33	6.50	5.91	95.0%
						Avg.	**94.0%**
						RSD	**1.1%**

Dynamic Spiking Data Sheet (Drift Corrected)

Facility name: Armstrong Date: 19-Jul-06 Time 9:03

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: GE/PSA

Estimated native Hg concentration: 25.8 □g/m^3

Serial number: Estimated unspiked sample flow rate 47.45 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.6 slpm

Preliminary Data

Target Level	**C_{target} (□g/m^3)**		**C^*_{spike} (□g/m^3)**		**Selected C_{spike} Value (□g/m^3)**	**Expected[1] C_{ss} (□g/m^3)**
	Upper	**Lower**	**Upper**	**Lower**		
High	51.7	46.5	292	239	290	51.4
Low	41.3	36.2	186	132	180	40.8

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	**Q_{probe} (lpm)**	**Q_{spike} (lpm)**	**C_{ss} (□g/m^3)**	**C_{native} (□g/m^3)**			**% Spike Recovery**
				Pre	**Post**	**Avg.**	
High	47.45	4.83	51.89	25.83	26.84	26.34	96.07%
	47.45	4.85	52.59	26.84	26.34	26.59	96.68%
	47.45	4.86	53.85	26.34	28.22	27.28	97.69%
	47.45	4.90	65.95	31.45	32.55	32.00	X 100.2% X
						Avg.	**96.8%**
						RSD	**0.8%**
Low	47.45	4.81	43.41	28.22	28.42	28.32	98.06%
	47.45	4.82	44.22	28.42	30.36	29.39	96.19%
	47.45	4.84	49.31	30.36	31.45	30.90	97.45%
						Avg.	**97.2%**
						RSD	**1.0%**

Dynamic Spiking Data Sheet (Oxydized Cal Error Corrected)

Facility name: Armstrong Date: 6-Jul-06 Time 9:25

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Tekran

Estimated native Hg concentration: 5.2 □g/m^3

Serial number: Estimated unspiked sample flow rate 48.30 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.7 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	10.4	9.4	59	48	44	9.0
Low	8.3	7.3	37	27	39	8.5

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High	48.18	4.71	7.86	5.21	5.62	5.41	X 78.7% X
	48.48	4.72	10.07	6.44	5.80	6.12	X 79.8% X
	48.27	4.72	7.37	4.65	4.36	4.50	93.4%
	48.43	4.71	8.34	4.36	5.46	4.91	X 110.7% X
	48.38	4.73	9.51	5.56	5.93	5.74	96.0%
	48.23	4.69	9.46	6.07	5.66	5.87	97.1%
						Avg.	**95.5%**
						RSD	**2.0%**
Low	48.27	4.71	9.71	6.68	7.61	7.15	X 86.5% X
	48.40	4.72	10.53	7.61	7.88	7.74	92.6%
	48.31	4.72	10.22	7.88	6.89	7.38	93.1%
	48.27	4.72	8.62	6.00	5.56	5.78	95.4%
						Avg.	**93.7%**
						RSD	**1.6%**

Facility name: Armstrong Date: 11-Jul-06 Time 19:30

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Tekran

Estimated native Hg concentration: 21.6 □g/m^3

Serial number: Estimated unspiked sample flow rate 48.30 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.6 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	43.2	38.9	248	203	180	36.7
Low	34.6	30.2	158	112		

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High	48.22	2.47	29.31	21.60	20.20	20.90	X 93.0% X
	48.21	4.63	36.82	20.20	21.30	20.75	105.46%
	48.17	4.63	37.43	21.30	20.32	20.81	109.49%
	48.48	4.62	34.64	20.32	21.61	20.97	X 93.2% X
	48.31	4.62	37.19	21.61	20.70	21.15	107.07%
						Avg.	**107.3%**
						RSD	**1.9%**
Low							
						Avg.	
						RSD	

Facility name: Armstrong Date: 12-Jul-06 Time 7:45

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Tekran
Estimated native Hg concentration: 19.7 □g/m^3
Serial number: Estimated unspiked sample flow rate 48.23 slpm
Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.7 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	39.4	35.4	222	181		
Low	31.5	27.6	141	101	109	28.4

[1]Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High							
						Avg.	
						RSD	
Low	48.43	4.63	28.61	19.69	20.77	20.23	98.51%
	48.32	4.63	28.86	20.77	20.64	20.70	97.69%
	48.23	4.63	29.47	20.64	20.88	20.76	101.57%
						Avg.	**99.3%**
						RSD	**2.1%**

Facility name: Armstrong Date: 18-Jul-06 Time 9:12

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Tekran

Estimated native Hg concentration: 6.6 □g/m^3

Serial number: Estimated unspiked sample flow rate 48.25 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 4.7 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	Lower	Upper	Lower		
High	13.2	11.9	75	61	69	12.7
Low	10.6	9.3	47	34	46	10.5

[1]Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	Post	Avg.	
High	48.22	4.66	11.55	6.62	7.24	6.93	X 104.2% X
	48.08	4.66	11.45	7.24	7.49	7.36	X 94.3% X
	48.29	4.66	12.97	7.49	7.76	7.62	103.10%
	48.31	4.67	14.09	7.76	8.30	8.03	102.95%
	48.42	4.67	14.48	8.30	8.49	8.39	103.86%
	48.26	4.67	13.80	8.49	8.31	8.40	X 93.2% X
						Avg.	**103.3%**
						RSD	**0.5%**
Low	48.33	4.66	12.93	8.31	9.32	8.82	X 111.7% X
	48.34	4.65	12.59	9.32	9.08	9.20	X 96.6% X
	48.35	4.66	13.05	9.08	9.26	9.17	107.17%
	48.23	4.66	13.24	9.26	9.80	9.53	103.80%
	48.37	4.66	14.04	9.80	10.47	10.13	109.41%
						Avg.	**106.8%**
						RSD	**2.6%**

Dynamic Spiking Data Sheet (Oxidized Cal Error Corrected)

Facility name: Armstrong Date: 5-Jul-06 Time 12:13

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Thermo

Estimated native Hg concentration: 8.9 □g/m^3

Serial number: Estimated unspiked sample flow rate 24.47 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 2.25 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	17.8	16.0	105	86	99	17.2
Low	14.2	12.4	67	48	52	12.8

[1]Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High	24.39	2.24	12.91	8.88	9.02	8.95	X 61.1% X
	24.40	2.25	16.28	8.89	8.62	8.75	91.03%
	24.49	2.25	15.87	8.58	8.32	8.45	90.21%
	24.63	2.25	15.46	8.10	8.22	8.16	90.15%
						Avg.	**90.5%**
						RSD	**0.5%**
Low	24.43	2.24	10.47	7.12	6.47	6.79	89.38%
	24.49	2.24	10.88	6.98	6.34	6.66	100.68%
	24.60	2.24	10.30	5.96	6.12	6.04	101.40%
						Avg.	**97.2%**
						RSD	**6.9%**

Facility name: Armstrong Date: 13-Jul-06 Time 20:27

Unit(s) tested: Unit 2Test personnel: JEB, NFR Analyzer make & model: Thermo

Estimated native Hg concentration: 14.4 □g/m^3

Serial number: Estimated unspiked sample flow rate 24.52 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 2.6 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	28.7	25.9	150	123	150	28.8
Low	23.0	20.1	96	69	50	18.1

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High	24.49	2.57	26.30	14.37	14.84	14.60	79.89%
	24.51	2.56	26.35	14.84	12.85	13.84	X 92.5% X
	24.55	2.57	23.06	12.85	11.39	12.12	79.85%
	24.51	2.58	19.69	11.39	11.06	11.23	81.58%
						Avg.	**80.4%**
						RSD	**1.2%**
Low	24.47	2.58	12.42	8.90	8.32	8.61	77.92%
	24.55	2.58	11.00	7.32	7.34	7.33	88.74%
	24.61	2.57	11.76	6.75	9.92	8.34	97.08%
						Avg.	**87.9%**
						RSD	**10.9%**

Facility name: Armstrong Date: 14-Jul-06 Time 21:23

Unit(s) tested: Unit 2 Test personnel: JEB, NFR Analyzer make & model: Thermo

Estimated native Hg concentration: 8.4 □g/m^3

Serial number: Estimated unspiked sample flow rate 24.51 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 2.45 slpm

Preliminary Data

Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	16.8	15.1	93	76		
Low	13.5	11.8	59	42	52	12.8

