

**Long-Term Field Evaluation of Mercury
(Hg) Continuous Emission Monitoring
Systems: Coal-Fired Power Plant
Burning Eastern Bituminous Coal
and Equipped With Selective Catalytic
Reduction (SCR), Electrostatic
Precipitator (ESP), and
Wet Scrubber:
Field Activities From
November 2004 to September 2005**

Final Report

Volume 1 (of 3)—Text

**For
U.S. Environmental Protection Agency**

EPA Contract GS-10F-0127J

MRI Project No. 110489

November 29, 2006

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**For
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Measurement Technology Group
Research Triangle Park, North Carolina 27711**

Attn: Mr. Bill Grimley

EPA Contract GS-10F-0127J

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Preface

This report was prepared by Midwest Research Institute (MRI) for the U.S. Environmental Protection Agency (EPA) under Contract No. GS-10F-0127J. Mr. Bill Grimley is the EPA Project Manager. Field work activities for the report were performed from November 2004 through September 2005. This report was prepared on a follow-up contract as the original contract expired in September, 2005.

The test program was conducted in MRI's Applied Engineering Division, with Mr. John Hosenfeld serving as MRI's Project Leader. In this report, MRI presents a summary of activities surrounding installation of mercury Continuous Emissions Monitoring System (Hg CEMS), certification results including the final Relative Accuracy Test Audit (RATA), and the long-term monitoring phase.

MIDWEST RESEARCH INSTITUTE



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September 29, 2006

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Section 1.

Introduction

1.1 Study Overview

The US Environmental Protection Agency (EPA) has recently promulgated regulations for mercury (Hg) emissions from coal-fired electric utilities, which include provisions for use of mercury Continuous Emission Monitoring Systems (Hg CEMS) as well as other monitoring approaches (FR 5/18/05, 70(95), 28606). The implementation of Hg CEMS could be enhanced greatly by the collection of data demonstrating application of monitoring technologies to the source category. As a result, EPA conducted the field testing described to evaluate Hg CEMS technologies on a long-term continuous basis.

The purpose of this field test program was to collect data to assess the ability of commercially available Hg CEMS to provide reliable and accurate data over an extended time period, while meeting certification, durability, data availability, and set-up/maintenance requirements. In particular, data were collected to assess the ability of the Hg CEMS to satisfy the requirements of Performance Specification 12A (PS-12A) and the 40 *CFR* Part 75 mercury monitoring provisions (FR 5/18/05, 70(95), 28606).

This report presents a summary of the certification test results and other information collected from November 2004, through September 2005. The test facility was a coal-fired utility boiler burning eastern bituminous coal and equipped with a selective catalytic reduction (SCR) system with ammonia injection that is operated during ozone season (May 1 through September 30), an electrostatic precipitator, and a wet limestone scrubber.

The work was separated into two phases, Phase 1 and Phase 2. Phase 1 field work was performed from November 2004 through February 2005 and consisted of:

- Installation and shakedown of four mercury Continuous Emission Monitoring Systems (Hg CEMS);
- Phase 1 certification testing during the first two weeks of continuous Hg CEMS operation (with Relative Accuracy Test Audit [RATA], February 22 - 26);
- Evaluation while the selective catalytic reduction (SCR) system was bypassed; and
- Information gathering on the Hg CEMS operation, durability, and maintenance.

Phase 2 field work was performed from March through September 2005 and consisted of:

- Installation of two additional Hg CEMS in early May (in addition to the four which were previously in operation);
- Phase 2 certification testing after more than a month of continuous operation by the additional two Hg CEMS (with RATA July 7-12);

- Removal of two Hg CEMS when vendors elected to have their systems removed from the test program;
- Evaluation while the SCR was in operation; and
- Information gathering on the Hg CEMS operation, durability, and maintenance.

1.2 Performance Testing

Table 1-1 summarizes the certification test acceptance criteria used during this test program. Sorbent trap monitoring was conducted according to 40 *CFR* Part 75 Appendix K (Appendix K) by RMB Associates, and the data are provided in a separate report. Dynamic spiking and data collection were also performed using the Tekran Hg CEMS to assess potential criteria for a draft instrumental test method for mercury; results of this test are provided in Section 4.1.3 of this report.

Table 1-1. Summary of Certification and Relative Accuracy Test Performance Criteria

Activity	Frequency	Gas type	Performance criteria	Reference
7-day Calibration Error. Check at 2 pts, zero and upscale. ^a	Once per day for 7-day consecutive days	Elemental mercury	≤ 5% of span; or, if spanned at lowest range of 10 µg/m ³ , then ≤ 1 µg/m ³	Part 75, App A, Section 3.1; (FR 5/18/05, 70(95), 28691)
Linearity Check at 3 pts: low, mid, and high. ^b Performed in nonrepetitive triplicates.	Once, at beginning of certification test	Elemental mercury	≤ 10% of ref tag value; or ≤ 1 µg/m ³ , whichever is less restrictive	Part 75, App A, Section 3.2; (FR 5/18/05, 70(95), 28691)
System Integrity. Check at 3 pts: zero, mid, and high. ^b	Once, at beginning of certification test	Oxidized mercury	≤ 5% of span	Part 75, App A, Section 3.2; (FR 5/18/05, 70(95), 28691) and PS-12A, Sections 8.3 and 13.1
Cycle Time	Once, at beginning of certification test	Elemental mercury	≤ 15 min	Same as existing Part 75, App A, Section 3.5
Relative Accuracy (RA), performed after certification checks	One set of 12 duplicate test runs, at beginning of Phase 1 evaluation test program, and again during Phase 2 long-term evaluation	Stack Gas	≤ 20%; or for low emitters with avg. conc. < 5 µg/m ³ , ≤ 1 µg/m ³ difference	Part 75, App. A, Section 3.3 (FR 5/18/05, 70(95), 28691) and PS-12A Section 13.4

^a Conducting the 7-day Cal Error test allows for determination of the Zero and Upscale Drift specification of PS-12A, which cannot exceed 5% of span (Sections 13.2 and 13.3).

^b By collecting linearity check data and system integrity check data (per Part 75 requirements), the PS-12A Measurement Error and Converter Efficiency tests are also effectively performed, except that the PS-12A criterion is ≤5% of span with no alternative criteria when the stack concentration is ≤1 µg/m³.

1.3 Test Site

The facility at which the evaluation testing was conducted consists of a coal-fired generating unit referred to as Unit 1. Unit 1 is 14 years old with a capacity of 550 MW. The facility was designed with state-of-the-art pollution controls that include ammonia injection and selective catalytic reduction (SCR) for NO_x control, an electrostatic precipitator for particulate control, and a wet limestone slurry scrubber for SO₂ control. The facility has been permitted according to EPA criteria for Best Achievable Control Technology (BACT). Fuel for the facility is eastern bituminous coal.

The sampling location was at ~ 350 ft up the stack. Section 3 provides further details on the test facility and sampling locations.

1.4 Summary of Systems Evaluated

This study was designed to evaluate Hg CEMS that use the latest technology, i.e., dry converter or alternative systems rather than the older wet converter systems. A summary of the Hg CEMS that were evaluated during Phase 1 using the performance certification test criteria is provided in Table 1-2. A summary of the Hg CEMS that were evaluated during Phase 2 is provided in Table 1-3.

Table 1-2. Phase 1 Summary of Hg CEMS Evaluated

Parameter	Forney/Genesis CEM	Horiba/Nippon DM-6D	Tekran 3300	Thermo Electron
Gas Conditioning System	Glass fiber particulate filter, thermocatalytic converter, chilled KOH impinger, chilled moisture removal impinger, acid mist filter.	Glass fiber particulate filter, thermocatalytic converter, vapor separator, chilled dehumidifier tube at probe. Chilled KOH impinger at detector.	Inertial filter and dilution system at probe. Thermo-catalytic converter, water wash system at sample conditioner.	Inertial filter, dilution system, thermocatalytic converter at probe.
Mercury Detector	Cold vapor atomic absorption	Cold vapor atomic absorption	Cold vapor atomic fluorescence	Cold vapor atomic fluorescence
Measurement Range	0-50 µg/m ³	0-50 µg/m ³	Dilution system allows multiple ranges	0-15 µg/m ³
Resolution	0.1 µg/m ³	0.1 µg/m ³	0.001 µg/m ³	0.01 µg/m ³
Response Delay	Update every 1 second	Update every 1 second	2.5 minutes per cycle	None. Continuous reading via 4-20 mA output, user configurable time averaging on instrument display.
Sample Flow Rate	3 LPM	0.5 LPM	0.5 LPM	0.75 LPM
Zero Point Adjustment	Automatic, once per hour	Automatic, once per hour	None	Automatic, daily
Daily Calibration Requirements	None. Factory calibrated prior to installation.	None. Factory calibrated prior to installation.	Daily automatic detector calibration via internal Hg gas generator	Daily system calibration via Hg calibration gas generator
Output	4-20 mA	4-20 mA	System control computer	4-20 mA
Reporting Temperature	25°C	0°C	0°C	20°C
Power Supply	110, 208 VAC	110 VAC	110 VAC	110, 220 VAC
Other Utilities Required	None	DI water at probe.	Compressed air, argon gas, DI water, drain.	Compressed air.

Table 1-3. Phase 2 Summary of Hg CEMS Evaluated

Parameter	Durag	Forney/Genesis CEM ¹	Horiba/Nippon DM-6D ²	Opsis	Tekran 3300	Thermo Electron
Gas Conditioning System	Ceramic filter, heated sample line, thermocatalytic converter	NA ¹	NA ²	Inertial filter, dilution system, and thermocatalytic converter at probe	Inertial filter and dilution system at probe. Thermocatalytic converter, water wash system at sample conditioner.	Inertial filter, dilution system, thermocatalytic converter at probe.
Mercury Detector	Cold vapor atomic absorption	NA ¹	NA ²	Cold vapor atomic absorption	Cold vapor atomic fluorescence	Cold vapor atomic fluorescence
Measurement Range	0-20 µg/dscm multiple ranges	NA ¹	NA ²	0-15 µg/m ³	Dilution system allows multiple ranges	0-15 µg/m ³
Resolution	0-1 µg/dscm (0.01 Bg/dscm if required)	NA ¹	NA ²	0.05 µg/m ³	0.001 µg/m ³	0.01 µg/m ³
Response Delay	None. Continuous reading via 4-20 mA output, user configurable time averaging on instrument display.	NA ¹	NA ²	5 minutes per cycle	2.5 minutes per cycle	None. Continuous reading via 4-20 mA output, user configurable time averaging on instrument display.
Sample Flow Rate	2 LPM	NA ¹	NA ²	1.0 LPM	0.5 LPM	0.75 LPM
Zero Point Adjustment	Automatic, every 2 h up to every 99 h	NA ¹	NA ²	None	None	Automatic, daily
Daily Calibration Requirements	Daily system calibration via Hg calibration with gas cylinder, if required (automatic daily calibration module with ionic mercury will be available in 2006)	NA ¹	NA ²	Daily: None Monthly-Quarterly Calibrations	Daily automatic detector calibration via internal Hg gas generator	Daily system calibration via Hg calibration gas generator
Output	4-20 mA	NA ¹	NA ²	4-20 mA/0-10V/RS232	System control computer	4-20 mA
Reporting Temperature	0°C	NA ¹	NA ²	0°C/20°C	0°C	20°C
Power Supply	110, 220 VAC	NA ¹	NA ²	110 VAC	110 VAC	110, 220 VAC
Other Utilities Required	None	NA ¹	NA ²	Compressed instrument air	Compressed air, argon gas, DI water, drain.	Compressed air.

NOTES:

¹ Forney/Genesis CEM: This instrument was withdrawn from the test program late in Phase 2 testing at the vendor's request.

² Horiba/Nippon DM-6D: This instrument was removed at the vendor's request prior to the second RA test series.

The Durag Inc., Forney Corporation/Genesis Laboratory Systems Inc., Opsis Inc., Horiba/Nippon, and ThermoElectron Corporation systems were connected to the MRI data logger via their 4 to 20 mA data outputs. The MRI data logger converted each output to a 0 to 10 VDC signal which was then used to calculate the instruments' readings. The computer display on the MRI data logger was verified to match the display on each of these instruments.

Rather than a 4 to 20 mA output, the Tekran Inc. system provided instrument readings in real-time via its system control computer. The MRI data logger retrieved the data over a local area network installed between the trailer and the stack Hg CEM shelter.

The Horiba International Corporation/Nippon Instruments Corporation CEMS tested in the Phase 1 work was inoperative during Phase 2, and the vendor elected to have their system removed from further testing. The Forney/Genesis CEMS also elected to have their CEMS removed from the test program late in the Phase 2 testing.

1.5 Test Program Organization

The following individuals are the key personnel in the management and execution of this test project:

The EPA Work Assignment Manager (WAM) was:

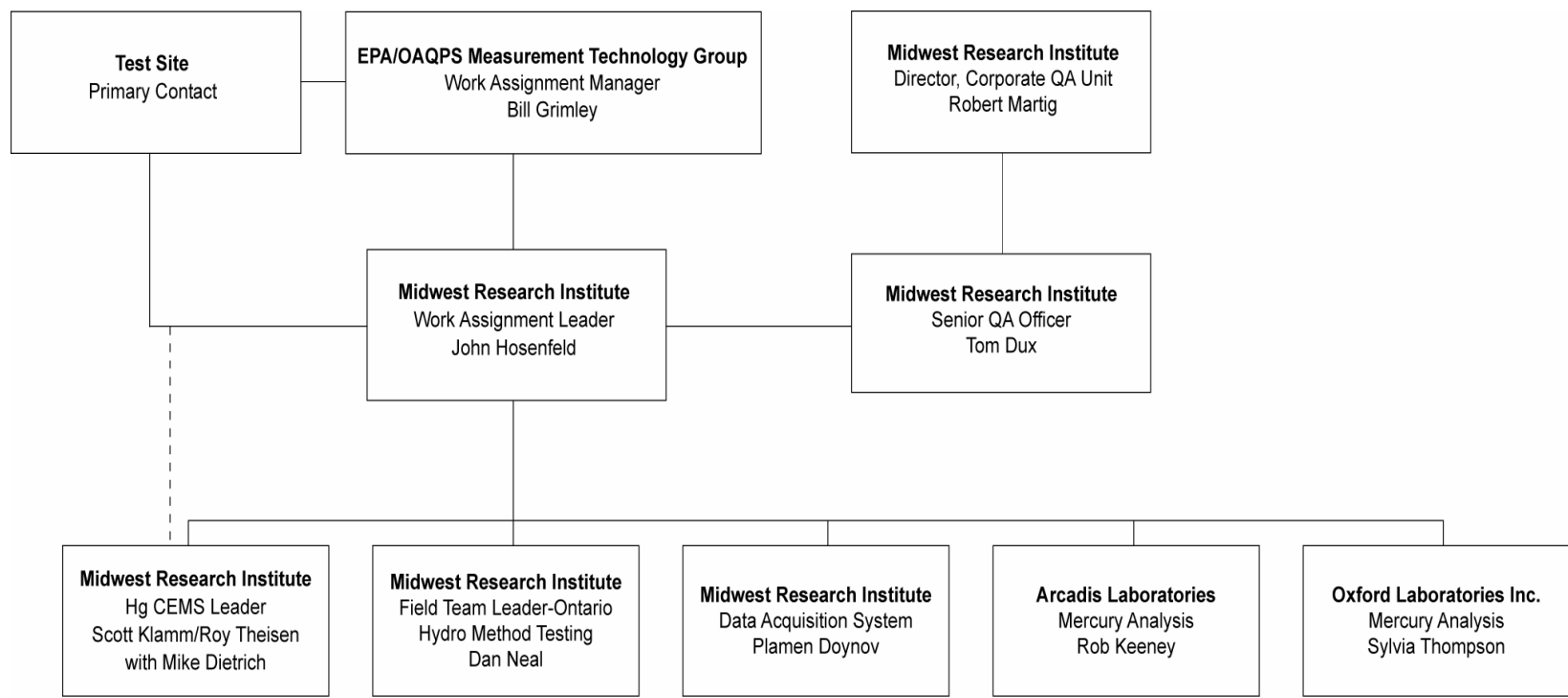
Mr. Bill Grimley
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The MRI Work Assignment Leader (WAL) for this test project was:

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Figure 1-1 presents the test program organization, major lines of communication, names, and phone numbers of responsible individuals. Midwest Research Institute was responsible for the project under contract to EPA's Office of Air Quality Planning and Standards.