[1] Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High							
						Avg.	
						RSD	
Low	24.50	2.45	12.34	8.41	8.57	8.49	X 92.8% X
	24.50	2.46	12.65	8.57	8.60	8.58	95.84%
	24.67	2.47	12.90	8.60	8.62	8.61	98.48%
	24.64	2.46	12.69	8.62	8.34	8.48	97.91%
	24.76	2.46	11.99	8.34	7.97	8.16	X 89.6% X
						Avg.	**97.4%**
						RSD	**1.4%**

Facility name: Armstrong Date: 18-Jul-06 Time 8:09

Unit(s) tested: Unit 2Test personnel: JEB, NFR Analyzer make & model: Thermo

Estimated native Hg concentration: 6.0 □g/m^3

Serial number: Estimated unspiked sample flow rate 24.47 slpm

Calibration span 20 □g/m^3 Estimated spike gas flow rate: 2.45 slpm

Preliminary Data

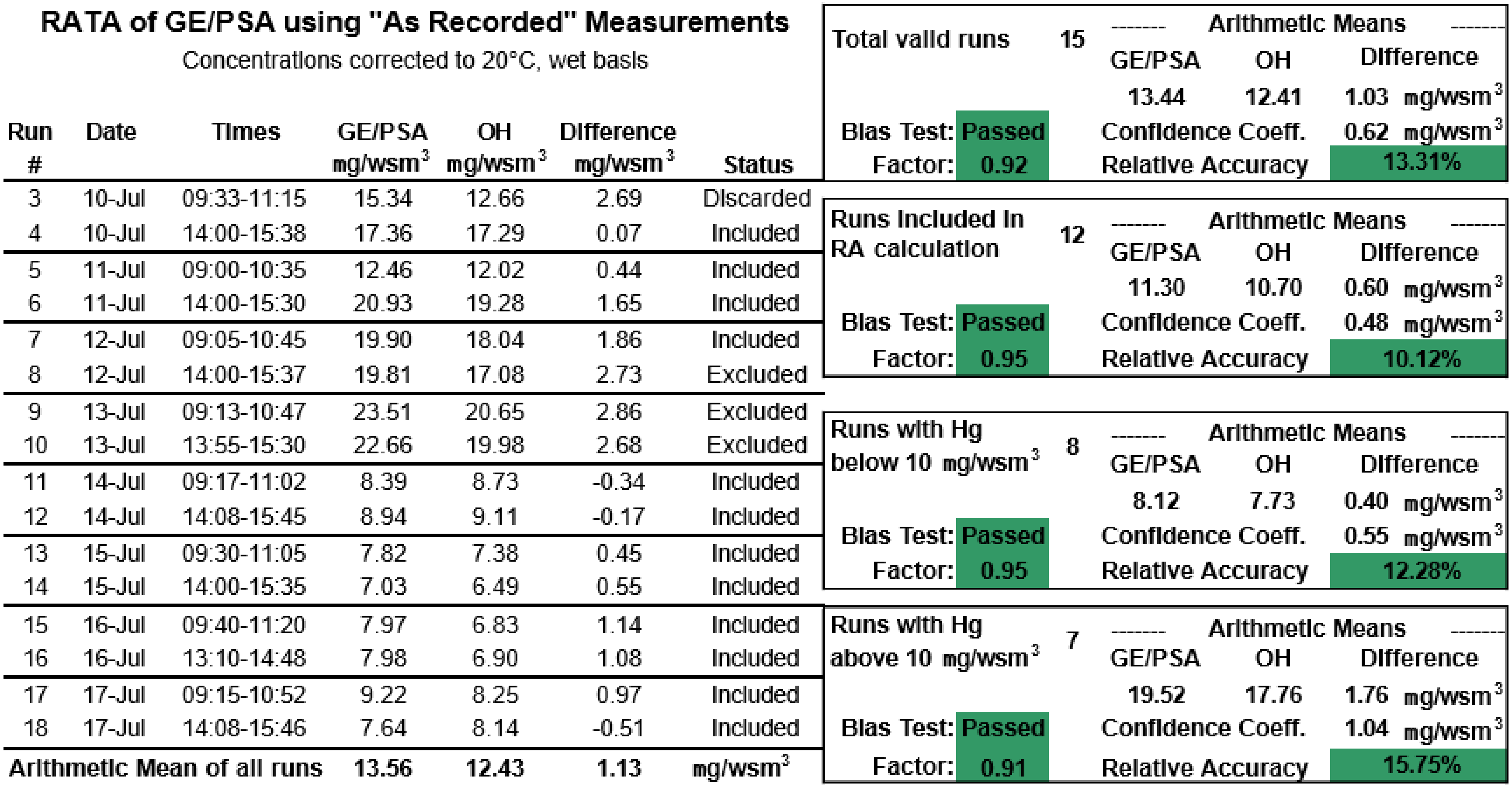
Target Level	C_{target} (□g/m^3)		C^*_{spike} (□g/m^3)		Selected C_{spike} Value (□g/m^3)	Expected[1] C_{ss} (□g/m^3)
	Upper	**Lower**	**Upper**	**Lower**		
High	12.0	10.8	66	54	55	10.9
Low	9.6	8.4	42	30	42	9.6

[1]Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} (□g/m^3)	C_{native} (□g/m^3)			% Spike Recovery
				Pre	**Post**	**Avg.**	
High	24.49	2.46	11.17	6.02	5.85	5.93	X 91.8% X
	24.45	2.47	10.43	5.85	5.57	5.71	84.41%
	24.47	2.47	10.26	5.57	6.23	5.90	85.35%
	24.49	2.48	10.62	6.23	6.41	6.32	84.84%
	24.54	2.42	10.45	6.41	6.79	6.60	X 85.8% X
	24.64	2.45	10.64	6.79	6.84	6.81	X 83.4% X
	24.45	2.43	10.79	6.84	7.03	6.93	X 85.2% X
						Avg.	**84.9%**
						RSD	**0.6%**
Low	24.47	2.44	10.11	7.03	7.06	7.05	89.76%
	24.55	2.45	10.20	7.06	7.18	7.12	90.02%
	24.49	2.47	10.03	7.18	6.72	6.95	88.26%
						Avg.	**89.3%**
						RSD	**1.1%**

Appendix D. RATA Summary Sheets



RATA of GE/PSA using "As Recorded" Measurements

Concentrations corrected to 20°C, wet basis

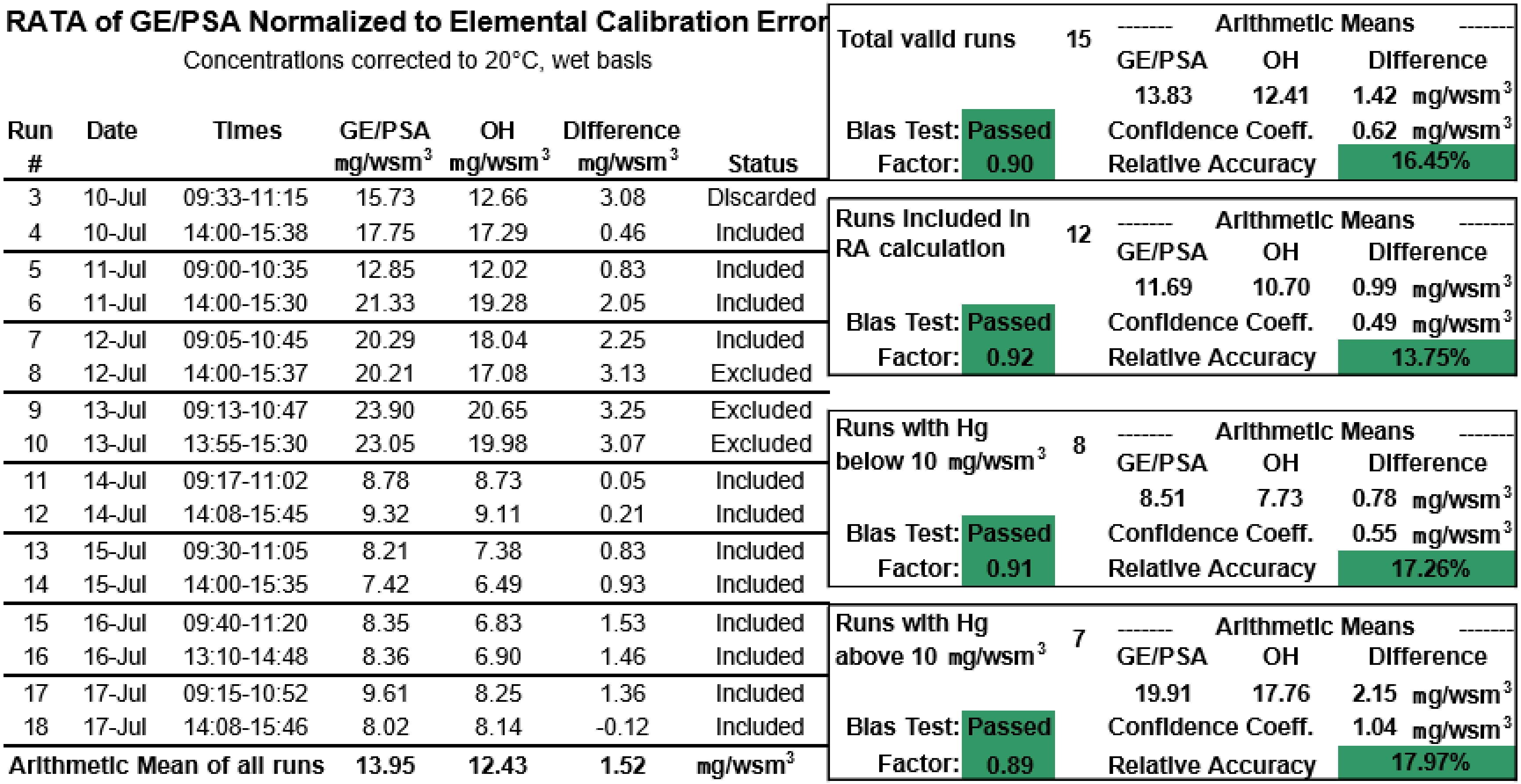
Run #	Date	Times	GE/PSA mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	15.34	12.66	2.69	Discarded
4	10-Jul	14:00-15:38	17.36	17.29	0.07	Included
5	11-Jul	09:00-10:35	12.46	12.02	0.44	Included
6	11-Jul	14:00-15:30	20.93	19.28	1.65	Included
7	12-Jul	09:05-10:45	19.90	18.04	1.86	Included
8	12-Jul	14:00-15:37	19.81	17.08	2.73	Excluded
9	13-Jul	09:13-10:47	23.51	20.65	2.86	Excluded
10	13-Jul	13:55-15:30	22.66	19.98	2.68	Excluded
11	14-Jul	09:17-11:02	8.39	8.73	-0.34	Included
12	14-Jul	14:08-15:45	8.94	9.11	-0.17	Included
13	15-Jul	09:30-11:05	7.82	7.38	0.45	Included
14	15-Jul	14:00-15:35	7.03	6.49	0.55	Included
15	16-Jul	09:40-11:20	7.97	6.83	1.14	Included
16	16-Jul	13:10-14:48	7.98	6.90	1.08	Included
17	17-Jul	09:15-10:52	9.22	8.25	0.97	Included
18	17-Jul	14:08-15:46	7.64	8.14	-0.51	Included
Arithmetic Mean of all runs			13.56	12.43	1.13	mg/wsm^3

Total valid runs	15	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		13.44	12.41	1.03 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.62 mg/wsm^3
Factor:	0.92	Relative Accuracy		13.31%

Runs included in RA calculation	12	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		11.30	10.70	0.60 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.48 mg/wsm^3
Factor:	0.95	Relative Accuracy		10.12%

Runs with Hg below 10 mg/wsm^3	8	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		8.12	7.73	0.40 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.55 mg/wsm^3
Factor:	0.95	Relative Accuracy		12.28%

Runs with Hg above 10 mg/wsm^3	7	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		19.52	17.76	1.76 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		1.04 mg/wsm^3
Factor:	0.91	Relative Accuracy		15.75%



RATA of GE/PSA Normalized to Elemental Calibration Error

Concentrations corrected to 20°C, wet basis

Run #	Date	Times	GE/PSA mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	15.73	12.66	3.08	Discarded
4	10-Jul	14:00-15:38	17.75	17.29	0.46	Included
5	11-Jul	09:00-10:35	12.85	12.02	0.83	Included
6	11-Jul	14:00-15:30	21.33	19.28	2.05	Included
7	12-Jul	09:05-10:45	20.29	18.04	2.25	Included
8	12-Jul	14:00-15:37	20.21	17.08	3.13	Excluded
9	13-Jul	09:13-10:47	23.90	20.65	3.25	Excluded
10	13-Jul	13:55-15:30	23.05	19.98	3.07	Excluded
11	14-Jul	09:17-11:02	8.78	8.73	0.05	Included
12	14-Jul	14:08-15:45	9.32	9.11	0.21	Included
13	15-Jul	09:30-11:05	8.21	7.38	0.83	Included
14	15-Jul	14:00-15:35	7.42	6.49	0.93	Included
15	16-Jul	09:40-11:20	8.35	6.83	1.53	Included
16	16-Jul	13:10-14:48	8.36	6.90	1.46	Included
17	17-Jul	09:15-10:52	9.61	8.25	1.36	Included
18	17-Jul	14:08-15:46	8.02	8.14	-0.12	Included
Arithmetic Mean of all runs			**13.95**	**12.43**	**1.52**	mg/wsm^3

------- Arithmetic Means -------

Total valid runs	15	GE/PSA	OH	Difference	
		13.83	12.41	1.42	mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.62	mg/wsm^3
Factor:	0.90	Relative Accuracy		16.45%	

------- Arithmetic Means -------

Runs included in RA calculation	12	GE/PSA	OH	Difference	
		11.69	10.70	0.99	mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.49	mg/wsm^3
Factor:	0.92	Relative Accuracy		13.75%	

------- Arithmetic Means -------

Runs with Hg below 10 mg/wsm^3	8	GE/PSA	OH	Difference	
		8.51	7.73	0.78	mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.55	mg/wsm^3
Factor:	0.91	Relative Accuracy		17.26%	

------- Arithmetic Means -------

Runs with Hg above 10 mg/wsm^3	7	GE/PSA	OH	Difference	
		19.91	17.76	2.15	mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		1.04	mg/wsm^3
Factor:	0.89	Relative Accuracy		17.97%	

RATA of GE/PSA Normalized to Oxidized Calibration Error

Concentrations corrected to 20°C, wet basis

Run #	Date	Times	GE/PSA mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.19	12.66	3.53	Discarded
4	10-Jul	14:00-15:38	18.28	17.29	0.99	Included
5	11-Jul	09:00-10:35	13.20	12.02	1.18	Included
6	11-Jul	14:00-15:30	21.99	19.28	2.71	Included
7	12-Jul	09:05-10:45	20.92	18.04	2.87	Included
8	12-Jul	14:00-15:37	20.83	17.08	3.75	Excluded
9	13-Jul	09:13-10:47	24.66	20.65	4.01	Excluded
10	13-Jul	13:55-15:30	23.78	19.98	3.80	Excluded
11	14-Jul	09:17-11:02	8.98	8.73	0.25	Included
12	14-Jul	14:08-15:45	9.54	9.11	0.43	Included
13	15-Jul	09:30-11:05	8.39	7.38	1.01	Included
14	15-Jul	14:00-15:35	7.57	6.49	1.08	Included
15	16-Jul	09:40-11:20	8.54	6.83	1.71	Included
16	16-Jul	13:10-14:48	8.55	6.90	1.65	Included
17	17-Jul	09:15-10:52	9.84	8.25	1.59	Included
18	17-Jul	14:08-15:46	8.19	8.14	0.05	Included
Arithmetic Mean of all runs			14.34	12.43	1.91	mg/wsm^3

Total valid runs	15	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		14.22	12.41	1.81 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.73 mg/wsm^3
Factor:	0.87	Relative Accuracy		20.41%

Runs included in RA calculation	12	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		12.00	10.70	1.29 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.56 mg/wsm^3
Factor:	0.89	Relative Accuracy		17.30%

Runs with Hg below 10 mg/wsm^3	8	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		8.70	7.73	0.97 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.55 mg/wsm^3
Factor:	0.89	Relative Accuracy		19.73%

Runs with Hg above 10 mg/wsm^3	7	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		20.52	17.76	2.76 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		1.15 mg/wsm^3
Factor:	0.87	Relative Accuracy		21.99%