The companies supplying the Hg CEMS for evaluation during the performance testing were Durag, Forney/Genesis, Horiba/Nippon Instruments Corporation, Opsis, Tekran, and Thermo Electron. The EPA is appreciative of these vendors for their participation in this test program.



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Figure 1-1. Test Program Organization

Section 2.

Durability, Availability, and Maintenance of CEMS

The following describes the maintenance related to Hg CEMS operation during the commissioning, setup, and ongoing operation of the systems at the test site. Summaries of Phase 1 and 2 maintenance events are provided in Tables 2-1 and 2-2, respectively.

There were two types of maintenance performed on the Hg CEMS: preventative and corrective. Preventative maintenance consisted of tasks performed to prevent system failure. Corrective maintenance consisted of tasks performed to bring the system back into normal operation. Corrective maintenance on the Hg CEMS generally fell onto one of six primary categories related to system components/configurations:

- Calibration
- Temperature Adjustment
- Sample Transfer
- Catalyst/Sample Conditioning
- Filter Replacement
- Analyzer Replacement

Corrective maintenance performed on the systems during the setup phase did not attempt to differentiate between required maintenance caused by a natural instrument failure and maintenance required by operator intervention to system while performing routine checks and measurements. A few examples of maintenance caused by operator intervention are:

- Instrument offset required by unintentional over-pressurization or under-pressurization of the system while introducing daily audit gases.
- Cleaning a blocked orifice caused by introducing contamination to system while making connections for system integrity tests.
- Maintenance caused by accidentally bumping the probe, transfer lines, or analyzer and dislodging accumulated scale or sludge into downstream components.
- Maintenance caused by temperature overcompensation when opening probe enclosures to make measurement attachments.

Table 2-1. Summary of Phase 1 Maintenance Events for Hg CEMS (Nov 2004-Feb 2005)

Forney/Genesis	Horiba/Nippon	Tekran	ThermoElectron
The 450-ft heated line between sample conditioner and analyzer cabinet was found to have severe contamination. Repeated attempts at cleaning failed. The heated line was abandoned and the analyzer was moved to the stack platform	System leaks: replaced a damaged union and most Teflon fittings	Critical orifice in probe became clogged: Added particulates filter.	A tear was found in pump diaphragm: pump was replaced
	A crack in the probe moisture sensor allowed leakage: replaced the sample line with smaller diameter Teflon tubing	Stack thermocouple broke loose from probe: remaining parts were removed and the port plugged	Data output failed shortly before the start of Run 11: swapped components from an unused data output channel
Short heated line between sample conditioner and probe was contaminated and was replaced	Data output showed excessive amounts of electrical noise: installed a filtering circuit to correct	A hole in the "stinger" portion of the probe allowed leakage of acid gases into the heater causing failure	Low flow through probe's critical orifice: changed dilution ratio temporarily until probe was cleaned
Several analyzers failed over a period of several months: acid mist filter just prior to the analyzer was installed (also prevents condensation from reaching the analyzer)	Repeated condensation in sample transfer line: replaced with heated line between probe and analyzer	About every 2 months material buildup on probe's main sample loop created blockage: periodically cleaned sample loop and replaced motive air heater	
Impingers used for SO ₂ removal were found to cause significant loss of mercury in sample gas. Impingers were modified.	Calcium deposits were accumulating at the inlet of the KOH impinger: connected hourly water wash system		
Probe blowback system was disabled and used as the sample line after the original sample line became unusable	Analyzer exhaust line was blocked: installed heated exhaust assembly to prevent condensation from freezing		
Problems with condensation in the sample line between conditioner and analyzer. Improvements made to chiller efficiency	Gas/liquid separator and dehumidifier tube had signs of selenium contamination: connected 3X daily water wash system		
Ceramic probe filter caused loss of mercury in sample gas. Replacement with glass fiber filter did not help.	Before and during the RATA, the catalytic converter suffered from buildup of calcium: replacement would remedy for 2 to 5 days		
Data output showed excessive amounts of electrical noise with intermittent output signal. Output module was replaced			

Table 2-2. Summary of Phase 2 Maintenance Events for Hg CEMS (Mar-Sept 2005)

Durag	Forney/ Genesis	Horiba/ Nippon	Opsis	Tekran	ThermoElectron
Low airflow; replaced filter to UV detector	Vendor elected to have their system removed from the test program		Replaced broken glass tube in analyzer (improper overtightening) to correct leak	Replaced probe and analyzer components	Closed pressure bypass dump four consecutive times.
Replaced converter after attempting to fix by increasing temperature and recalibration			Replaced RTD thermocouple connector on temperature controller to correct overheating	Replaced eductor module to correct plugged orifice	Cleaned out stinger and return port. Zero and span check performed afterward
Rotated UV light filter by 90° and recalibrated to correct for non-linearity			Replaced probe filter and acid scrubber to improve response time	Corrected program controlling test sequence, loop flow, and zero calibration gas delivery	Installed new inertial filter, probe draw tube, & probe cabinet doors. Changed draw orifice and added time-controlled external probe blowback system
Increased converter temperature then replaced catalyst and cleaned probe port to correct for slow response time			Melted Teflon on converter caused overheating of probe. Temporarily replaced RTD thermocouple with a K-type	Replaced eductor module, repaired melted Teflon gas connection line to correct measurement of zero stack gas concentration	Stack gas values measure at zero; closed pressure bypass dump port four consecutive times which did not help. Unspecified repairs made over next two days then cleaned out residual debris from fast loop tubing, cleaned lines from probe to analyzer. Increased probe temperature to burn off potential contamination. Installed redesigned probe front end assembly, added tee to probe to allow injection of system integrity gas to be introduced upstream of the inertial filter. Replaced four solenoid valves in analyzed and cleaned out probe stinger.
Increased probe temperature to remove accumulated Hg			Removed thermocouple from temperature controller and serviced Gold trap	Repaired heat tape and heated eductor module to correct for low measurement readings	System did not measure stack gas for 5 days because an operator left the system in "probe zero" mode after performing daily reference gas measurement
Replaced probe filter			Span adjusted to match audit gas	Replaced inertial filter	
New software installed to allow system to operate at higher probe temperature			Changed system span and offset	Removed return loop flow tube and cleaned venturi lines + stack gas return tube to correct for zero measurement readings	
Manually zeroed and increased probe temperature			Replaced dilution pump due to failed bearing	Replaced venturi pressure transducer to correct high loop flow measurements	
Replaced probe filter to correct for low airflow rates			Replaced orifice filter on probe		
			System span adjusted	Cleaned out return probe port to correct improper proportional valve measurement	Analog output to MRI data logger failed resulting in loss of data for several days
			Replaced filter disk at probe (possible caused by plant startup)	Removed and cleaned plug in the eductor orifice.	
			Maintenance to verify that orifice gasket orientation is correct	Cleaned out return probe	
			Replaced probe filter during July RATA	Replaced: sample extraction assembly (including orifice), PMT & power base, Hg conditioner filter, sample filter on Hg analyzer; installed clean inertial filter, and new lamp on Hg analyzer	
			Changed probe filter and blew out orifice ports. Also adjusted system span	Reset software to correct software lockup. Data logger lost synchronization with output link; lost 6 days of data.	
			Tightened 3 hinged flange bolts to correct low measurement values		
			Changed analyzer pump, probe filter, and increased span adjustment to correct low measurement values		
	Adjusted analyzer pump voltage, analyzer temperature, and system span to correct low measurement values				
	Replaced voltage power distribution board in analyzer. Adjusted span and offset				

2.1 Durag

The Durag system was installed by manufacturer representatives during the week of May 9. The system was commissioned to stack measurements on May 11. The system was programmed to provide a probe blowback and zero offset check every 2 hours. This procedure typically takes less than 5 minutes. The system span and zero adjustments were performed manually and verified daily by plant personnel throughout the week, Monday through Friday. The system was removed from the site on August 11. The total operation period was three months.

2.1.1 Preventative Maintenance and Checks

Routine preventative maintenance and checks included recording the system sample flow, system pressure, and the zero offset value to verify the parameters were within normal operating ranges. A system leak check was performed periodically to verify the system was leak-free. Also included in the routine preventative maintenance was checking and emptying the fluid level of the condensation collection container. The container is sized to allow up to 2 months of collection before necessary emptying.

The probe filter change was performed June after a plant outage. The excessive emissions resulting from fuel oil used during plant start-up had a tendency to plug CEM filters and this filter change was a preventative measure.

2.1.2 Corrective Maintenance

The system operated throughout a 3-month period at the site with some downtime for preventative or corrective maintenance. The corrective maintenance activities to the Durag system are described below.

The span and offset adjustments were performed several times during the initial system commissioning to confirm proper system measurements. Thereafter, the span and offset were adjusted approximately every month.

The sample conditioning catalyst was changed twice during the 3 months of operation. The catalyst was changed the first time in June due to damage resulting from increasing the catalyst temperature beyond the recommended temperature limit. The catalyst was changed the second time in July prior to the RATA to improve the degrading response time.

In June the analyzer glass cuvet light filter was suspected to be delaminating after 1 ½ months of operation. The glass cuvet was rotated 90 degrees to bring the system back into normal operation.

The probe and catalyst temperatures were increased several times during the 3-month period. The temperature increases were performed in an effort to overcome the system's delayed response. The delayed response occurred 15 minutes after each 2-hour system blowback and zero offset check. The time required for system to measure pre-blowback stack concentration values increased from a nominal 5 minutes to more than 1 hour. In July, the vendor installed new software to allow the probe temperature to be set above the original high temperature limit. When the probe temperature was increased, the system stack concentration measurements also increased more than 50% above the original measurements.

The probe filter was changed twice to correct system problems. The first probe filter change was performed in July during the middle of a RATA test due to higher than normal Hg measurements. The second probe filter change was performed in August to increase the system flow rate that was measuring below the low limit threshold.

2.2 Forney/Genesis

The Forney/Genesis system was installed in early November 2004 by personnel from Forney Corporation and Genesis Laboratory Systems. The system seemed functional, but exhibited anomalous responses. Testing throughout the first three months following installation yielded anomalous responses to both reference gas and zero gas (e.g., reference gases were detected at lower than expected concentrations and zero gas read as though it had a high background mercury content).

The Forney/Genesis system, though not operational, remained in the stack throughout the period between the February RATA and the May certification testing. During the week before the May certification tests, Forney representatives were on-site to perform corrective maintenance. Daily corrective and preventative maintenance was required to keep the system operating. Efforts to continue corrective and preventative maintenance were then ceased due to lack of replacement parts, and the system was not operational.

A Forney representative was on-site to perform corrective maintenance during the last day of the June certification tests and during the July RATA. Eventually efforts to continue corrective and preventative maintenance were completely stopped. No further maintenance was performed on the system after Forney determined that it was discontinuing its efforts at the site. The system was removed during the second week in August.

Because the Forney system was rarely operational between corrective maintenance visits during Phase 2 of the demonstration project, maintenance efforts have not been included in Table 2-2.

2.3 Horiba/Nippon

The Nippon DM-6D system was installed in early November 2004 by technicians from Horiba Instruments and Nippon Instruments Corporation. Though the system performed well immediately after installation, leaks and other problems caused deterioration of the system. Further visits were made by Horiba personnel in mid-November and early December, and a Nippon representative was on-site in early January. Maintenance details for this time period are included in Table 2-1.

No preventative or corrective maintenance was performed on the Horiba system between February and July. The system was removed at the vendor's request prior to the second RATA test series. When the system was removed from the port, the stainless steel probe was discovered to be completely corroded away, leaving nothing but the Teflon sample line.

2.4 Opsis

The Opsis system was installed by manufacturer representatives during the week of May 2. The system was commissioned to stack measurements on May 6. The system was programmed to provide a zero check at the top of every hour. This procedure typically takes less than 5 minutes. The system span and zero adjustments are performed manually and verified daily by plant personnel throughout the week (Monday through Friday).

2.4.1 Preventative Maintenance and Checks

Routine preventative maintenance to the system included recording the probe temperature, the regulated compressed air pressure, and the dilution pump vacuum to ensure they were within the manufacturer's setpoint. Periodic preventative maintenance included replacing the probe filter.

2.4.2 Corrective Maintenance

Maintenance during the first month (May) was mainly performed to address a temperature control problem and slow response time. A broken glass tube was also replaced to correct a leak caused by improper over tightening of a mounting screw.

Much of the maintenance during the third month (August) was performed to address low measurement values.

During the period of operation, the system had a slow response to known changes in Hg concentrations, i.e., from challenges with the reference gases. Corrective maintenance during this period included multiple changes of the probe filters. The probe filters were

changed six times during the 4-month period. The number of probe filter changes was high compared to other instruments.

The instrument output span was adjusted routinely by the Opsis maintenance representatives during the 4-month period. Eight known span adjustments were performed to bring the instrument output measurements back into alignment with the external reference gas concentrations.

2.5 Tekran

Technicians from Tekran Systems, Incorporated arrived in mid-November and installed the system. The Tekran system remained operating on stack emissions throughout the period between installation and system shutdown for project completion in mid-September. Periodic preventative and corrective maintenance was necessary during this period to keep the system operating. The Tekran system has a programmable automatic blow back incorporated into the normal operation that occurs every 2 to 4 hours. The instrument zero and span is also checked automatically daily.

2.5.1 Preventative Maintenance

Preventative maintenance on the system included recording the air supply pressures daily, recording the Argon gas cylinder pressure daily and replacing it as needed, adding deionized water to the scrubber reservoir, emptying the wasted water reservoir every week or as needed, and cleaning the air filter to the probe electronics cabinet weekly.

The Tekran system has a built-in Hg calibrator. This feature allows the system to be programmed to introduce a single or multiple known Hg concentrations to the probe, the orifice, or the analyzer. This feature allowed for either self-calibration or diagnostic purposes. However, the stack gas concentration could not be monitored while performing the self-calibrations or self-diagnostics. As configured, the system conducted its daily checks and calibrations over a 4-hour period during the early morning hours, during which the system did not monitor the stack gas Hg concentration.

2.5.2 Corrective Maintenance

A Tekran representative visited the site in December to make repairs and probe modifications. The primary causes for corrective maintenance during the period between February and May was due to the loop flow or the dilution eductor orifice becoming plugged. The most notable failure was when the plant had a scheduled shut down to switch on the SCR system. The Tekran loop flow became plugged immediately after the plant came back online. The Tekran system successfully maintained operation after two unscheduled plant outages and restarts during June and July.

During the months between May and the end of the field evaluation in September the following corrective maintenance issues were addressed. The loop flow return port became plugged nearly each month and required cleaning to dislodge the obstruction. The dilution eductor orifice also became plugged nearly each month and required disassembly and cleaning. The inertial filter was typically cleaned or replaced during the same time as when the dilution eductor was cleaned. The dilution eductor heat tape also required replacing twice during the period between May and September primarily due to damage caused by repeated disturbing the heat tape to remove the dilution eductor.

The analyzer portion of the system required corrective maintenance every three months. The corrective maintenance included replacing the UV lamp, replacing the sample and conditioning filters, and flushing out the photo cartridges. Also included in the analyzer corrective maintenance in May was replacing the valve assembly.

2.6 Thermo

The Thermo system has remained in the stack throughout the duration between the February RATA and the May certification testing. Periodic preventative and corrective maintenance was necessary during this period to keep the system operating. The Thermo, as tested, had no automated method for zero and span checks. Blowback was added later as discussed in the corrective maintenance section below.

2.6.1 Preventative Maintenance

Preventative maintenance included recording the air regulator pressure to the system daily. Frequently, the orifice became plugged and required closing the ambient bleed port at the probe for thirty seconds to dislodge the orifice obstruction. However, the system remained operating after the plant had a scheduled 4-day shutdown in late April to bring the SCR system on-line. The Thermo system continued to operate after the plant start-up. The system also successfully maintained operation after two unscheduled plant outages and restarts during June and July. The Thermo, as tested, had no automated method for zero and span checks, but they could be done manually. Blowback was added later as discussed in the corrective maintenance section below.