RATA of GE/PSA Normalized to Integrity/Drift Checks

Concentrations corrected to 20°C, wet basis

Run #	Date	Times	GE/PSA mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.90	12.66	4.24	Discarded
4	10-Jul	14:00-15:38	19.11	17.29	1.83	Excluded
5	11-Jul	09:00-10:35	12.23	12.02	0.20	Included
6	11-Jul	14:00-15:30	20.54	19.28	1.26	Included
7	12-Jul	09:05-10:45	18.22	18.04	0.18	Included
8	12-Jul	14:00-15:37	18.14	17.08	1.06	Included
9	13-Jul	09:13-10:47	22.95	20.65	2.30	Excluded
10	13-Jul	13:55-15:30	22.12	19.98	2.14	Excluded
11	14-Jul	09:17-11:02	8.93	8.73	0.20	Included
12	14-Jul	14:08-15:45	9.51	9.11	0.40	Included
13	15-Jul	09:30-11:05	8.14	7.38	0.76	Included
14	15-Jul	14:00-15:35	7.32	6.49	0.83	Included
15	16-Jul	09:40-11:20	8.11	6.83	1.28	Included
16	16-Jul	13:10-14:48	8.12	6.90	1.22	Included
17	17-Jul	09:15-10:52	9.64	8.25	1.39	Included
18	17-Jul	14:08-15:46	7.99	8.14	-0.16	Included
Arithmetic Mean of all runs			13.62	12.43	1.19	mg/wsm^3

Total valid runs	15	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		13.40	12.41	0.99 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.41 mg/wsm^3
Factor:	0.93	Relative Accuracy		11.32%

Runs included in RA calculation	12	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		11.41	10.69	0.72 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.34 mg/wsm^3
Factor:	0.94	Relative Accuracy		9.90%

Runs with Hg below 10 mg/wsm^3	8	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		8.47	7.73	0.74 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.47 mg/wsm^3
Factor:	0.91	Relative Accuracy		15.62%

Runs with Hg above 10 mg/wsm^3	7	-------	Arithmetic Means	-------
		GE/PSA	OH	Difference
		19.04	17.76	1.28 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.80 mg/wsm^3
Factor:	0.93	Relative Accuracy		11.71%

RATA of Ohio Lumex using "As Recorded" Measurements

Concentrations corrected to 20°C, wet basis

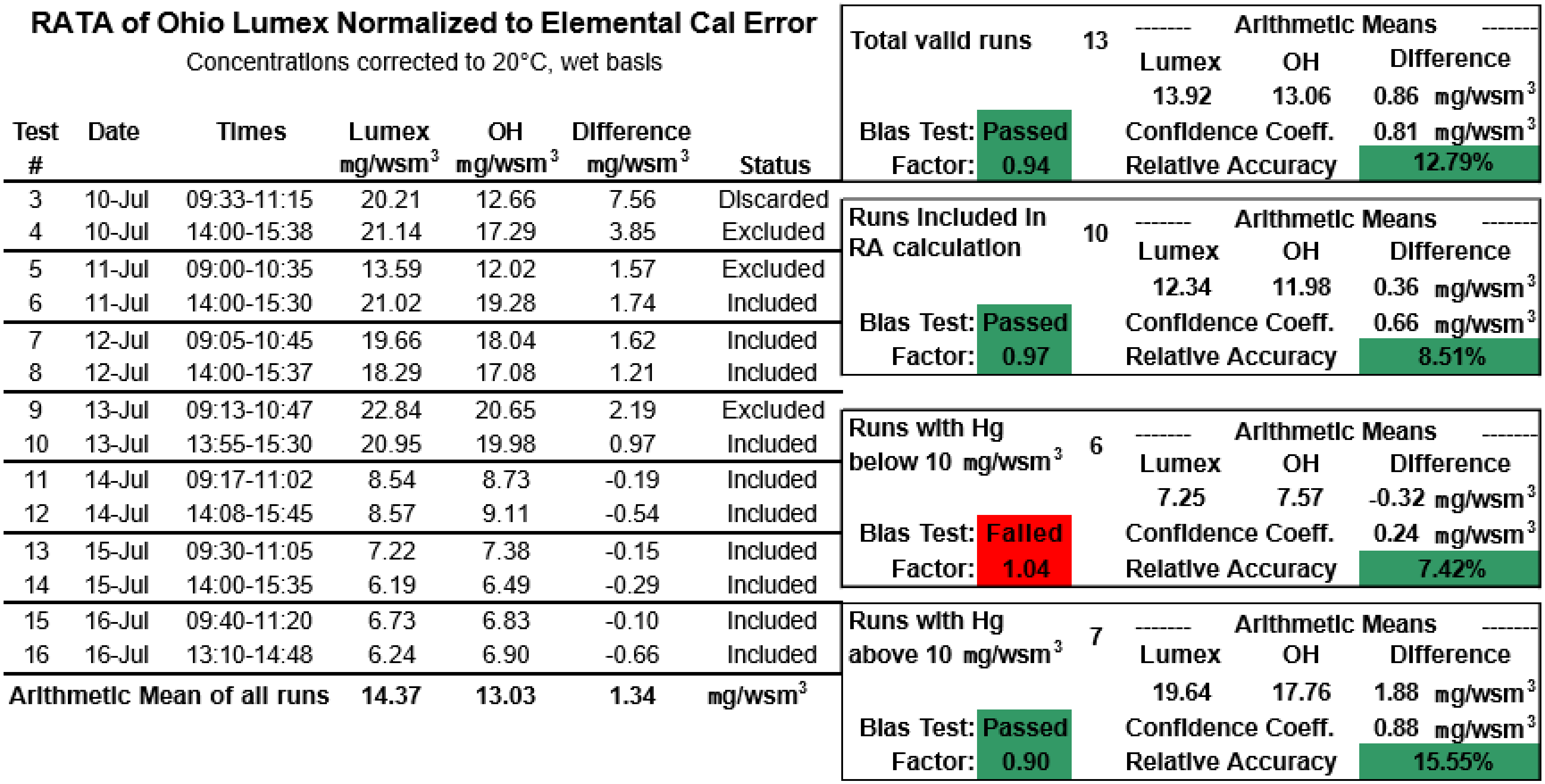
Test #	Date	Times	Lumex mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	19.74	12.66	7.08	Discarded
4	10-Jul	14:00-15:38	20.63	17.29	3.34	Excluded
5	11-Jul	09:00-10:35	13.35	12.02	1.33	Excluded
6	11-Jul	14:00-15:30	20.52	19.28	1.24	Included
7	12-Jul	09:05-10:45	19.20	18.04	1.16	Included
8	12-Jul	14:00-15:37	17.89	17.08	0.80	Included
9	13-Jul	09:13-10:47	22.27	20.65	1.62	Excluded
10	13-Jul	13:55-15:30	20.45	19.98	0.47	Included
11	14-Jul	09:17-11:02	8.47	8.73	-0.26	Included
12	14-Jul	14:08-15:45	8.51	9.11	-0.61	Included
13	15-Jul	09:30-11:05	7.21	7.38	-0.17	Included
14	15-Jul	14:00-15:35	6.21	6.49	-0.27	Included
15	16-Jul	09:40-11:20	6.73	6.83	-0.10	Included
16	16-Jul	13:10-14:48	6.26	6.90	-0.64	Included
Arithmetic Mean of all runs			**14.10**	**13.03**	**1.07**	mg/wsm^3

Total valid runs	**13**	-------	**Arithmetic Means**	-------
		Lumex	**OH**	**Difference**
		13.67	**13.06**	**0.61** mg/wsm^3
Bias Test:	**Passed**	**Confidence Coeff.**		**0.69** mg/wsm^3
Factor:	**0.96**	**Relative Accuracy**		**9.92%**

Runs included in RA calculation	**10**	-------	**Arithmetic Means**	-------
		Lumex	**OH**	**Difference**
		12.14	**11.98**	**0.16** mg/wsm^3
Bias Test:	**Passed**	**Confidence Coeff.**		**0.50** mg/wsm^3
Factor:	**0.99**	**Relative Accuracy**		**5.55%**

Runs with Hg below 10 mg/wsm^3	**6**	-------	**Arithmetic Means**	-------
		Lumex	**OH**	**Difference**
		7.23	**7.57**	**-0.34** mg/wsm^3
Bias Test:	**Failed**	**Confidence Coeff.**		**0.24** mg/wsm^3
Factor:	**1.05**	**Relative Accuracy**		**7.65%**

Runs with Hg above 10 mg/wsm^3	**7**	-------	**Arithmetic Means**	-------
		Lumex	**OH**	**Difference**
		19.19	**17.76**	**1.42** mg/wsm^3
Bias Test:	**Passed**	**Confidence Coeff.**		**0.86** mg/wsm^3
Factor:	**0.93**	**Relative Accuracy**		**12.83%**



RATA of Ohio Lumex Normalized to Elemental Cal Error

Concentrations corrected to 20°C, wet basis

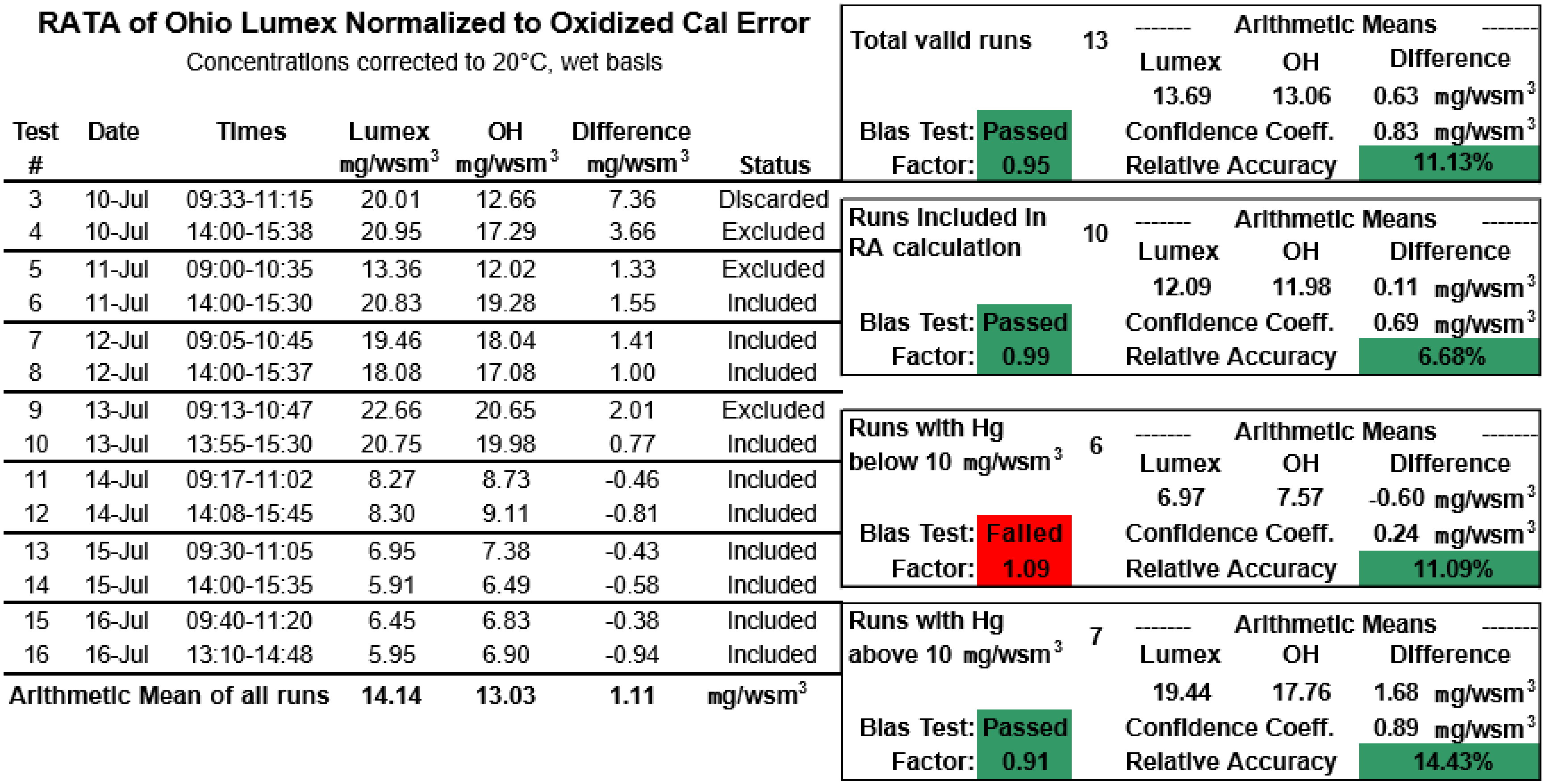
Test #	Date	Times	Lumex mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	20.21	12.66	7.56	Discarded
4	10-Jul	14:00-15:38	21.14	17.29	3.85	Excluded
5	11-Jul	09:00-10:35	13.59	12.02	1.57	Excluded
6	11-Jul	14:00-15:30	21.02	19.28	1.74	Included
7	12-Jul	09:05-10:45	19.66	18.04	1.62	Included
8	12-Jul	14:00-15:37	18.29	17.08	1.21	Included
9	13-Jul	09:13-10:47	22.84	20.65	2.19	Excluded
10	13-Jul	13:55-15:30	20.95	19.98	0.97	Included
11	14-Jul	09:17-11:02	8.54	8.73	-0.19	Included
12	14-Jul	14:08-15:45	8.57	9.11	-0.54	Included
13	15-Jul	09:30-11:05	7.22	7.38	-0.15	Included
14	15-Jul	14:00-15:35	6.19	6.49	-0.29	Included
15	16-Jul	09:40-11:20	6.73	6.83	-0.10	Included
16	16-Jul	13:10-14:48	6.24	6.90	-0.66	Included
Arithmetic Mean of all runs			**14.37**	**13.03**	**1.34**	**mg/wsm^3**

Total valid runs	**13**	**------- Arithmetic Means -------**		
		Lumex	**OH**	**Difference**
		13.92	**13.06**	**0.86 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.81 mg/wsm^3**
Factor:	**0.94**	**Relative Accuracy**		**12.79%**

Runs Included in RA calculation	**10**	**------- Arithmetic Means -------**		
		Lumex	**OH**	**Difference**
		12.34	**11.98**	**0.36 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.66 mg/wsm^3**
Factor:	**0.97**	**Relative Accuracy**		**8.51%**

Runs with Hg below 10 mg/wsm^3	**6**	**------- Arithmetic Means -------**		
		Lumex	**OH**	**Difference**
		7.25	**7.57**	**-0.32 mg/wsm^3**
Bias Test:	**Failed**	**Confidence Coeff.**		**0.24 mg/wsm^3**
Factor:	**1.04**	**Relative Accuracy**		**7.42%**

Runs with Hg above 10 mg/wsm^3	**7**	**------- Arithmetic Means -------**		
		Lumex	**OH**	**Difference**
		19.64	**17.76**	**1.88 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.88 mg/wsm^3**
Factor:	**0.90**	**Relative Accuracy**		**15.55%**