2.6.2 Corrective Maintenance

The corrective maintenance during the months between May and September included cleaning the probe stinger and return port on a monthly basis. The inertial filter required replacing every 2 months. A probe blowback system was added to the system on June 8. On occasion the orifice became plugged and required closing the ambient bleed port at the probe for thirty seconds to dislodge the orifice obstruction.

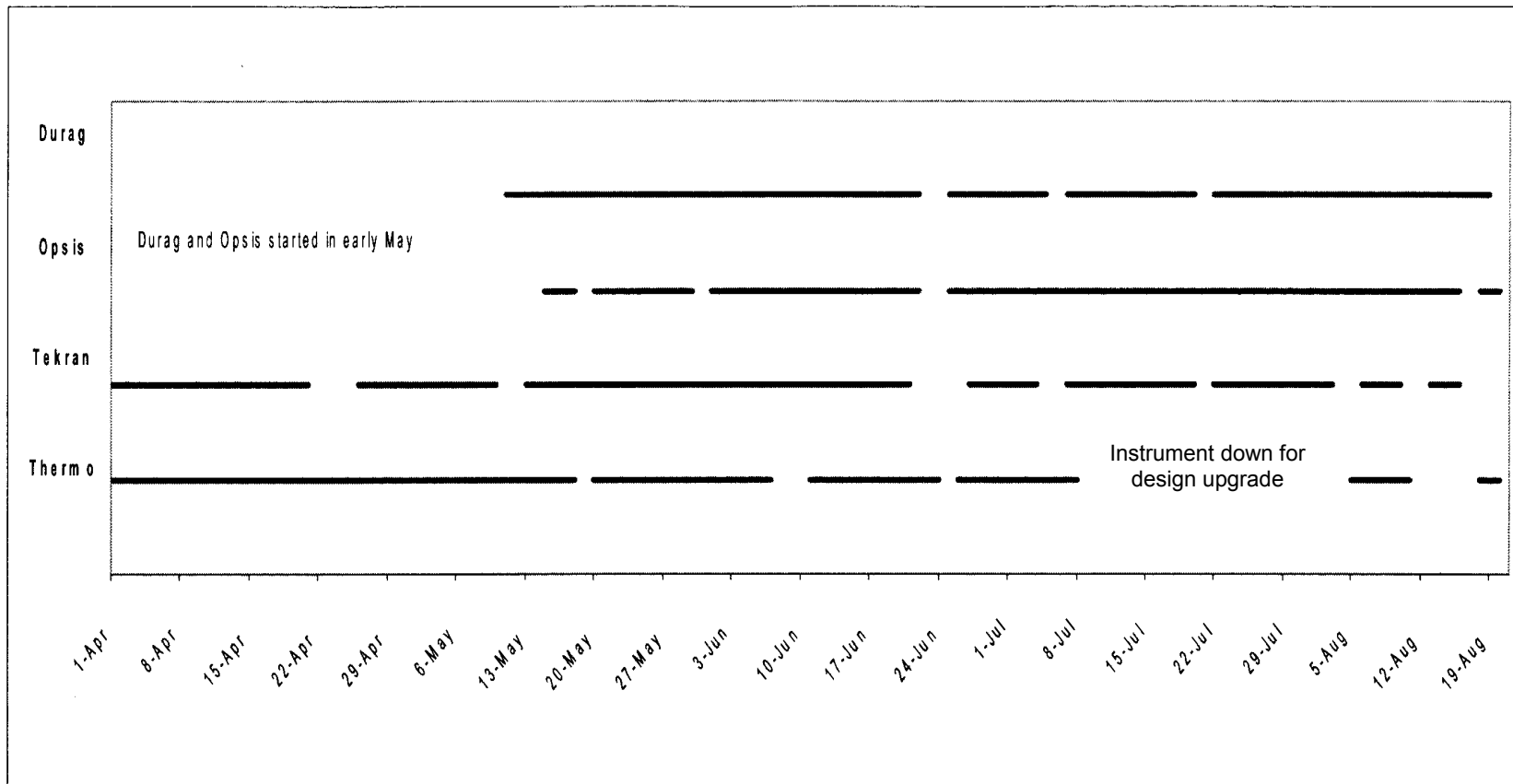
On July 9, the system failed during the seventh RATA run. The output measurements remained high after a routine system blowback then slowly leveled off to zero concentrations and remained there. Thermo maintenance personnel were on-site during the week of July 11 to repair the system. The probe heater was turned off overnight to allow the system to cool for maintenance. The next morning condensation was found in all of the sample lines up to the analyzer. Several attempts were made to clean and repair the system during the following 3 weeks. The repair attempts included cleaning the fast loop assembly, replacing the complete probe sample conditioning assembly with a third generation design sample conditioning assembly, replacing the inertial filter, cleaning the probe stinger and return port, replacing the analyzer UV lenses, and replacing four process control solenoid valves in the analyzer. The system was back in operation on August 4.

On August 12, the operator left the system in “probe zero” mode which prevented the system from measuring stack gas. The status was corrected during the next week visit on August 17. Although the system was not measuring stack gas during this period, the system was functioning.

2.7 Summary

Figure 2-1 shows a summary of the long-term operations for each of the CEMS. This summary is presented to clearly illustrate operational gaps due to mechanical or computer failure encountered to date by the various units. Operational periods do not take into account passing/failure of daily/weekly QA/QC checks and no data are shown past August 20. All of the instruments evaluated during this study required preventative maintenance. The systems also required corrective maintenance. The primary preventative maintenance requirements were probe-related (including probe blockage), loop flow blockage, temperature regulation, sample conditioning-related, and routine filter changing.

The analyzer portions of the systems were reliable but required quarterly corrective maintenance to keep them functioning properly.



NOTE: Horiba/Nippon and Forney/Genesis data not shown as they elected to remove their systems from the test program.

Figure 2-1. Phase 1 and 2 Long-Term Monitoring Periods

Section 3. Sampling

3.1 Process Data

Phase 1 and Phase 2 plant CEMS data as run averages are provided in Tables 3-1 and 3-2.

3.2 Flue Gas Sampling Location

The Hg CEMS and manual ASTM D6784-02 (Ontario Hydro) mercury sampling locations were located on the active stack, approximately 345 ft above ground level, 180 ft (10 duct diameters) above the nearest flow restriction, and 410 ft (> 22 duct diameters) from the outlet. The layout of ports, Hg CEMS, Appendix K sampling, and manual sampling during Phase 1 testing are shown in Figure 3-1. The layout during Phase 2 testing is shown in Figure 3-2.

The Ontario Hydro Method samples were collected isokinetically at a single point approximately 5 ft within the stack. This effective distance was based on traverse information provided by the facility. Note that single point sampling is a deviation from the method, but it is appropriate for this test program where the goal was to verify Hg CEMS accuracy against the reference method. Assessing Hg CEMS probe placement in the stack was not part of this test program.

All of the sampling ports are on the same level, thereby allowing the Hg CEMS and Appendix K probes to sample gases similar to those sampled by the Ontario Hydro Method. Figure 3-3 indicates elevations of ports relative to flow restrictions and top of stack for both phases of testing. The Horiba/Nippon analyzer was in the trailer with its own reference gas delivery system while the Durag, Forney/Genesis, Opsis, Tekran, and Thermo/Electron analyzers were on the stack platform with a separate reference gas delivery system. The Forney/Genesis system initially was operated from the trailer, but the analyzer was moved to the stack platform when problems persisted with the heated sample line. Figure 3-4 indicates the sampling configuration during Phase 1 and Figure 3-5 indicates the sampling configuration during Phase 2.

3.3 Ontario Hydro Method

This section provides information on the reference method for the mercury sampling and analysis used for the project.

Table 3-1. Phase 1 Average Plant CEM Data

Run No.	SO ₂ low range ppm	NO _x conc. raw ppm	CO ₂ conc. raw %	Exit opacity %	Stack flow 10 ⁶ std. ft ³ /hr	Chim gas Exit 1 temp. °F
1	115	211	12	9	65.29	127
2	107	206	12	9	64.38	126
3	70	189	12	11	63.98	127
4	106	201	12	11	64.71	127
5	108	201	12	11	65.82	128
6	103	215	12	10	64.60	126
7	89	211	12	10	64.93	125
8	100	211	12	11	64.25	126
9	81	211	12	11	63.97	125
10	93	210	12	11	64.07	127
11	67	226	12	11	63.40	127
12	142	200	12	10	62.61	128

Table 3-2. Phase 2 Average Plant CEM Data

Run No.	SO ₂ low range ppm	NO _x conc. raw ppm	CO ₂ conc. raw %	Exit opacity %	Stack flow 10 ⁶ std. ft ³ /hr	Chim gas Exit 1 temp. °F
1	244	10	12	10	71	131
2	201	20	12	10	71	131
3	173	15	12	11	70	132
4	169	13	12	10	69	131
5	137	16	12	9	70	130
6	142	17	12	9	70	130
7	241	11	12	8	69	131
8	231	10	12	8	69	131
9	148	16	12	9	69	131
10	159	16	12	10	68	132
11	224	14	12	10	71	132
12	179	15	12	10	71	132

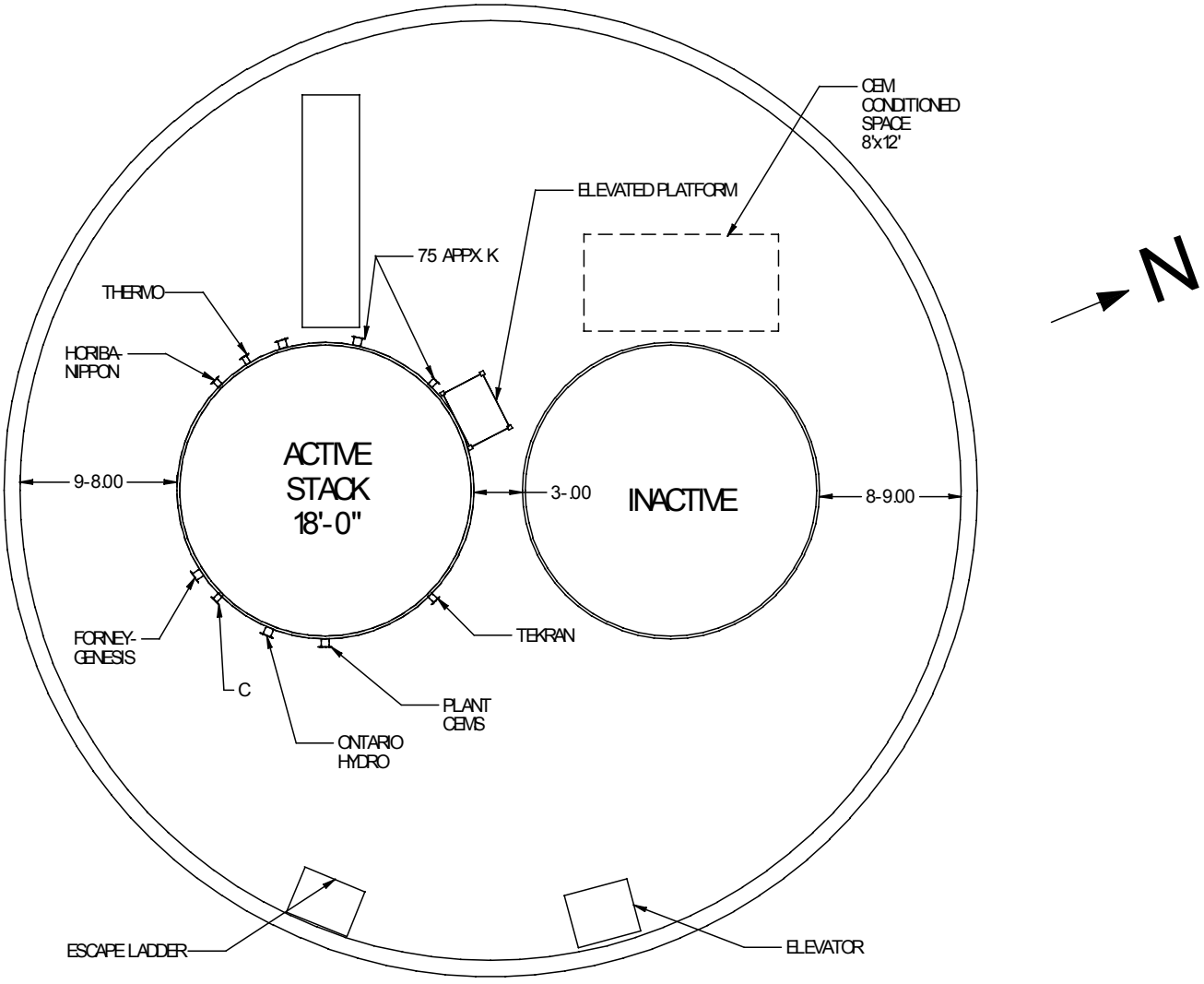


Figure 3-1. Layout of Sampling Ports and Hg CEMS and Other Sampling Systems During Phase 1 RATA Test

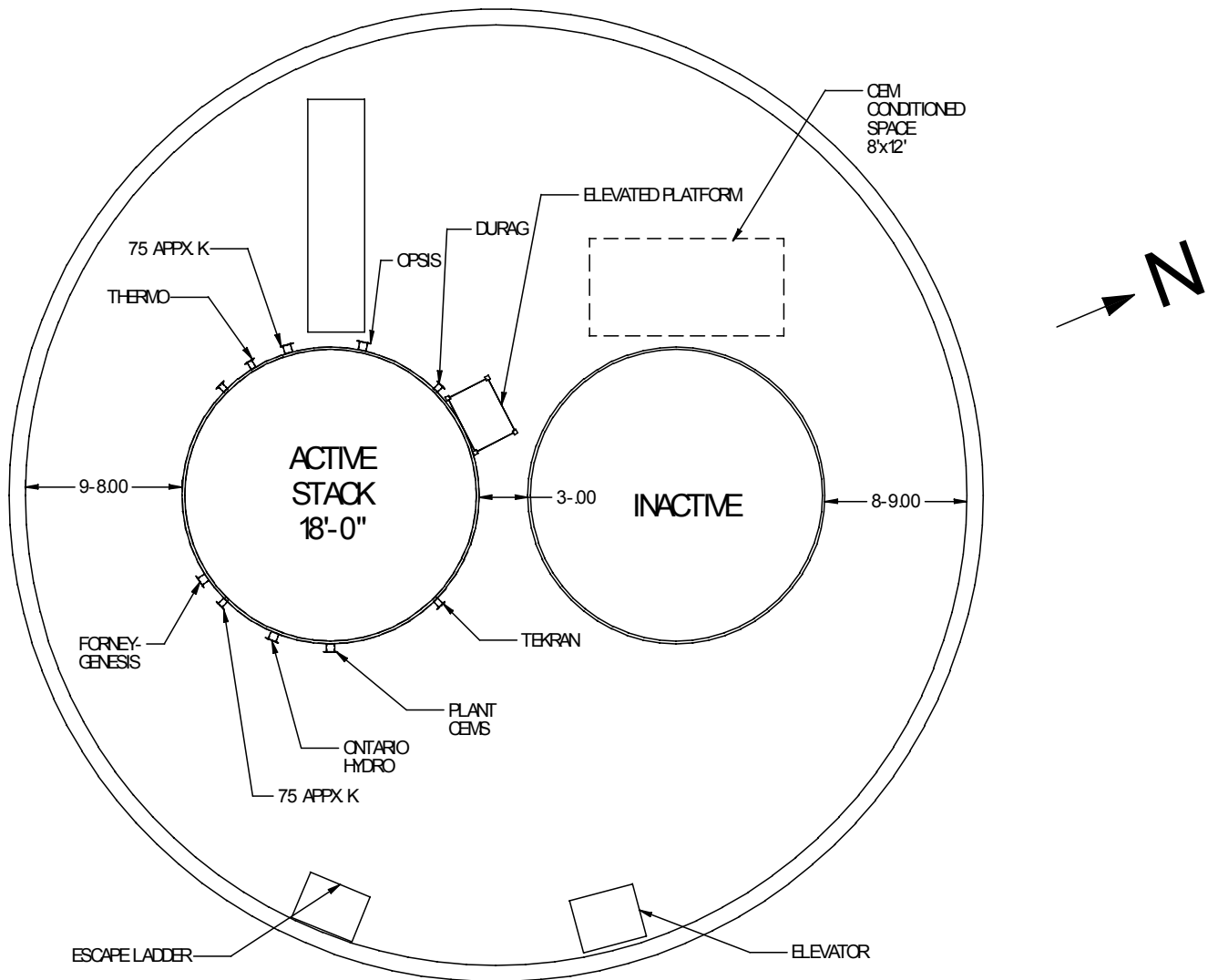


Figure 3-2. Layout of Sampling Ports and Hg CEMS and Other Sampling Systems During Phase 2 RATA Test

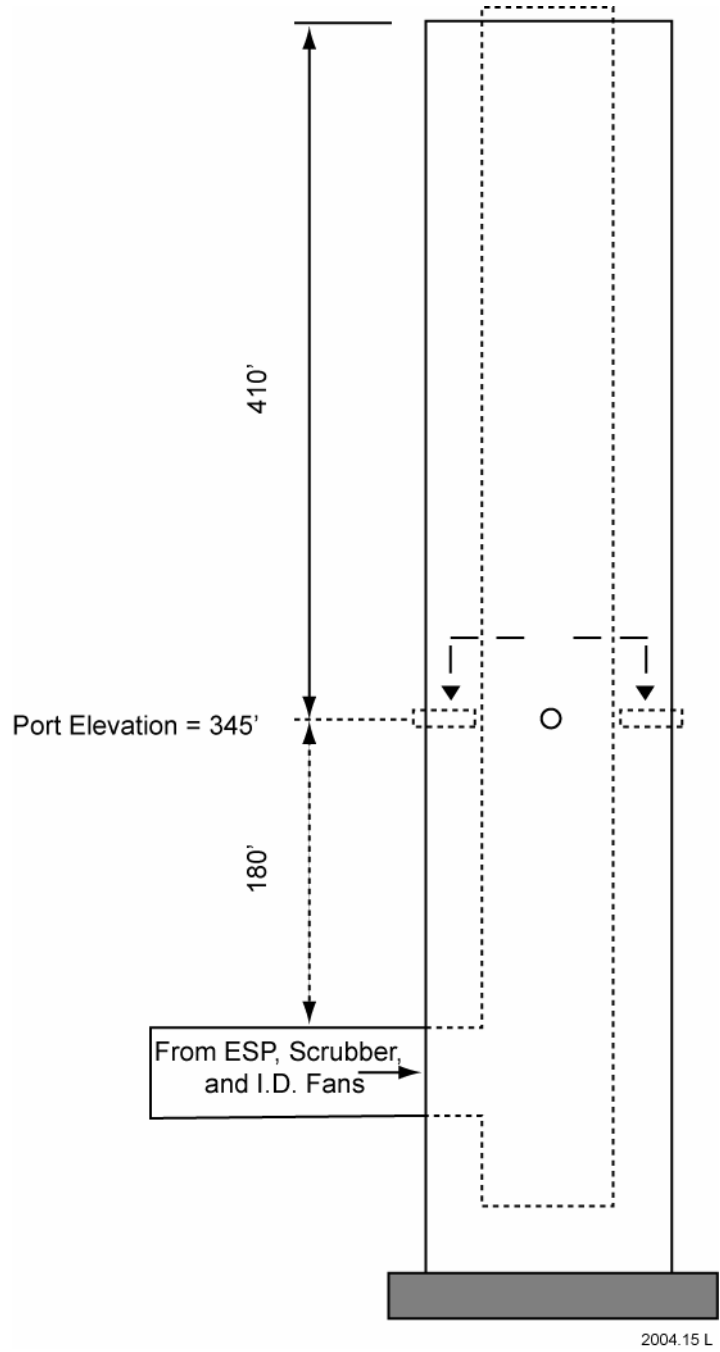


Figure 3-3. Sampling Location at the Unit #1 Stack North Inlet Duct

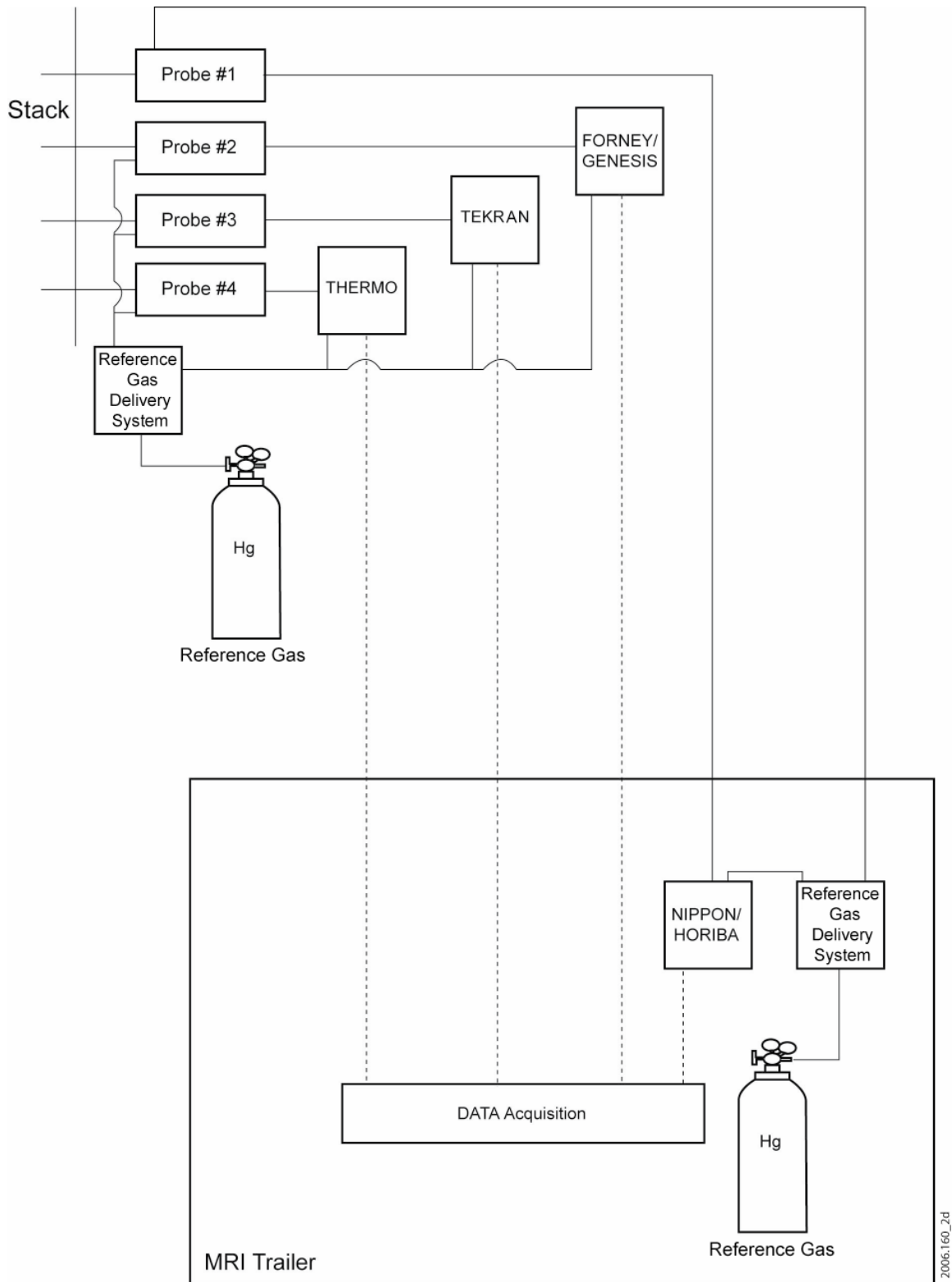


Figure 3-4. Hg CEMS Sampling Configuration During Phase 1 RATA

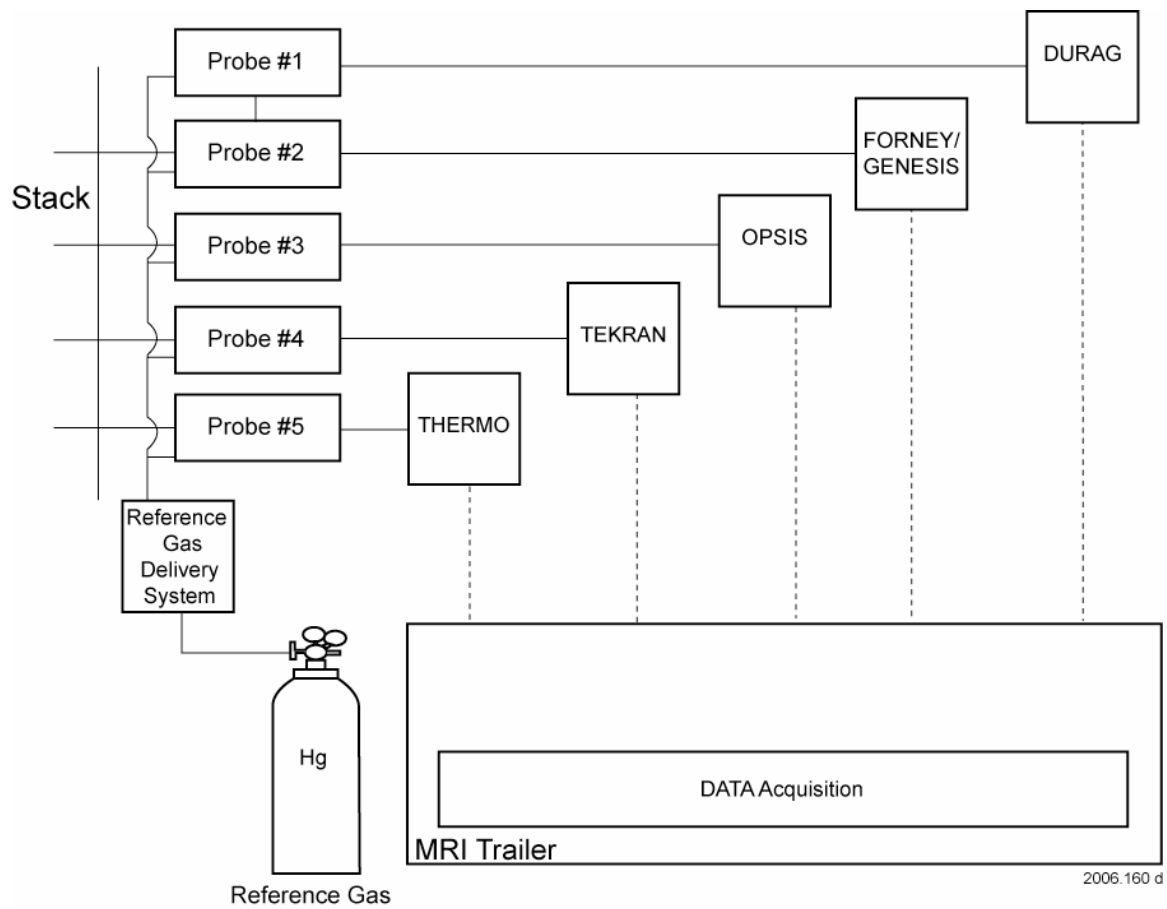


Figure 3-5. Hg CEMS Sampling Configuration During Phase 2 RATA

3.3.1 Method Summary

The ASTM D 6784-02 “Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method),” was used as the reference method per Part 75, Appendix A, Section 6.5.10 (FR 5/18/05, 70(95), 2 8691). A schematic of a sampling train is presented in Figure 3-6. Further clarifications on the use of the Ontario Hydro method for this project were:

- Two 2-hr paired-train samples were collected isokinetically from a single point within the stack for each test run.
- Quartz fiber filters were used, and had the same specifications as those described in the method. Filter supports used in the filter holders were 100% Teflon.
- The $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples were stored and shipped at water ice temperature; the rest of the samples were stored and shipped at room temperature. This was done as directed by EPA representatives in response to the paper, “The Ontario Hydro Method for Speciated Mercury Measurements: Issues and Considerations,” by Jeffery V. Ryan and Robert M. Keeney.
- The sample recovery scheme is presented in Figure 3-7.

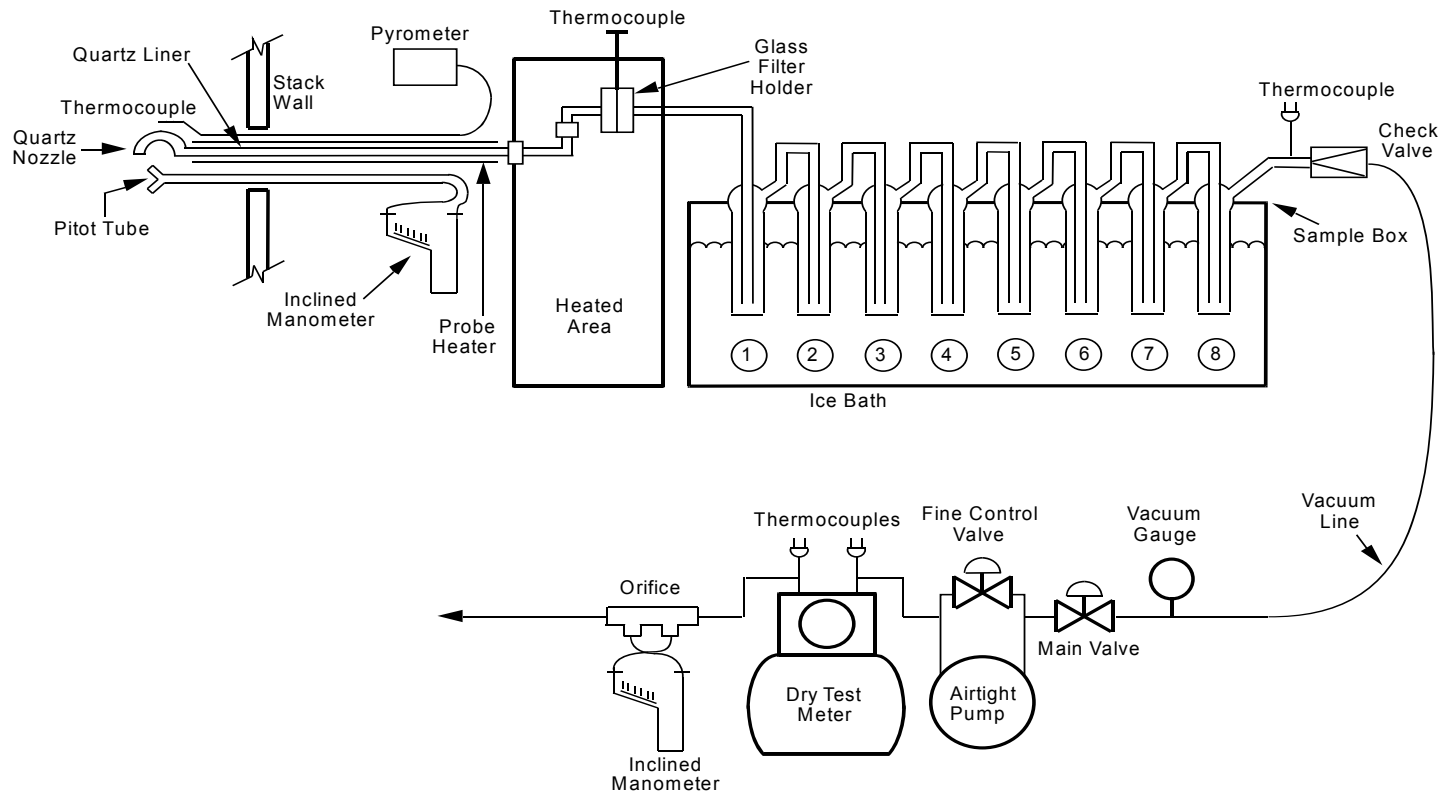
3.3.2 Determination of Gas Velocity at Sampling Point

Method 2 in Appendix A of 40 *CFR* 60 was used to measure the gas velocity with a Type S pitot tube during sampling with the Ontario Hydro Method sampling train. Results of the Method 2 testing were used to determine the isokinetic sampling rate for the single-point sampling.

An aneroid barometer calibrated against a calibrated mercury barometer was used to measure atmospheric pressure at the sampling location.