RATA of Ohio Lumex Normalized to Oxidized Cal Error

Concentrations corrected to 20°C, wet basis

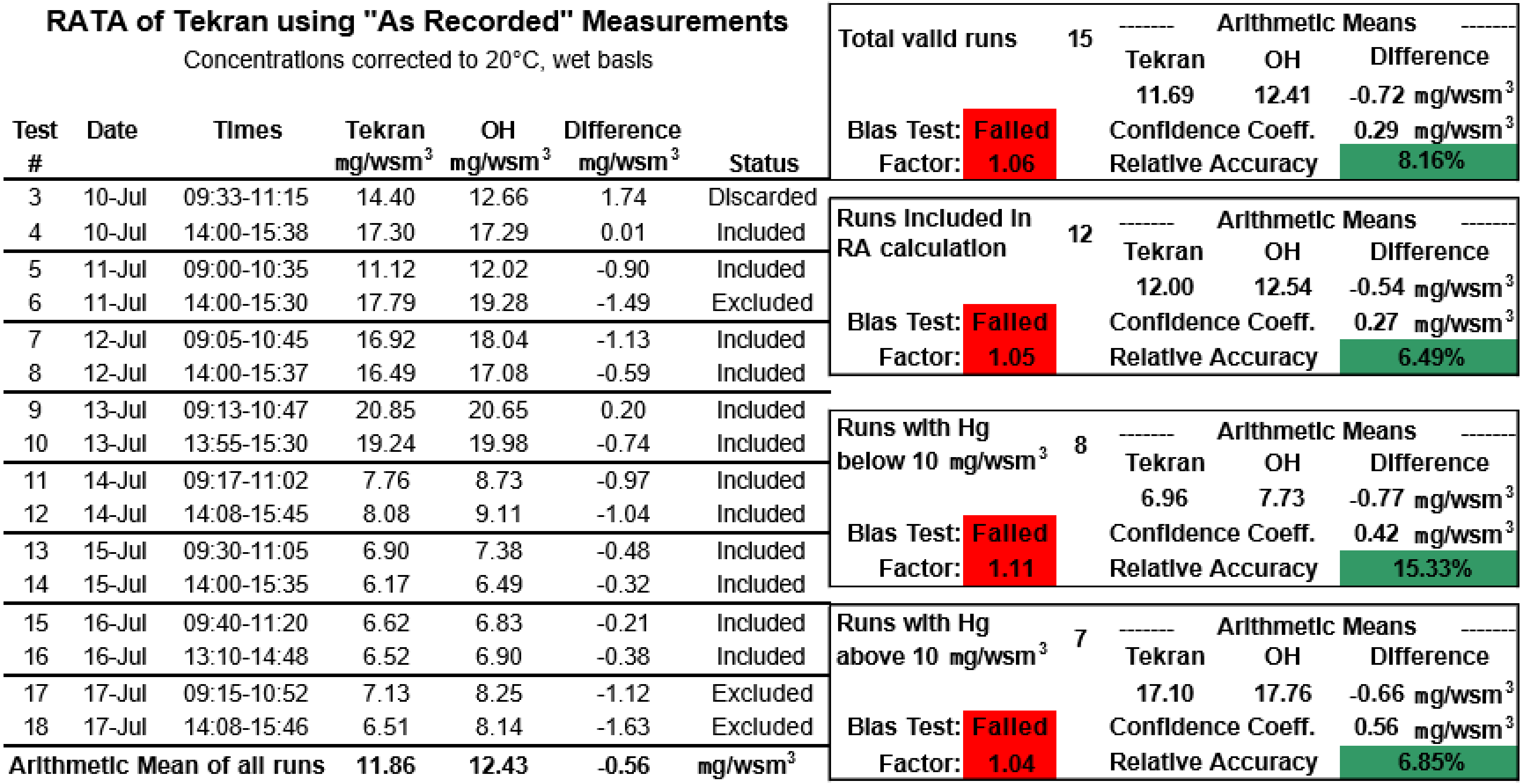
Test #	Date	Times	Lumex mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	20.01	12.66	7.36	Discarded
4	10-Jul	14:00-15:38	20.95	17.29	3.66	Excluded
5	11-Jul	09:00-10:35	13.36	12.02	1.33	Excluded
6	11-Jul	14:00-15:30	20.83	19.28	1.55	Included
7	12-Jul	09:05-10:45	19.46	18.04	1.41	Included
8	12-Jul	14:00-15:37	18.08	17.08	1.00	Included
9	13-Jul	09:13-10:47	22.66	20.65	2.01	Excluded
10	13-Jul	13:55-15:30	20.75	19.98	0.77	Included
11	14-Jul	09:17-11:02	8.27	8.73	-0.46	Included
12	14-Jul	14:08-15:45	8.30	9.11	-0.81	Included
13	15-Jul	09:30-11:05	6.95	7.38	-0.43	Included
14	15-Jul	14:00-15:35	5.91	6.49	-0.58	Included
15	16-Jul	09:40-11:20	6.45	6.83	-0.38	Included
16	16-Jul	13:10-14:48	5.95	6.90	-0.94	Included
Arithmetic Mean of all runs			**14.14**	**13.03**	**1.11**	mg/wsm^3

Total valid runs	13	------- Arithmetic Means -------		
		Lumex	OH	Difference
		13.69	13.06	0.63 mg/wsm^3
Bias Test:	🟩 Passed	Confidence Coeff.		0.83 mg/wsm^3
Factor:	🟩 0.95	Relative Accuracy		🟩 11.13%

Runs included in RA calculation	10	------- Arithmetic Means -------		
		Lumex	OH	Difference
		12.09	11.98	0.11 mg/wsm^3
Bias Test:	🟩 Passed	Confidence Coeff.		0.69 mg/wsm^3
Factor:	🟩 0.99	Relative Accuracy		🟩 6.68%

Runs with Hg below 10 mg/wsm^3	6	------- Arithmetic Means -------		
		Lumex	OH	Difference
		6.97	7.57	-0.60 mg/wsm^3
Bias Test:	🟥 Failed	Confidence Coeff.		0.24 mg/wsm^3
Factor:	🟥 1.09	Relative Accuracy		🟩 11.09%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Lumex	OH	Difference
		19.44	17.76	1.68 mg/wsm^3
Bias Test:	🟩 Passed	Confidence Coeff.		0.89 mg/wsm^3
Factor:	🟩 0.91	Relative Accuracy		🟩 14.43%



RATA of Tekran using "As Recorded" Measurements

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Tekran mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	14.40	12.66	1.74	Discarded
4	10-Jul	14:00-15:38	17.30	17.29	0.01	Included
5	11-Jul	09:00-10:35	11.12	12.02	-0.90	Included
6	11-Jul	14:00-15:30	17.79	19.28	-1.49	Excluded
7	12-Jul	09:05-10:45	16.92	18.04	-1.13	Included
8	12-Jul	14:00-15:37	16.49	17.08	-0.59	Included
9	13-Jul	09:13-10:47	20.85	20.65	0.20	Included
10	13-Jul	13:55-15:30	19.24	19.98	-0.74	Included
11	14-Jul	09:17-11:02	7.76	8.73	-0.97	Included
12	14-Jul	14:08-15:45	8.08	9.11	-1.04	Included
13	15-Jul	09:30-11:05	6.90	7.38	-0.48	Included
14	15-Jul	14:00-15:35	6.17	6.49	-0.32	Included
15	16-Jul	09:40-11:20	6.62	6.83	-0.21	Included
16	16-Jul	13:10-14:48	6.52	6.90	-0.38	Included
17	17-Jul	09:15-10:52	7.13	8.25	-1.12	Excluded
18	17-Jul	14:08-15:46	6.51	8.14	-1.63	Excluded
Arithmetic Mean of all runs			**11.86**	**12.43**	**-0.56**	mg/wsm^3

Total valid runs	15	------- Arithmetic Means -------		
		Tekran	OH	Difference
		11.69	12.41	-0.72 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.29 mg/wsm^3
Factor:	1.06	Relative Accuracy		8.16%

Runs included in RA calculation	12	------- Arithmetic Means -------		
		Tekran	OH	Difference
		12.00	12.54	-0.54 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.27 mg/wsm^3
Factor:	1.05	Relative Accuracy		6.49%

Runs with Hg below 10 mg/wsm^3	8	------- Arithmetic Means -------		
		Tekran	OH	Difference
		6.96	7.73	-0.77 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.42 mg/wsm^3
Factor:	1.11	Relative Accuracy		15.33%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Tekran	OH	Difference
		17.10	17.76	-0.66 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.56 mg/wsm^3
Factor:	1.04	Relative Accuracy		6.85%