3.3.3 Determination of Dry Gas Molecular Weight

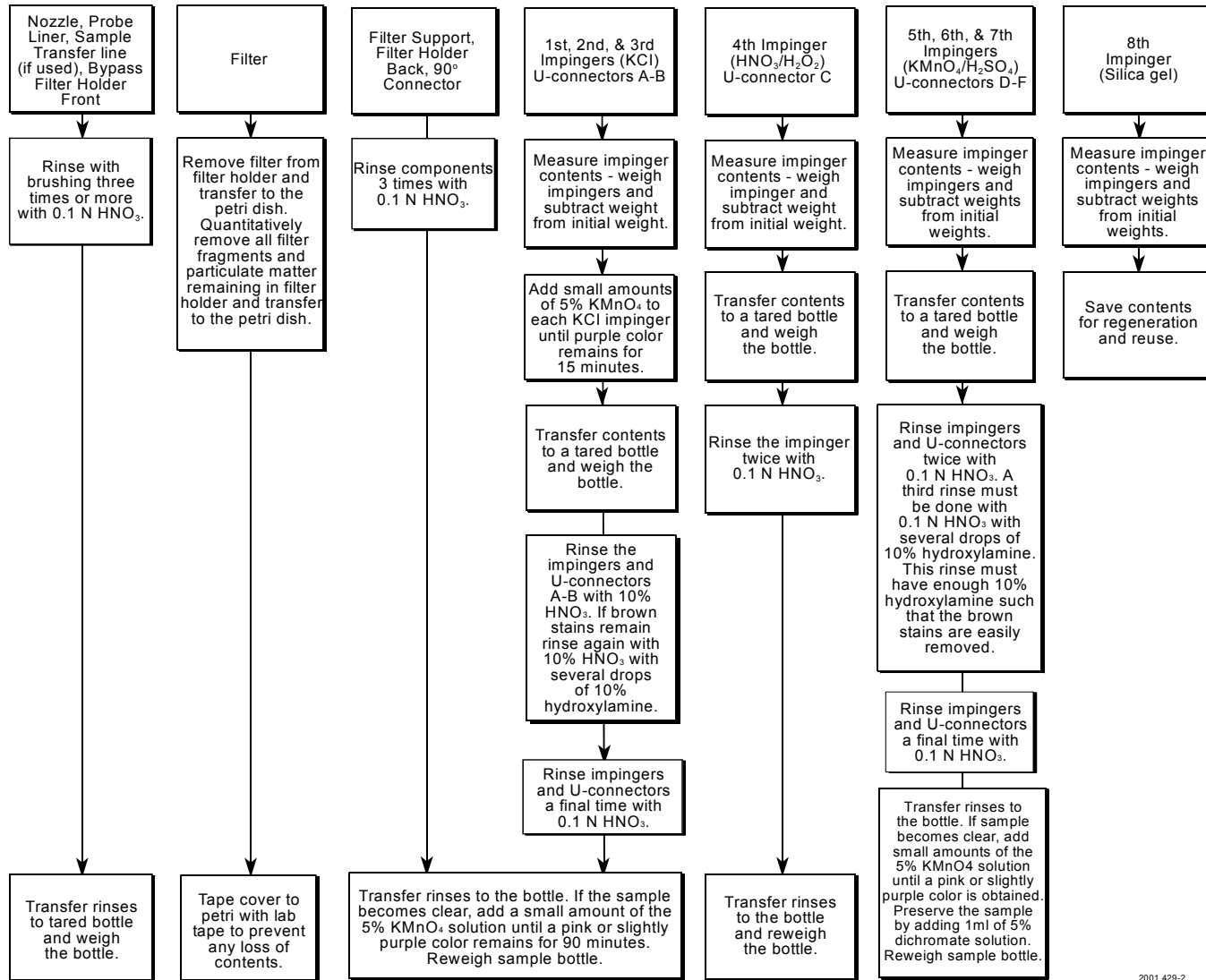
Method 3B in Appendix A of 40 *CFR* 60 was used to collect integrated gas bag samples simultaneously with the Ontario Hydro method point sampling for determination of dry gas molecular weight. The integrated gas sampling apparatus used to collect the samples is a component of the sampling train. An integrated gas sample is extracted at a constant rate from the exhaust of the sampling train just upstream from the outlet of the dry gas meter outlet orifice.



- | | |
|--|--|
| ① Modified Greenburg-Smith, 100 mL 1N KCl | ⑤ Modified Greenburg-Smith, 100 mL 4% KMnO_4 /10% H_2SO_4 |
| ② Modified Greenburg-Smith, 100 mL 1N KCl | ⑥ Modified Greenburg-Smith, 100 mL 4% KMnO_4 /10% H_2SO_4 |
| ③ Greenburg-Smith, 100 mL 1N KCl | ⑦ Greenburg-Smith, 100 mL 4% KMnO_4 /10% H_2SO_4 |
| ④ Modified Greenburg-Smith, 100 mL 5% HNO_3 /10% H_2O_2 | ⑧ Modified Greenburg-Smith, 200 g Silica Gel |

2001.429-1

Figure 3-6. Ontario Hydro Sampling Train



2001.429-2

Figure 3-7. Ontario Hydro Sample Recovery Scheme

3.3.4 Determination of Moisture Content

Method 4 in Appendix A of 40 *CFR* 60 incorporated as part of the Ontario Hydro method was used to determine the moisture (water vapor) content of the gas stream. Moisture collected during sampling was determined gravimetrically from the difference between the initial and final weights of all of the impingers in a train.

3.3.5 Mercury Analysis

The sample analysis was performed by Oxford Laboratories in Wilmington, North Carolina. The sample components recovered from the Ontario Hydro trains (i.e., rinses, filter, and impinger contents) were digested and analyzed according to the procedures specified in the method except as explained below. For analysis of the mercury, the Ontario Hydro Method incorporates Method 7470A, which is a procedure for cold vapor atomic absorption spectroscopy (CVAAS) for mercury previously published in “Test Methods for Evaluating Solid Waste, Physical/Chemical (SW-846).” It was discovered near the end of the test program that the laboratory had not been clarifying the KMnO_4 impingers prior to extracting an aliquot for analysis as described in Section 13.3.5 of the Ontario Hydro method. To recover from this omission, ARCADIS G&M, Inc. in Research Triangle Park, North Carolina, performed a reanalysis of the KMnO_4 impingers.

3.4 Reference Gases

MRI used compressed elemental mercury gas standards throughout the project to verify instrument response. The gases were also used extensively for troubleshooting problems with individual analyzers and specific components within each analyzer. The reference, or span, gas standards were purchased from Spectra Gases (Branchburg, New Jersey) with a nominal concentration range of 1 to 10 $\mu\text{g}/\text{m}^3$ of elemental mercury in nitrogen. Several gas cylinders were used over the course of the project, and Table 3-3 summarizes the concentrations of each gas cylinder used. Three linearity standards were also used during the precertification tests. All gases were certified by Spectra Gases based on a cylinder supplied by NIST (secondary certification). Gases have not been characterized to the point that the delivered concentration is accurate to a known uncertainty.

Table 3-3. Elemental Mercury Cylinders

Cylinder No.	Certified conc ($\mu\text{g}/\text{m}^3$)	Approx dates of use
CC19870	1.9	Dec. 04 - End of test program
CC133357	2.1	Nov. 04 - End of test program
CC191724	2.2	July - August 05
CC84954	2.3	Replacement - not used
CC134442	5.1	July - August 05
CC191854	5.8	June - July 05
CC173117	9.03	Nov. 04 - End of test program

3.4.1 HovaCal Gas

The Hovacal is a calibration gas generator used to introduce a known concentration of oxidized mercury gas (Hg^{2+}) to the Hg CEMS systems for comparing the Hg CEMS output measurement readings against a known concentration. The Hovacal performs this function by regulating the flow rate of a known concentration of oxidized mercury in an aqueous state and by regulating the mass flow rate of a nitrogen carrier gas to a heated evaporator where the gas-vapor mixture is introduced into the Hg CEM system prior to the converter.

The Hovacal instrument control parameters were certified by the factory prior to operation on November 02, 2004. The instrument mass flow meter, electronic balance mass, and temperature meter were checked on August 15, 2005. The check showed all of the control parameters were operating within factory tolerances.

3.4.2 Cylinder Gases

The Hg reference gas cylinders were provided by Spectra Gases Incorporated. The audit gases were provided with a factory concentration certification of $\pm 10\%$ of the stated concentration. The reference gases contain a vaporized elemental mercury concentration suspended in a nitrogen carrier gas.

3.4.3 Tekran 3310 Gas

The Tekran 3310 generates a range of elemental mercury concentrations by regulating the heat of an elemental mercury source to create a known vapor. Mass flow controllers are used to regulate the ratio of elemental mercury vapor and supplemental clean air to provide a known vapor concentration at a desired flow rate.

The output of the 3310 Hg calibrator was plumbed to a pressure relief bypass tee to prevent over pressurization of the calibrator. The output port of the tee dumped to atmosphere while the second output port of the tee was attached to input of the calibration gas flow regulator attached to the Hg CEM instrument under investigation.

Section 4.

Certification Test Results

The certification test results are presented in two parts—the initial certification test results (Phase 1) are presented in Subsection 4.1, and the second certification test results (Phase 2) are presented in Subsection 4.2. Within each subsection results are provided as certification testing minus the RATA, and then the RATA.

4.1 Phase 1 Certification Test Results

The certification testing is presented in two parts. Section 4.1.1 presents results from the Phase 1 measurement error test, 7-day calibration error test, the linearity test, system integrity test, the upscale/downscale drift test, and cycle time test. Section 4.1.2 presents results from the Phase 1 RATA test. Additional test results are presented in Section 4.1.3.

4.1.1 Phase 1 Certification (excluding RATA) Results

Phase 1 certification tests were conducted between February 15 and 28, 2005 according to Part 75 and PS-12A requirements. The results for each Hg CEMS are provided below. The initial certification for each CEMS included a 7-day calibration error test, a linearity check, a system integrity test (which checks converter efficiency), a measurement error test, and zero/upscale drift tests. The reported Hg CEMS values are based on the resolution of the analyzer even though the believed resolution is more likely 0.1 mg/m^3 . The Hg CEMS results are reported at 20°C . The span was defined at $10 \text{ } \mu\text{g/m}^3$, and values used to assess CEMS performance are summarized based on that span, as shown in Table 4-1 below.

Table 4-1. Summary of Phase 1 CEMS Certification Criteria and Performance (Excluding RATA)

Test	Criteria	Criteria Met? (Y/N)			
		Forney ^a	Horiba	Tekran	Thermo
7 Day Calibration Error Test	Error must be $\leq 5\%$ of span; or $\leq 1 \text{ } \mu\text{g/m}^3$ (alternative specification when span is defined at $10 \text{ } \mu\text{g/m}^3$).	N	Y	Y	Y
Linearity Test	Error must be $\leq 10\%$ of reference gas tag value or $\leq 1 \text{ } \mu\text{g/m}^3$, whichever is least restrictive.	N	N	Y	Y
System Integrity Test	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \text{ } \mu\text{g/m}^3$ of certified gas value).	N	Y	Y	Y
Cycle Time Test	Cycle times must be ≤ 15 minutes.	N	N	Y	Y
Measurement Error Test	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \text{ } \mu\text{g/m}^3$ of certified gas value).	N	N	Y	Y
Zero and Upscale Drift Test	Error must be $\leq 5\%$ of span (i.e., within $\pm 0.5 \text{ } \mu\text{g/m}^3$ of certified gas value).	N	Y	N	N

^a System was not functioning for most of the certification period.

4.1.1.1 Forney/Genesis

Results for the last two days of the Forney 7-day calibration error test are presented in Table 4-2. The system was not functioning except for the last 2 days of the certification period (February 25 and 26, 2005) and no data for the linearity check, system integrity test (which checks converter efficiency), measurement error test, and zero/upscale drift tests were obtained. The remaining tests were not performed due to a pending system upgrade being developed. This system as tested was configured to operate at the stack sampling elevation.

Table 4-2. Forney 7-Day Calibration Error Test—Phase 1

Reference Gas Concentration ($\mu\text{g}/\text{m}^3$):		1.3					
Date	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)		Error (difference) ($\mu\text{g}/\text{m}^3$)		Result	
		Zero	Reference	Zero	Reference	Zero	Reference
02/25/05	7:55:00	0.3	1.5	0.3	0.2	Pass	Pass
02/26/05	8:40:00	0.2	1.5	0.2	0.2	Pass	Pass
7 Day Cal Error Result:		Test not completed (system failure).					

4.1.1.2 Horiba/Nippon

The Horiba 7-day calibration error, and linearity check, system integrity test (which checks converter efficiency), and measurement error test results are presented in Tables 4-3 through 4-7. The 7-day calibration test was performed February 22 through 28, 2005. The linearity test was performed on February 28, 2005. The system integrity test was performed on February 15, 2005. The measurement error test was performed on February 27, 2005. The zero/upscale test was performed from February 22 through 28, 2005. The data table for the cycle time test is not provided because it could not be completed. The sample conditioning system (converter) was located at the stack sampling location and the converted sample was transported through a 450-ft heated line (100°F) to the analyzer in the on-site test trailer. All reported concentrations are corrected to 20°C. The Horiba met the criteria for the 7-day calibration error, system integrity, and zero/upscale drift tests, with the catalyst being replaced twice during this period. The Horiba system did not meet the criteria for the measurement error, linearity, and cycle time tests.

Table 4-3. Horiba/Nippon 7-Day Calibration Error Test—Phase 1

Reference Gas Concentration ($\mu\text{g}/\text{m}^3$):		1.3					
		CEMS reading ($\mu\text{g}/\text{m}^3$)		Error (difference) ($\mu\text{g}/\text{m}^3$)		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
02/22/05	9:50:00	0.09	0.9	0.1	0.4	Yes	Yes
02/23/05	10:10:00	-0.09	1.0	0.1	0.3	Yes	Yes
02/23/05	9:35:00	0.0	0.8	0.0	0.5	Yes	Yes
02/24/05	9:50:00	0.0	0.8	0.0	0.5	Yes	Yes
02/24/05	15:12:00	-0.2	0.8	0.2	0.5	Yes	Yes
02/25/05	15:52:00	0.5	1.5	0.5	0.2	Yes	Yes
02/25/05	10:05:00	0.00	1.1	0.0	0.2	Yes	Yes
02/26/05	10:05:00	-0.09	1.2	0.1	0.1	Yes	Yes
02/26/05	10:17:00	-0.2	1.0	0.2	0.3	Yes	Yes
02/27/05	10:27:00	-0.2	0.7	0.2	0.6	Yes	Yes
02/27/05	10:27:00	0.0	1.2	0.0	0.1	Yes	Yes
02/28/05	10:09:00	0.0	1.2	0.0	0.1	Yes	Yes
7 Day Cal Error Result:		Met criteria.					

NOTE: 2/24/05 at 18:37, longer response time observed.
 2/25/05 at 08:00 replaced Horiba catalyst.
 2/27/05 at 08:40, replaced Horiba catalyst.

Table 4-4. Horiba/Nippon Linearity Test—Phase 1

Low-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		1.3		
Mid-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		5.1		
High-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		10.4		
Test Date:		2/28/05		
	Cycle	Time	Gas type	CEMS reading ($\mu\text{g}/\text{m}^3$)
	1	11:03:00	Low	1.2
	1	11:27:00	Mid	3.4
	1	11:40:00	High	5.9
	Gas	Low	Mid	High
	Average	1.2	3.4	5.9
	% Rel. Diff.	3.9%	34%	44%
	Linear Error (Diff, $\mu\text{g}/\text{m}^3$)	0.0	1.7	4.5
	Criteria met?	Yes	No	No
Linearity Result:		Criteria not met. Only the first cycle was performed.		

Table 4-5. Horiba/Nippon System Integrity Test—Phase 1

Mid-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		3.5		
High-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		5.7		
Test Date:		02/15/05		
Time	Gas type	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error ($\mu\text{g}/\text{m}^3$)	Criteria met?
12:01:00	Zero	0.0	0.0	Yes
12:14:00	Mid	3.3	0.2	Yes
12:34:00	High	5.2	0.5	Yes
Test Result:		Criteria met.		

Table 4-6. Horiba/Nippon Measurement Error Test—Phase 1

Mid-Level Reference Gas, Elemental Mercury Conc. ($\mu\text{g}/\text{m}^3$):		5.1		
High-Level Reference Gas, Elemental Mercury Conc. ($\mu\text{g}/\text{m}^3$):		–		
Mid-Level Reference Gas, Oxidized Mercury Conc. ($\mu\text{g}/\text{m}^3$):		–		
High-Level Reference Gas, Oxidized Mercury Conc. ($\mu\text{g}/\text{m}^3$):		–		
Test Date:		2/27/2005		
Gas type	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error (difference) ($\mu\text{g}/\text{m}^3$)	Criteria met?
Zero	12:52	0.0	0.0	Yes
Hg Mid	13:27	3.3	1.8	No
Hg High	NC	NC	NC	NC
Oxidized Mercury Mid	NC	NC	NC	NC
Oxidized Mercury High	NC	NC	NC	NC
Measurement Error Result:		Test not completed; NC indicates check not completed.		

Table 4-7. Horiba/Nippon Zero/Upscale Drift Tests—Phase 1

Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		1.3					
Date	Time	CEMS Reading ($\mu\text{g}/\text{m}^3$)		Drift ($\mu\text{g}/\text{m}^3$)		Result	
		Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
02/22/05	17:29:00	0.09	0.9	0.1	0.4	Yes	Yes
02/23/05	7:19:00	-0.09	1.0	0.1	0.3	Yes	Yes
02/24/05	7:29:00	0.0	0.8	0.0	0.5	Yes	Yes
02/25/05	17:35:00	0.0	1.1	0.0	0.2	Yes	Yes
02/26/05	8:19:00	-0.09	1.2	0.1	0.1	Yes	Yes
02/27/05	13:30:00	0.0	1.2	0.0	0.1	Yes	Yes
02/28/05	11:03:00	0.0	1.2	0.0	0.1	Yes	Yes

NOTE: 2/25/05 at 08:00 catalyst replaced. 2/27/05 at 08:40 catalyst replaced

Zero Drift Result: Criteria met

Upscale Drift Result: Criteria met

4.1.1.3 Tekran

The Tekran 7-day calibration error test, linearity check, system integrity test (which checks converter efficiency), cycle time, measurement error test, and zero/upscale drift test results are presented in Tables 4-8 through 4-13. The 7-day calibration error test was performed between February 15 and 21, 2005. The linearity check and the system integrity and measurement error tests were performed on February 15, 2005. The cycle time and zero/upscale drift tests were performed on February 21, 2005. The system was located at the stack sampling platform and configured with a 50-ft heated line (190°C) to the analysis system in the CEM shelter on the platform. All reported concentrations are corrected to 20°C. The Tekran met the criteria for the 7-day calibration error, system integrity, measurement error, linearity, and cycle time tests. It did not meet the criteria for

the zero/upscale drift tests of PS 12A which does not have the alternative criteria allowance when the span is defined at 10 ug/m³.

Table 4-8. Tekran 7-Day Calibration Error Test—Phase 1

Reference Gas Concentration (mid, µg/m ³):		5.1					
		CEMS reading (µg/m ³)		Error (difference) (µg/m ³)		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
02/15/05	9:50:00	0.000	4.703	0.000	0.347	Yes	Yes
02/16/05	10:10:00	0.000	4.675	0.000	0.375	Yes	Yes
02/17/05	9:35:00	0.000	4.409	0.000	0.641	Yes	Yes
02/18/05	15:52:00	0.096	4.640	0.096	0.410	Yes	Yes
02/19/05	10:05:00	0.075	4.602	0.075	0.448	Yes	Yes
02/20/05	10:27:00	0.122	4.756	0.122	0.294	Yes	Yes
02/21/05	10:09:00	0.000	4.613	0.000	0.437	Yes	Yes
7-Day Cal Error Result: Criteria met.							

Table 4-9. Tekran Linearity Test—Phase 1

Low-Level Reference Gas Conc. (µg/m ³): *		2.5	
Mid-Level Reference Gas Conc. (µg/m ³): *		6.1	
High-Level Reference Gas Conc. (µg/m ³): *		9.8	
Test Date:		2/21/05	
Cycle	Time	Gas type	CEMS reading (µg/m ³)
1	2:12:00	Low	2.707
1	2:22:00	Mid	6.574
1	2:40:00	High	10.191
2	2:55:00	Low	3.002
2	3:02:00	Mid	6.743
2	3:25:00	High	10.356
3	3:40:00	Low	3.104
3	3:55:00	Mid	6.818
3	4:05:00	High	10.357
Gas	Low	Mid	High
Average	2.937	6.712	10.302
% Rel. Diff.	19.65%	9.345%	4.859%
Linear Error (Diff, µg/m ³)	0.302	0.124	0.242
Criteria met?	Yes	Yes	Yes

* Reference gas produced by Tekran 3310 generator

Linearity Result: Criteria met.

Table 4-10. Tekran System Integrity Test—Phase 1

Mid-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		3.5		
High-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		5.7		
Test Date:		02/15/05		
Time	Gas type	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error ($\mu\text{g}/\text{m}^3$)	Criteria met?
12:01:00	Zero	0.000	0.000	Yes
12:14:00	Mid	3.299	0.231	Yes
12:34:00	High	5.185	0.465	Yes

Test Result: Criteria met.

Table 4-11. Tekran Cycle Time—Phase 1

<u>Upscale Cycle Time Test</u>	
Date:	2/21/2005
Start Time:	4:15:00
Stable Time:	4:30:00
Step Change ($\mu\text{g}/\text{m}^3$):	8.834
95% of Step Change:	8.392
Time of 95% Change:	4:20:00
Upscale Cycle Time:	0:05:00
<u>Downscale Cycle Time Test</u>	
Date:	2/21/2005
Start Time:	9:22:30
Stable Time:	9:37:30
Step Change ($\mu\text{g}/\text{m}^3$):	2.165
95% of Step Change:	2.057
Time of 95% Change:*	9:22:30
Downscale Cycle Time:	0:00:00
Cycle Time: Criteria met	

* This is a semicontinuous reading instrument, so the step change occurred at the time the next reading was available, which was 2 min and 30 sec.

Table 4-12. Tekran Measurement Error Test—Phase 1

Mid-Level Reference Gas, Elemental Mercury Conc. ($\mu\text{g}/\text{m}^3$): ¹		6.1		
High-Level Reference Gas, Elemental Mercury Conc. ($\mu\text{g}/\text{m}^3$): ¹		9.8		
Mid-Level Reference Gas, Oxidized Mercury Conc. ($\mu\text{g}/\text{m}^3$): ²		3.5		
High-Level Reference Gas, Oxidized Mercury Conc. ($\mu\text{g}/\text{m}^3$): ²		5.7		
Test Date:		2/15/2005		
Gas Type	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error (difference) ($\mu\text{g}/\text{m}^3$)	Criteria met?
Zero	1:56	0.176	0.176	Yes
Elemental Hg Mid	2:26	6.574	0.464	Yes
Elemental Hg High	2:44	10.191	0.367	Yes
Oxidized Hg Mid	12:14	3.299	0.010	Yes
Oxidized Hg High	12:34	5.185	0.079	Yes

¹ Reference gas produced by Tekran 3310 generator, concentration at 20°C.

² Oxidized mercury gas produced by HovaCal unit.

Measurement Error Result: Criteria met.

Table 4-13. Tekran Zero/Upscale Drift Tests—Phase 1

Mid-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		5.05					
Date	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)		Drift ($\mu\text{g}/\text{m}^3$)		Result	
		Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
02/15/05	9:50:00	0.000	4.703	0.000	0.347	Yes	Yes
02/16/05	9:42:00	0.000	4.675	0.000	0.375	Yes	Yes
02/17/05	9:35:00	0.000	4.409	0.000	0.641	Yes	No
02/18/05	15:52:00	0.096	4.640	0.096	0.410	Yes	Yes
02/19/05	10:05:00	0.075	4.602	0.075	0.448	Yes	Yes
02/20/05	10:27:00	0.122	4.756	0.122	0.294	Yes	Yes
02/21/05	10:09:00	0.000	4.613	0.000	0.437	Yes	Yes

Zero Drift Result: Criteria met.

Criteria not met on

Upscale Drift Result: 2/17/05.

4.1.1.4 ThermoElectron

The ThermoElectron 7-day calibration error test, linearity check, system integrity (which checks converter efficiency), cycle time test, measurement error test, and zero/upscale drift test results are presented in Tables 4-14 through 4-19. The system was located at the stack sampling platform and was configured with a 50-ft heated line (165°C) to the analysis system in the CEMS shelter on this platform. The 7-day calibration error test was performed February 18 through 24, 2005. The linearity test was performed on February 26. The system integrity test was performed February 18, 2005. The cycle time test was performed on February 20 (downscale) and February 26 (upscale). The measurement error test was performed on February 18 and 26 and the zero/upscale drift test was performed on February 20. The Thermo met the criteria for the 7-day calibration error, system integrity, measurement error, linearity, and cycle time tests. It did not meet the criteria for the zero/upscale drift tests of PS 12A which does not have the alternative criteria allowance when the span is defined at 10 $\mu\text{g}/\text{m}^3$.

Table 4-14. Thermo 7-Day Calibration Error Test—Phase 1

Reference Gas Concentration ($\mu\text{g}/\text{m}^3$):		1.9					
		CEMS reading ($\mu\text{g}/\text{m}^3$)		Error (difference) ($\mu\text{g}/\text{m}^3$)		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met	Span criteria met
02/18/05	9:50:00	-0.07	1.84	0.07	0.06	Yes	Yes
02/19/05	10:10:00	0.04	1.93	0.04	0.03	Yes	Yes
02/20/05	9:35:00	0.09	2.32	0.09	0.42	Yes	Yes
02/21/05	9:50:00	0.00	2.74	0.00	0.84	Yes	Yes
02/22/05	15:12:00	0.00	2.31	0.00	0.41	Yes	Yes
02/23/05	15:52:00	0.00	1.95	0.00	0.05	Yes	Yes
02/24/05	10:09:00	-0.09	1.83	0.09	0.07	Yes	Yes

7 Day Cal Error Result: Criteria met.

Table 4-15. Thermo Linearity Test—Phase 1

Low-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		1.9	
Mid-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		5.6	
High-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		10.4	
Test Date:		2/26/05 and 2/27/05 ^a	
Cycle	Time	Gas type	CEMS reading ($\mu\text{g}/\text{m}^3$)
1	12:28:00	Low	1.68
1	12:32:00	Mid	5.27
1	8:58:00	High	10.23
2	14:24:00	Low	1.77
2	14:28:00	Mid	5.38
2	9:14:00	High	10.68
3	14:42:00	Low	2.20
3	14:47:00	Mid	5.44
3	9:27:00	High	10.72
Gas	Low	Mid	High
Average	1.88	5.36	10.54
% Rel. Diff.	0.88%	4.23%	1.38%
Linear Error (Diff, $\mu\text{g}/\text{m}^3$)	0.02	0.24	0.14
Criteria met?	Yes	Yes	Yes
Linearity Result:	Criteria met.		

^a High conc. 9.03 $\mu\text{g}/\text{m}^3$ cylinder was found to be defective; 10.4 $\mu\text{g}/\text{m}^3$ was substituted and was run on 2/27/05.

Table 4-16. Thermo System Integrity Test—Phase 1

Mid-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):	3.5			
High-Level Oxidized Mercury Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):	5.7			
Test Date:	02/18/05			
Time	Gas Type	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error ($\mu\text{g}/\text{m}^3$)	Criteria met?
14:45:00	Zero	0.06	0.06	Yes
16:41:00	Mid	3.43	0.10	Yes
17:08:00	High	5.80	0.15	Yes

Test Result: Criteria met.

Table 4-17. Thermo Cycle Time—Phase 1

Upscale Cycle Time Test	
Date:	2/26/2005
Start Time:	14:55:04
Stable Time:	15:08:04
Step Change ($\mu\text{g}/\text{m}^3$):	4.00
95% of Step Change:	3.80
Time of 95% Change:	15:04:44
Upscale Cycle Time:	0:09:40
Downscale Cycle Time Test	
Date:	2/20/2005
Start Time:	9:21:04
Stable Time:	9:29:54
Step Change ($\mu\text{g}/\text{m}^3$):	2.74
95% of Step Change:	2.60
Time of 95% Change:	9:23:44
Downscale Cycle Time:	0:02:40
Cycle Time Test: Criteria met.	

Table 4-18. Thermo Measurement Error Test—Phase 1

Mid-Level Reference Gas, Elemental Hg Conc. ($\mu\text{g}/\text{m}^3$):	5.6			
High-Level Reference Gas, Elemental Hg Conc. ($\mu\text{g}/\text{m}^3$):	10.4			
Mid-Level Reference Gas, Oxidized Hg Conc. ($\mu\text{g}/\text{m}^3$): ¹	3.5			
High-Level Reference Gas, Oxidized Hg Conc. ($\mu\text{g}/\text{m}^3$): ¹	5.7			
Test Dates:	2/18/2005 ² and 2/26/2005			
Gas type	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)	Error (difference) ($\mu\text{g}/\text{m}^3$)	Criteria met?
Zero	8:26	-0.26	0.26	Yes
Hg Mid	12:32	5.27	0.33	Yes
Hg High	8:58	10.23	0.17	Yes
Oxidized Hg Mid	16:41	3.43	0.1	Yes
Oxidized Hg High	17:08	5.8	0.15	Yes

¹ Oxidized Hg gas produced by HovaCal unit.

² Oxidized Hg tests.

Measurement Error Result: Criteria met.

Table 4-19. Thermo Zero/Upscale Drift Tests—Phase 1

Mid-Level Reference Gas Conc. ($\mu\text{g}/\text{m}^3$):		1.9					
Date	Time	CEMS reading ($\mu\text{g}/\text{m}^3$)		Drift ($\mu\text{g}/\text{m}^3$)		Result	
		Zero	Reference	Zero	Reference	Zero criteria met?	Reference criteria met?
02/18/05	9:50:00	-0.07	1.84	0.07	0.06	Yes	Yes
02/19/05	9:42:00	0.04	1.93	0.04	0.03	Yes	Yes
02/20/05	9:35:00	0.09	2.32	0.09	0.42	Yes	Yes
02/21/05	15:52:00	0.00	2.74	0.00	0.84	Yes	No
02/22/05	10:05:00	0.00	2.31	0.00	0.41	Yes	Yes
02/23/05	10:27:00	0.00	1.95	0.00	0.05	Yes	Yes
02/24/05	10:09:00	-0.09	1.83	0.09	0.07	Yes	Yes

Zero Drift Result: Criteria met.

Upscale Drift Result: Criteria not met on 2/21/05.

4.1.2 Phase 1 RATA Test Results

The data presented in this section are from the Initial RA test conducted during February 22-26, 2005. The testing consisted of 12 test runs comparing four mercury CEMS to the Ontario Hydro (OH) reference method. Overall, emissions as measured by OH appeared to remain fairly constant between 2 and 4 $\mu\text{g}/\text{m}^3$.

The Horiba/Nippon, Tekran, and Thermo instruments collected data for all 12 of the RA test runs and Forney/Genesis collected data for 7 RA tests runs. Duplicate OH sampling trains were used during all 12 RA test runs. Further details of the Ontario Hydro results and results for each mercury measurement system are presented in the sections that follow.

Mercury analysis results are provided in Appendix E of Volume 2 of this report. Mercury CEMS data collected during the RA test are provided in Appendix F of Volume 2 of this report.

4.1.2.1 Ontario Hydro Sample Results

Sampling times for the Ontario Hydro sampling method are provided in Table 4-20. All runs had the minimum sample collection time of 2 hr according to the method. Samples were collected over a period of several days in order to observe any variation in emission data that would be useful in evaluating CEMS response.

Table 4-20. Phase 1 RA Test Run Times

Run number	Date	Stack sampling intervals (in minutes per 24-hour clock)	Sampling time (min)
1	2/22/2005	10:30 - 12:30	120
2	2/22/2005	14:40 - 16:40	120
3	2/23/2005	09:20 - 11:20	120
4	2/23/2005	12:40 - 14:40	120
5	2/23/2005	15:50 - 17:50	120
6	2/24/2005	09:00 - 11:00	120
7	2/24/2005	12:05 - 14:05	120
8	2/24/2005	15:15 - 17:15	120
9	2/25/2005	08:40 - 10:40	120
10	2/25/2005	11:45 - 13:45	120
11	2/25/2005	14:50 - 16:50	120
12	2/26/2005	09:30 - 11:30	120

Table 4-21 summarizes the sampling conditions of the reference method train. Ontario Hydro sampling and recovery data are provided in Appendix C of Volume 2 of this report. Method 3B sample collection data and the Orsat analysis results for each sample are included in Appendix C of Volume 2. Sample traceability data sheets are provided in Appendix B and sampling equipment calibration results are provided in Appendix D of Volume 2.