RATA of Tekran Normalized to Elemental Calibration Error

Concentrations corrected to 20°C, wet basis

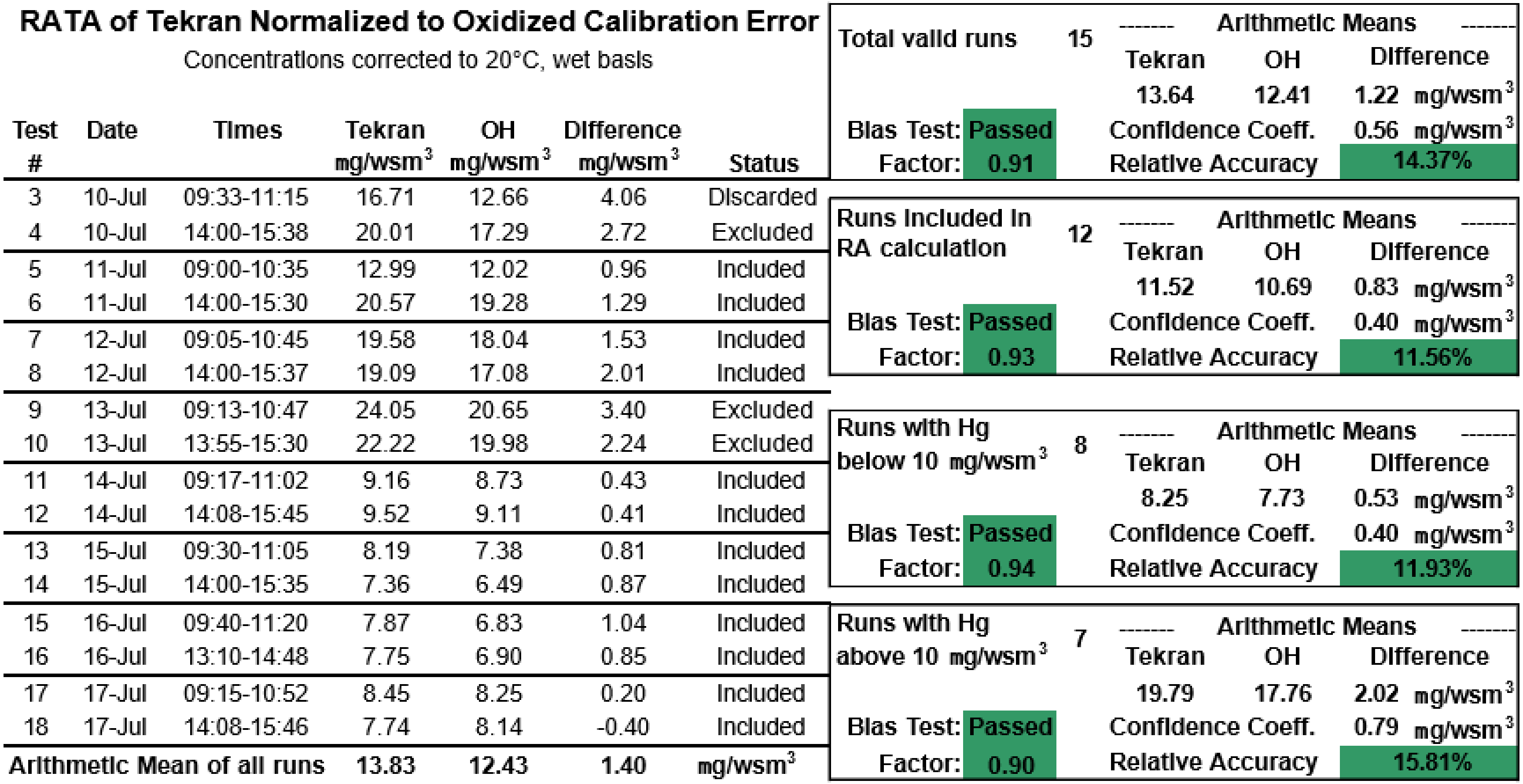
Test #	Date	Times	Tekran mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.29	12.66	3.63	Discarded
4	10-Jul	14:00-15:38	19.57	17.29	2.28	Excluded
5	11-Jul	09:00-10:35	12.58	12.02	0.56	Included
6	11-Jul	14:00-15:30	20.12	19.28	0.84	Included
7	12-Jul	09:05-10:45	19.14	18.04	1.09	Included
8	12-Jul	14:00-15:37	18.65	17.08	1.57	Included
9	13-Jul	09:13-10:47	23.58	20.65	2.93	Excluded
10	13-Jul	13:55-15:30	21.76	19.98	1.78	Excluded
11	14-Jul	09:17-11:02	8.78	8.73	0.05	Included
12	14-Jul	14:08-15:45	9.14	9.11	0.02	Included
13	15-Jul	09:30-11:05	7.81	7.38	0.43	Included
14	15-Jul	14:00-15:35	6.98	6.49	0.50	Included
15	16-Jul	09:40-11:20	7.49	6.83	0.67	Included
16	16-Jul	13:10-14:48	7.38	6.90	0.48	Included
17	17-Jul	09:15-10:52	8.07	8.25	-0.18	Included
18	17-Jul	14:08-15:46	7.36	8.14	-0.78	Included
Arithmetic Mean of all runs			**13.42**	**12.43**	**0.99**	mg/wsm^3

Total valid runs	15	------- Arithmetic Means -------		
		Tekran	OH	Difference
		13.23	12.41	0.82 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.54 mg/wsm^3
Factor:	0.94	Relative Accuracy		10.95%

Runs included in RA calculation	12	------- Arithmetic Means -------		
		Tekran	OH	Difference
		11.13	10.69	0.44 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.39 mg/wsm^3
Factor:	0.96	Relative Accuracy		7.74%

Runs with Hg below 10 mg/wsm^3	8	------- Arithmetic Means -------		
		Tekran	OH	Difference
		7.88	7.73	0.15 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.40 mg/wsm^3
Factor:	0.98	Relative Accuracy		7.06%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Tekran	OH	Difference
		19.34	17.76	1.58 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.77 mg/wsm^3
Factor:	0.92	Relative Accuracy		13.25%



RATA of Tekran Normalized to Oxidized Calibration Error

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Tekran mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.71	12.66	4.06	Discarded
4	10-Jul	14:00-15:38	20.01	17.29	2.72	Excluded
5	11-Jul	09:00-10:35	12.99	12.02	0.96	Included
6	11-Jul	14:00-15:30	20.57	19.28	1.29	Included
7	12-Jul	09:05-10:45	19.58	18.04	1.53	Included
8	12-Jul	14:00-15:37	19.09	17.08	2.01	Included
9	13-Jul	09:13-10:47	24.05	20.65	3.40	Excluded
10	13-Jul	13:55-15:30	22.22	19.98	2.24	Excluded
11	14-Jul	09:17-11:02	9.16	8.73	0.43	Included
12	14-Jul	14:08-15:45	9.52	9.11	0.41	Included
13	15-Jul	09:30-11:05	8.19	7.38	0.81	Included
14	15-Jul	14:00-15:35	7.36	6.49	0.87	Included
15	16-Jul	09:40-11:20	7.87	6.83	1.04	Included
16	16-Jul	13:10-14:48	7.75	6.90	0.85	Included
17	17-Jul	09:15-10:52	8.45	8.25	0.20	Included
18	17-Jul	14:08-15:46	7.74	8.14	-0.40	Included
Arithmetic Mean of all runs			13.83	12.43	1.40	mg/wsm^3

Total valid runs	15	------- Arithmetic Means -------		
		Tekran	OH	Difference
		13.64	12.41	1.22 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.56 mg/wsm^3
Factor:	0.91	Relative Accuracy		14.37%

Runs Included in RA calculation	12	------- Arithmetic Means -------		
		Tekran	OH	Difference
		11.52	10.69	0.83 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.40 mg/wsm^3
Factor:	0.93	Relative Accuracy		11.56%

Runs with Hg below 10 mg/wsm^3	8	------- Arithmetic Means -------		
		Tekran	OH	Difference
		8.25	7.73	0.53 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.40 mg/wsm^3
Factor:	0.94	Relative Accuracy		11.93%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Tekran	OH	Difference
		19.79	17.76	2.02 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.79 mg/wsm^3
Factor:	0.90	Relative Accuracy		15.81%

RATA of Tekran Normalized to Integrity/Drift Checks

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Tekran mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.62	12.66	3.96	Discarded
4	10-Jul	14:00-15:38	19.96	17.29	2.67	Excluded
5	11-Jul	09:00-10:35	12.99	12.02	0.97	Included
6	11-Jul	14:00-15:30	20.78	19.28	1.50	Included
7	12-Jul	09:05-10:45	20.24	18.04	2.20	Included
8	12-Jul	14:00-15:37	19.72	17.08	2.64	Included
9	13-Jul	09:13-10:47	24.77	20.65	4.12	Excluded
10	13-Jul	13:55-15:30	22.85	19.98	2.88	Excluded
11	14-Jul	09:17-11:02	9.12	8.73	0.39	Included
12	14-Jul	14:08-15:45	9.49	9.11	0.38	Included
13	15-Jul	09:30-11:05	8.22	7.38	0.84	Included
14	15-Jul	14:00-15:35	7.35	6.49	0.87	Included
15	16-Jul	09:40-11:20	7.79	6.83	0.96	Included
16	16-Jul	13:10-14:48	7.67	6.90	0.77	Included
17	17-Jul	09:15-10:52	8.30	8.25	0.05	Included
18	17-Jul	14:08-15:46	7.57	8.14	-0.57	Included
Arithmetic Mean of all runs			13.97	12.43	1.54	mg/wsm^3