Mercury analysis results are presented in Table 4-22 and were obtained by partially following the Ontario Hydro (OH) method analytical procedures. Because it was discovered very late in the test program that the analytical laboratory was not performing a critical step in the Ontario Hydro method (they had not been clarifying the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impinger sample prior to extracting an aliquot for analysis), the elemental mercury results for the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers are suspect. This omission affects both accuracy and precision.

Data are presented separately for each sample train component. Tables 4-23 and 4-24 combine the mercury analysis results with the stack sampling results and provide the mercury emissions on a concentration basis. All test runs used duplicate trains, and precision information is summarized in Table 4-25. Figure 4-1 shows concentrations of the total gaseous and oxidized fraction of mercury along with scatter points from each train. The estimated maximum amount of mercury that could be expected to have been introduced from the solution blanks is also shown for comparison purposes.

Table 4-21. Phase 1 RA Test Stack Sampling Data

	Sampling time (min)	Gas volume (dscm)	Water (%)	Avg. stack temp. (°F)	Iso- kinetic (%)
Run 1	120	3.127	13.6	125.3	101.3
Run 1 dup	120	3.023	13.5	125.0	101.1
Run 2	120	2.529	13.3	124.4	101.3
Run 2 dup	120	2.412	13.3	123.7	102.1
Run 3	120	2.343	13.6	125.5	98.8
Run 3 dup	120	2.298	13.0	123.8	98.8
Run 4	120	2.559	13.5	125.2	101.6
Run 4 dup	120	2.433	12.8	123.4	100.9
Run 5	120	2.514	14.2	127.0	102.4
Run 5 dup	120	2.445	13.6	125.2	99.4
Run 6	120	2.519	13.4	124.7	100.0
Run 6 dup	120	2.386	13.0	123.6	100.0
Run 7	120	2.467	13.1	123.7	97.3
Run 7 dup	120	2.451	12.5	122.1	100.0
Run 8	120	2.504	13.3	124.2	100.1
Run 8 dup	120	2.379	12.7	122.8	100.0
Run 9	120	2.461	12.8	123.0	100.0
Run 9 dup	120	2.441	12.3	121.8	99.9
Run 10	120	2.510	13.4	124.9	100.0
Run 10 dup	120	2.423	12.8	123.3	100.0
Run 11	120	2.406	13.7	125.5	100.0
Run 11 dup	120	2.356	13.2	124.1	100.1
Run 12	120	2.432	14.1	126.7	100.6
Run 12 dup	120	2.307	13.4	124.9	100.1

Table 4-22. Phase 1 RA Test Ontario Hydro Mercury Analysis Results (µg)

Field ID	Particle Bound Phase			Gaseous Phase							Total (µg)
				Ionic ^a		Elemental				Gas phase subtotal	
	Filter	Probe rinse	Part. bound subtotal	KCl impingers	KCl blank corrected amt. ^b	HNO ₃ /H ₂ O ₂ Impinger	HNO ₃ /H ₂ O ₂ imp. blank corrected amt. ^b	KMnO ₄ /H ₂ SO ₄ impingers (see Note)	Elemental subtotal		
Run 1	< 0.005	< 0.012	< 0.017	0.165 ^e	0.148	0.037 ^{c,e}	0.033	9.32	9.35	9.50	9.50
Run 1 dup	< 0.005	< 0.011	< 0.016	0.712	0.641	0.038 ^c	0.034	9.99	10.02	10.66	10.66
Run 2	< 0.005	< 0.013	< 0.018	0.705	0.635	0.059	0.053	7.04	7.09	7.73	7.73
Run 2 dup	< 0.005	0.031	0.031	0.556	0.500	0.028 ^c	0.025	7.62	7.64	8.14	8.18
Run 3	< 0.005	0.029	0.029	0.771	0.693	0.031 ^c	0.027	8.42	8.44	9.14	9.16
Run 3 dup	< 0.005	0.019	0.019	0.727	0.654	0.015 ^c	0.014	6.26	6.27	6.92	6.94
Run 4	< 0.005	< 0.011	< 0.016	0.871	0.784	0.036 ^c	0.032	6.71	6.74	7.53	7.53
Run 4 dup	< 0.005	< 0.010	< 0.015	1.006	0.905	0.035 ^c	0.032	8.20	8.23	9.14	9.14
Run 5	< 0.005	< 0.012	< 0.017	1.040	0.936	0.026 ^{c,e}	0.024	8.81	8.83	9.77	9.77
Run 5 dup	< 0.005	0.016	0.016	1.075	0.968	0.032 ^c	0.028	7.95	7.97	8.94	8.96
Run 6	< 0.006 ^e	< 0.011	< 0.017	0.890	0.801	0.028 ^{c,e}	0.025	11.75	11.77	12.58	12.58
Run 6 dup	< 0.005	< 0.012 ^e	< 0.017	0.938	0.844	0.026 ^c	0.024	8.22	8.25	9.09	9.09
Run 7	< 0.005	0.020	0.020	0.767	0.690	0.031 ^{c,e}	0.028	7.94	7.97	8.66	8.68
Run 7 dup	0.011 ^a	0.020 ^e	0.030 ^a	0.972	0.874	0.030 ^c	0.027	8.13	8.15	9.03	9.06
Run 8	0.016 ^a	< 0.017	0.016 ^a	0.906	0.815	0.033 ^c	0.030	7.09	7.12	7.93	7.95
Run 8 dup	0.006 ^a	< 0.010	0.006 ^a	0.992	0.893	0.020 ^{c,e}	0.018	6.28	6.29	7.19	7.19
Run 9	< 0.005	0.012 ^e	0.012	1.190	1.071	0.028 ^c	0.025	7.78	7.80	8.87	8.88
Run 9 dup	< 0.005	0.026	0.026	1.125	1.013	0.029 ^c	0.026	7.31	7.34	8.35	8.37
Run 10	< 0.005	0.025	0.025	0.980	0.882	0.031 ^c	0.027	8.07	8.09	8.97	9.00
Run 10 dup	< 0.005	< 0.012 ^e	< 0.017	1.020	0.918	0.029 ^c	0.026	8.43	8.45	9.37	9.37
Run 11	0.006 ^a	< 0.014	0.006 ^a	0.943	0.848	0.027 ^c	0.024	7.65	7.67	8.52	8.52
Run 11 dup	< 0.005	0.033	0.033	0.935	0.842	0.068	0.062	7.58	7.64	8.48	8.51
Run 12	< 0.005	0.016 ^e	0.016	0.949	0.854	0.038 ^c	0.034	6.25	6.28	7.13	7.15
Run 12 dup	< 0.005	0.022	0.022	0.944	0.849	0.023 ^c	0.021	8.37	8.39	9.23	9.26
FB	0.016 ^e	< 0.006		0.475		0.008 ^{c,e}		0.014			
SB	< 0.005	< 0.005		0.002		0.004		< 0.001			
Est'd. Max. Contribution from hydroxylamine ^d :				0.002				0.008			

FB = Field Blank Train; SB = Solution Blank plus Filter Blank

^a The Field Blank Train result exceeded 30% of the measured value; however, the contribution does not significantly impact total results.

^b Blank corrections performed per OH method.

^c The Solution Blank exceeded 10% of the measured value; however, the contribution does not significantly impact total results.

^d A maximum of approximately 0.2 mL (1-2 drops) in KCl impingers and 0.5 mL in KMnO₄/H₂SO₄ impingers was used during recovery; amount in blank was 0.01565 µg/mL.

^e Reanalysis result; original results did not meet < 10% difference for duplicate analyses.

NOTE: KMnO₄/H₂SO₄ impinger results are suspect due to improper sample preparation. See Section 5 for details.

Table 4-23. Phase 1 RA Total OH Mercury Concentrations

	Particle-bound subtotal		Gaseous-phase subtotal ^b	
	Mass (µg)	Concentration (µg/dscm)	Mass (µg)	Concentration (µg/dscm)
Run 1	< 0.017	N/D	9.50	3.04
Run 1 dup	< 0.016	N/D	10.66	3.53
Avg.				3.28
Run 2	< 0.018	N/D	7.73	3.06
Run 2 dup	0.031	0.013	8.14	3.38
Avg.				3.22
Run 3	0.029	0.012	9.14	3.90
Run 3 dup	0.019	0.008	6.92	3.01
Avg.				3.46
Run 4	< 0.016	N/D	7.53	2.94
Run 4 dup	< 0.015	N/D	9.14	3.76
Avg.				3.35
Run 5	< 0.017	N/D	9.77	3.89
Run 5 dup	0.016	0.006	8.94	3.66
Avg.				3.77
Run 6	< 0.017 ^a	N/D ^a	12.58	4.99
Run 6 dup	< 0.017	N/D	9.09	3.81
Avg.				4.40
Run 7	0.020	0.008	8.66	3.51
Run 7 dup	0.030 ^a	0.012 ^a	9.03	3.68
Avg.				3.60
Run 8	0.016 ^a	0.006 ^a	7.93	3.17
Run 8 dup	0.006 ^a	0.003 ^a	7.19	3.02
Avg.				3.09
Run 9	0.012	0.005	8.87	3.61
Run 9 dup	0.026	0.010	8.35	3.42
Avg.				3.51
Run 10	0.025	0.010	8.97	3.58
Run 10 dup	< 0.017	N/D	9.37	3.87
Avg.				3.72
Run 11	0.006 ^a	0.002 ^a	8.52	3.54
Run 11 dup	0.033	0.014	8.48	3.60
Avg.				3.57
Run 12	0.016	0.007	7.13	2.93
Run 12 dup	0.022	0.009	9.23	4.00
Avg.				3.47

^a The field blank train result exceeded 30% of the measured value; these results are not used in the gaseous-phase mercury concentration calculations.

^b Results for the elemental mercury portion (KM_nO₄/H₂SO₄ impinger samples) of the gaseous-phase are considered suspect due to improper sample preparation. See Section 5 for details.

Table 4-24. Phase 1 Gaseous-Phase OH Mercury

	Elemental portion ^a		Oxidized portion		Total gaseous	% Oxidized ^c (Ionic)
	Mass (µg)	Concentration (µg/dscm)	Mass ^b (µg)	Concentration (µg/dscm)	Concentration (µg/dscm)	
Run 1	9.35	2.99	0.15	0.05	3.04	1.6
Run 1 dup	10.02	3.316	0.64	0.21	3.53	6.0
Avg.		3.15		0.13	3.28	3.9
Run 2	7.09	2.80	0.63	0.25	3.06	8.2
Run 2 dup	7.64	3.17	0.50	0.21	3.38	6.1
Avg.		2.99		0.23	3.22	7.1
Run 3	8.44	3.60	0.69	0.30	3.90	7.6
Run 3 dup	6.27	2.73	0.65	0.28	3.01	9.4
Avg.		3.17		0.29	3.46	8.4
Run 4	6.74	2.63	0.78	0.31	2.94	10.4
Run 4 dup	8.23	3.38	0.91	0.37	3.76	9.9
Avg.		3.01		0.34	3.35	10.1
Run 5	8.83	3.51	0.94	0.37	3.89	9.6
Run 5 dup	7.97	3.26	0.97	0.40	3.66	10.8
Avg.		3.39		0.38	3.77	10.2
Run 6	11.77	4.675	0.801	0.318	4.99	6.4
Run 6 dup	8.25	3.46	0.84	0.35	3.81	9.3
Avg.		4.07		0.34	4.40	7.6
Run 7	7.97	3.23	0.69	0.28	3.51	8.0
Run 7 dup	8.15	3.33	0.87	0.36	3.68	9.7
Avg.		3.28		0.32	3.60	8.9
Run 8	7.12	2.84	0.81	0.33	3.17	10.3
Run 8 dup	6.29	2.64	0.89	0.38	3.02	12.4
Avg.		2.74		0.35	3.09	11.3
Run 9	7.80	3.17	1.07	0.44	3.61	12.1
Run 9 dup	7.34	3.01	1.01	0.41	3.42	12.1
Avg.		3.09		0.43	3.51	12.1
Run 10	8.09	3.22	0.88	0.35	3.58	9.8
Run 10 dup	8.45	3.49	0.92	0.38	3.87	9.8
Avg.		3.36		0.37	3.72	9.8
Run 11	7.67	3.19	0.85	0.35	3.54	10.0
Run 11 dup	7.64	3.24	0.84	0.36	3.60	9.9
Avg.		3.21		0.35	3.57	9.9
Run 12	6.28	2.58	0.85	0.35	2.93	12.0
Run 12 dup	8.39	3.64	0.85	0.37	4.00	9.2
Avg.		3.11		0.36	3.47	10.4

^a The KMnO₄/H₂SO₄ impinger data are considered suspect due to improper sample preparation. See Section 5 for details.

^b The field blank train result exceeded 30% of the measured value; however, the contribution does not significantly impact total results.

^c % Oxidized = (Oxidized Concentration / Total Concentration) * 100.

Table 4-25. Phase 1 Duplicate OH Train Relative Deviation

Run avg.	Concentration RD (%)		
	Oxidized (KCl)	Elemental ^a	Gaseous phase ^a
Run 1	63%	5%	7%
Run 2	10%	6%	5%
Run 3	2%	14%	13%
Run 4	10%	12%	12%
Run 5	3%	4%	3%
Run 6	5%	15%	13%
Run 7	12%	1%	2%
Run 8	7%	4%	2%
Run 9	2%	3%	3%
Run 10	4%	4%	4%
Run 11	1%	1%	1%
Run 12	2%	17%	15%

The PS-12A objective is $\leq 10\%$ RD for gaseous phase mercury, where $\% \text{ RD} = 100 * (\text{Abs}(a-b)) / (a+b)$.

Values shown in bold for Gaseous Phase have a RD > 10%.

^a Results for the elemental mercury portion (KMnO₄/H₂SO₄ impinger samples) are considered suspect due to improper sample preparation. See Section 5 for details.

NOTE: Nondetected results in the Particle Bound fraction prevented % RD calculations.