Total valid runs	15	-------	Arithmetic Means	-------
		Tekran	OH	Difference
		13.79	12.41	1.38 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.70 mg/wsm^3
Factor:	0.90	Relative Accuracy		16.76%

Runs included in RA calculation	12	-------	Arithmetic Means	-------
		Tekran	OH	Difference
		11.61	10.69	0.92 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.56 mg/wsm^3
Factor:	0.92	Relative Accuracy		13.82%

Runs with Hg below 10 mg/wsm^3	8	-------	Arithmetic Means	-------
		Tekran	OH	Difference
		8.19	7.73	0.46 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.44 mg/wsm^3
Factor:	0.94	Relative Accuracy		11.63%

Runs with Hg above 10 mg/wsm^3	7	-------	Arithmetic Means	-------
		Tekran	OH	Difference
		20.19	17.76	2.43 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.94 mg/wsm^3
Factor:	0.88	Relative Accuracy		18.95%

RATA of Thermo using "As Recorded" Measurements

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Thermo mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	16.05	12.66	3.39	Discarded
4	10-Jul	14:00-15:38	19.78	17.29	2.49	Excluded
5	11-Jul	09:00-10:35	12.61	12.02	0.59	Included
6	11-Jul	14:00-15:30	21.08	19.28	1.80	Excluded
7	12-Jul	09:05-10:45	18.41	18.04	0.37	Included
8	12-Jul	14:00-15:37	17.89	17.08	0.81	Included
9	13-Jul	09:13-10:47	22.38	20.65	1.73	Excluded
10	13-Jul	13:55-15:30	21.10	19.98	1.12	Included
11	14-Jul	09:17-11:02	8.61	8.73	-0.12	Included
12	14-Jul	14:08-15:45	9.07	9.11	-0.04	Included
13	15-Jul	09:30-11:05	7.47	7.38	0.09	Included
14	15-Jul	14:00-15:35	6.67	6.49	0.19	Included
15	16-Jul	09:40-11:20	7.04	6.83	0.21	Included
16	16-Jul	13:10-14:48	7.03	6.90	0.13	Included
17	17-Jul	09:15-10:52	7.75	8.25	-0.50	Included
18	17-Jul	14:08-15:46	7.05	8.14	-1.09	Included
Arithmetic Mean of all runs			**13.12**	**12.43**	**0.70**	mg/wsm^3

Total valid runs	**15**	-------	**Arithmetic Means**	-------
		Thermo	**OH**	**Difference**
		12.93	**12.41**	**0.52 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.52 mg/wsm^3**
Factor:	**0.96**	**Relative Accuracy**		**8.37%**

Runs Included in RA calculation	**12**	-------	**Arithmetic Means**	-------
		Thermo	**OH**	**Difference**
		10.89	**10.75**	**0.15 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.37 mg/wsm^3**
Factor:	**0.99**	**Relative Accuracy**		**4.78%**

Runs with Hg below 10 mg/wsm^3	**8**	-------	**Arithmetic Means**	-------
		Thermo	**OH**	**Difference**
		7.59	**7.73**	**-0.14 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.37 mg/wsm^3**
Factor:	**1.02**	**Relative Accuracy**		**6.66%**

Runs with Hg above 10 mg/wsm^3	**7**	-------	**Arithmetic Means**	-------
		Thermo	**OH**	**Difference**
		19.04	**17.76**	**1.27 mg/wsm^3**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.71 mg/wsm^3**
Factor:	**0.93**	**Relative Accuracy**		**11.14%**

RATA of Thermo Normalized to Oxidized Calibration Error

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Thermo mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	13.50	12.66	0.84	Discarded
4	10-Jul	14:00-15:38	16.49	17.29	-0.80	Included
5	11-Jul	09:00-10:35	10.75	12.02	-1.28	Included
6	11-Jul	14:00-15:30	17.53	19.28	-1.75	Included
7	12-Jul	09:05-10:45	15.40	18.04	-2.65	Excluded
8	12-Jul	14:00-15:37	14.97	17.08	-2.11	Included
9	13-Jul	09:13-10:47	18.58	20.65	-2.07	Included
10	13-Jul	13:55-15:30	17.55	19.98	-2.43	Excluded
11	14-Jul	09:17-11:02	7.54	8.73	-1.19	Included
12	14-Jul	14:08-15:45	7.91	9.11	-1.20	Included
13	15-Jul	09:30-11:05	6.63	7.38	-0.75	Included
14	15-Jul	14:00-15:35	5.99	6.49	-0.50	Included
15	16-Jul	09:40-11:20	6.28	6.83	-0.55	Included
16	16-Jul	13:10-14:48	6.27	6.90	-0.62	Included
17	17-Jul	09:15-10:52	6.85	8.25	-1.40	Included
18	17-Jul	14:08-15:46	6.30	8.14	-1.85	Excluded
Arithmetic Mean of all runs			11.16	12.43	-1.27	mg/wsm^3

Total valid runs	15	------- Arithmetic Means -------		
		Thermo	OH	Difference
		11.00	12.41	-1.41 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.39 mg/wsm^3
Factor:	1.13	Relative Accuracy		14.49%

Runs Included in RA calculation	12	------- Arithmetic Means -------		
		Thermo	OH	Difference
		10.48	11.67	-1.18 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.36 mg/wsm^3
Factor:	1.11	Relative Accuracy		13.24%

Runs with Hg below 10 mg/wsm^3	8	------- Arithmetic Means -------		
		Thermo	OH	Difference
		6.72	7.73	-1.01 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.40 mg/wsm^3
Factor:	1.15	Relative Accuracy		18.21%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Thermo	OH	Difference
		15.89	17.76	-1.87 mg/wsm^3
Bias Test:	Failed	Confidence Coeff.		0.60 mg/wsm^3
Factor:	1.12	Relative Accuracy		13.91%

RATA of Thermo Normalized to Integrity/Drift Checks

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	Thermo mg/wsm^3	OH mg/wsm^3	Difference mg/wsm^3	Status
3	10-Jul	09:33-11:15	14.57	12.66	1.91	Discarded
4	10-Jul	14:00-15:38	17.96	17.29	0.67	Included
5	11-Jul	09:00-10:35	11.55	12.02	-0.47	Included
6	11-Jul	14:00-15:30	19.31	19.28	0.03	Included
7	12-Jul	09:05-10:45	17.46	18.04	-0.58	Included
8	12-Jul	14:00-15:37	16.96	17.08	-0.12	Included
9	13-Jul	09:13-10:47	21.44	20.65	0.79	Excluded
10	13-Jul	13:55-15:30	20.21	19.98	0.23	Included
11	14-Jul	09:17-11:02	8.79	8.73	0.06	Included
12	14-Jul	14:08-15:45	9.26	9.11	0.14	Included
13	15-Jul	09:30-11:05	7.37	7.38	-0.01	Included
14	15-Jul	14:00-15:35	6.58	6.49	0.10	Included
15	16-Jul	09:40-11:20	6.82	6.83	0.00	Included
16	16-Jul	13:10-14:48	6.82	6.90	-0.08	Included
17	17-Jul	09:15-10:52	7.69	8.25	-0.56	Excluded
18	17-Jul	14:08-15:46	7.00	8.14	-1.14	Excluded
Arithmetic Mean of all runs			12.49	12.43	0.06	mg/wsm^3

Total valid runs	15	------- Arithmetic Means -------		
		Thermo	OH	Difference
		12.35	12.41	-0.06 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.27 mg/wsm^3
Factor:	1.01	Relative Accuracy		2.67%

Runs Included in RA calculation	12	------- Arithmetic Means -------		
		Thermo	OH	Difference
		12.42	12.43	0.00 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.20 mg/wsm^3
Factor:	1.00	Relative Accuracy		1.65%

Runs with Hg below 10 mg/wsm^3	8	------- Arithmetic Means -------		
		Thermo	OH	Difference
		7.54	7.73	-0.19 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.37 mg/wsm^3
Factor:	1.02	Relative Accuracy		7.20%

Runs with Hg above 10 mg/wsm^3	7	------- Arithmetic Means -------		
		Thermo	OH	Difference
		17.84	17.76	0.08 mg/wsm^3
Bias Test:	Passed	Confidence Coeff.		0.49 mg/wsm^3
Factor:	1.00	Relative Accuracy		3.19%