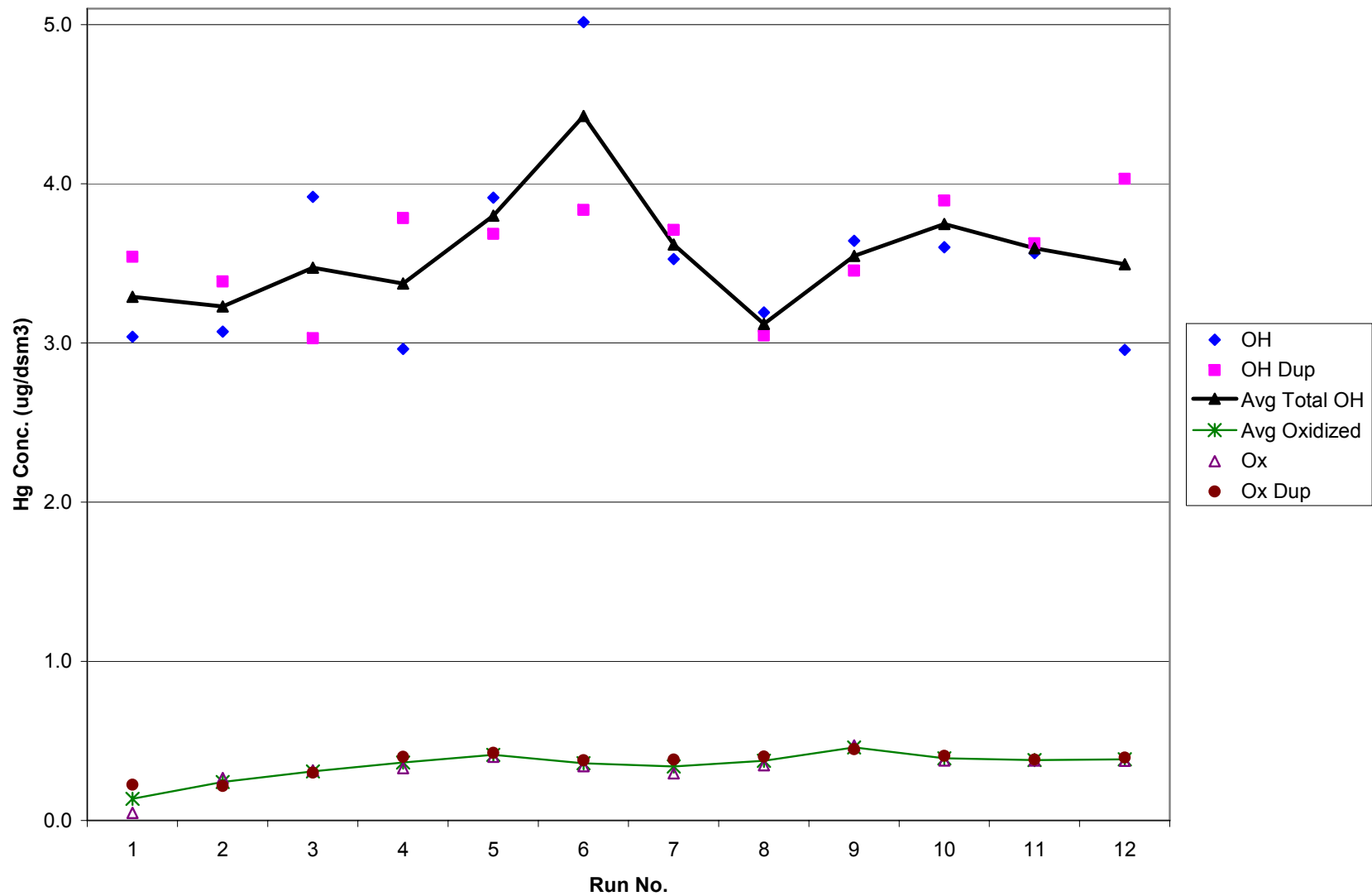


Figure 4-1. Phase 1 OH Gaseous Phase Mercury Concentrations

The OH sampling was performed isokinetically from a single point at a similar effective sampling location as the Hg CEMS and sorbent trap. As specified in Part 75 requirements for mercury monitoring and PS-12A, only the ionic (oxidized) and elemental fractions of the OH results are included in the gaseous phase concentration values used for the RATA calculations. Therefore, the mercury CEMS and the OH results are on a similar basis (i.e., gaseous phase only, concentrations per dry standard volume). The particle-bound fraction, which constituted less than 1% of the total mercury, is reported only for informational purposes.

The field blank train KCl impinger results on Table 4-22 are noteworthy due to the presence of mercury at levels greater than 30% of sample values. The cause is not known. As indicated at the bottom of Table 4-22, the calculated contribution from hydroxylamine (used in train recovery for the KCl and KMnO₄ impingers) could be as high as 0.002 µg and 0.008 µg for the KCl and KMnO₄ impingers, respectively. The field blank train used glassware from the recovered Run 1 train, which remarkably has a low sample result. An initial concern was that the Run 1 train recovery was incomplete. However, that seems unlikely because no significant increase was observed from recovery of this glassware when used for the next run (the same glassware was re-used for even and odd numbered runs). Even though the mercury levels in the field blank train were greater than 30% of the ionic fraction, it should be noted that the ionic fraction constitutes only about 10% of the total mercury in the train. This can be seen in Table 4-24 and Figure 4-1.

In order to verify that the field blank KCl impinger sample and the Run 1 KCl impinger sample had not been switched, the laboratory was contacted. The two sample volumes were rechecked and were verified to be correct for each sample type. These two samples were also reanalyzed with similar results. No explanation can be given for the unusual results obtained from these two samples.

Results from the remaining field blank samples revealed the presence of mercury in the filter, H₂O₂ impinger, and KMnO₄ impinger at levels near the detection limit. Also, two of the six solution blanks indicated the presence of mercury near the detection limit (the hydroxylamine solution result was higher). The laboratory method blanks showed no levels of mercury above detection limits.

The estimated contribution from solution blanks was between 0.5% and 0.7% of the total amount of mercury found in the samples. Thus, even though mercury was found in the solution blank samples, it did not appear to have an appreciable effect on the overall result. The KCl and HNO₃/H₂O₂ samples were blank corrected using the decision tree shown in Figure 4-2.

The relative deviation (RD) results in Table 4-25 indicate that even though the Run 1 KCl impinger result was anomalous, it did not have an appreciable impact on the overall result (8% RD). Most significantly, the RD for four of the 12 runs ranged between 12% to 15% RD which is greater than the 10% RD criteria in PS-12A. A review of other sampling parameters (O₂, CO₂, and H₂O) indicates that all parameters for all runs were within 10% of each other, with the exception of Run 7 O₂ with a difference of 11.5%.

Thus sampling variations do not appear to be contributing to the RD variances for those four runs (3, 4, 6, and 12). The RD calculation is Equation 12A-1 from the proposed revision to PS-12A, which was previously called RSD.

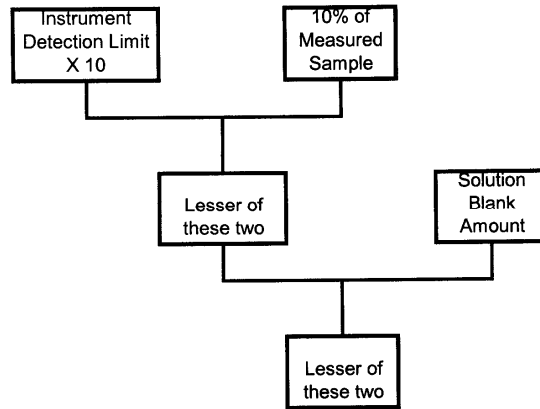


Figure 4-2. Decision Tree for Blank Corrections

4.1.2.2 CEMS and Appendix K RA Results

Table 4-26 summarizes the relative accuracy calculations for each of the Hg CEMS tested. Runs 3, 6, and 12 were not used because the RD values were > 10%. The Run 4 results were used (RD of 12%) in order to provide a 9th run for the RA calculation. Calculations followed the procedures of promulgated Part 75, and are provided in Table 4-27 through 4-31. Results for each Hg CEMS are briefly discussed below. Emissions appeared to remain fairly constant around 3 $\mu\text{g}/\text{m}^3$. Because mercury was observed in the solution blanks, blank corrections were used for the OH results in accordance with Section 13.4.3.1 of the Ontario Hydro Method. Still, Hg levels measured with the OH method were higher than all average Hg CEM values.

The reported values in the RA tables are based on the resolution of the analyzer; however, the believed resolution is more likely 0.1 $\mu\text{g}/\text{m}^3$. The Hg CEMS results are reported at 20°C.

Table 4-26 and Figure 4-2 show the OH results are consistently higher than CEMS results. Three possible reasons for this difference are (1) OH train contamination, (2) CEMS catalyst failure, or (3) other CEMS system component failure. Relative accuracy calculations were performed in three ways. First, relative accuracy was calculated using the average of Run 4 OH data. A second and third relative accuracy calculation was then performed using either the Run 4 train or the Run 4 duplicate train results. Comparing OH RD values with RA results sometimes helps to identify outliers or common trends.

Table 4-26. Phase 1 Summary of All RA Results for All CEMS

Run number	Use for RA?	OH gaseous mercury	CEMS ($\mu\text{g}/\text{dscm}$)				Appx. K ^e
			Forney	Horiba	Tekran	Thermo	
1	Yes	3.284	N/A	1.8	2.844	2.82	2.611
2	Yes	3.216	N/A	1.9	2.805	2.91	2.606
3	No	3.455	N/A	1.7	2.510	2.38	2.485
4	Yes ^a	3.348	N/A	1.7 ^b	2.657	2.42	2.457
5	Yes	3.771	N/A	2.1	3.106	3.10	2.789
6	No	4.402	1.9	1.7	3.414	3.11	2.955
7	Yes	3.597	1.7	1.5 ^b	2.982	2.48	2.743
8	Yes	3.095	4.0	1.3	2.997	2.47	2.865
9	Yes	3.513	2.3	2.1	3.099	2.23	2.698
10	Yes	3.721	1.5	2.3	3.076	2.00	2.633
11	Yes	3.570	1.6	2.3	3.132	2.22 ^d	2.814
12	No	3.468	2.0	2.2	3.583	3.18	3.127
Relative Accuracy (5 Runs)			81.9%	–	–	–	–
Relative Accuracy Using Avg Run 4 OH				51.9%	18.4%	37.5%	27.7%
Relative Accuracy Using Run 4 OH				51.0%	17.2%	37.2%	27.0%
Relative Accuracy Using Run 4 OH Dup				52.9%	21.3%	38.7%	29.9%

^a Run 4 OH result was 2.941 $\mu\text{g}/\text{dscm}$, Run 4 Dup OH result was 3.755 (Avg. of 3.348).

^b Data from half of run was lost.

^c Data from first 1-1/2 minutes were lost.

^d Results provided by Thermo software due to 4-20 mA output failure to data logger.

^e From proposed 40 CFR Part 75, Appendix K method.

NA indicates instrument not available to collect data.

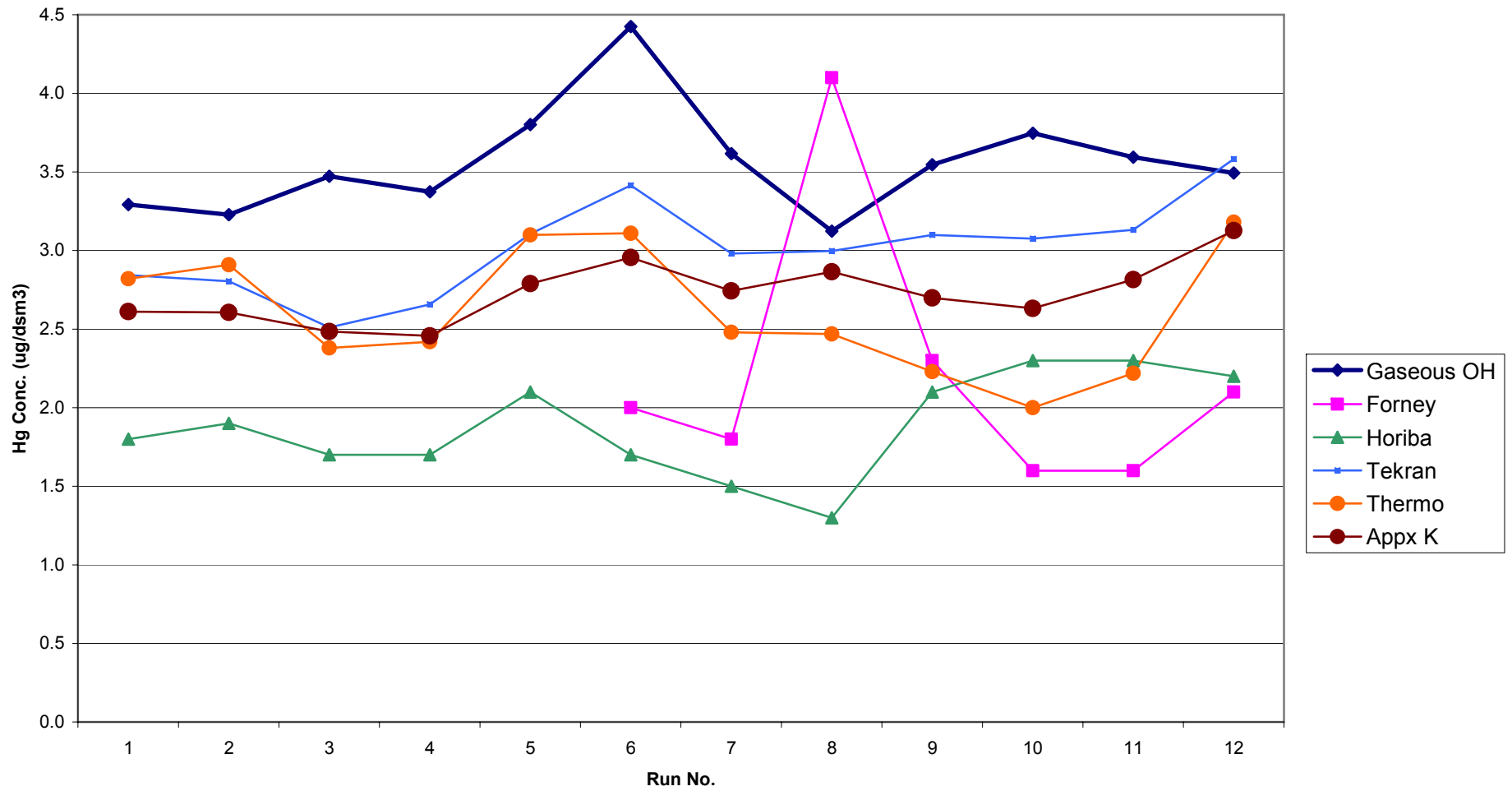


Figure 4-3. Summary of RA Phase 1 Tests

Calculations for Forney/Genesis system produced a relative accuracy (RA) of 82% for the five available test runs. The Horiba/Nippon system relative accuracy was around 52%. The Thermo system and Appendix K system RA results were similar at 38% and 28%, respectively. The Tekran system RA results were around 18%. Note that the RA criteria is $\leq 20\%$ RA or, if the average reference method concentration is less than $5 \mu\text{g}/\text{m}^3$, within $1 \mu\text{g}/\text{m}^3$. The Hg CEMS with a difference within $1 \mu\text{g}/\text{m}^3$ were the Tekran, the Thermo, and the Appendix K systems.

Figure 4-2 shows that with the exception of the Forney/Genesis, the CEMS and Appendix K values generally tracked with the OH results even if they were all slightly lower than the OH results. Figures 4-3 through 4-6 show plots of the run-by-run data for each analyzer, and Tables 4-27 through 4-31 show RA results for each analyzer compared with the OH method. The Appendix K RA results were provided by EPA and are reported here for comparison purposes only.

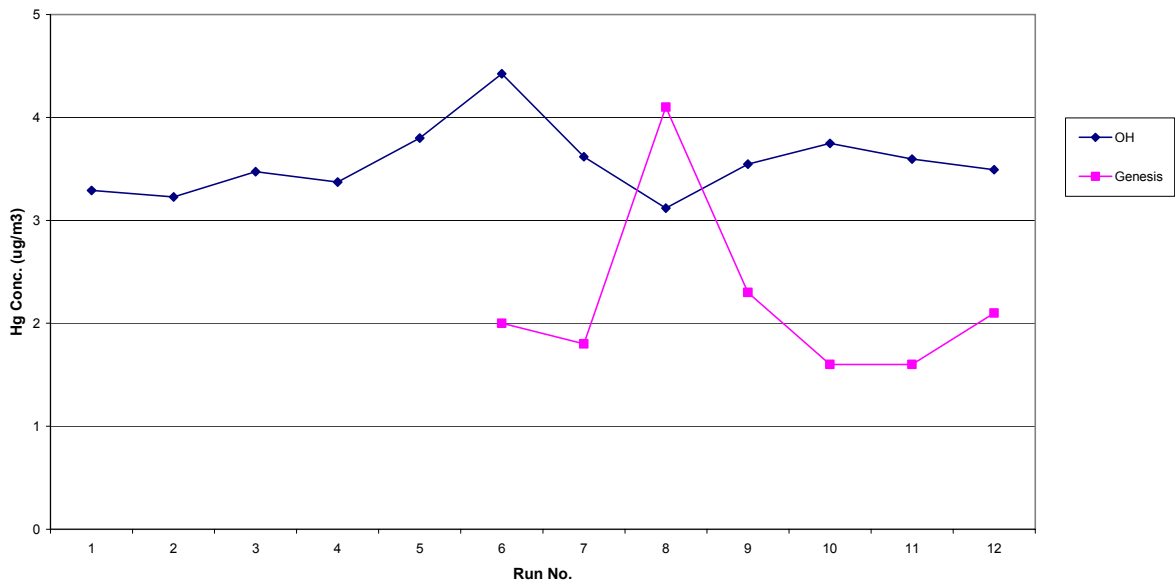


Figure 4-4. Phase 1 RA—OH Versus Forney/Genesis

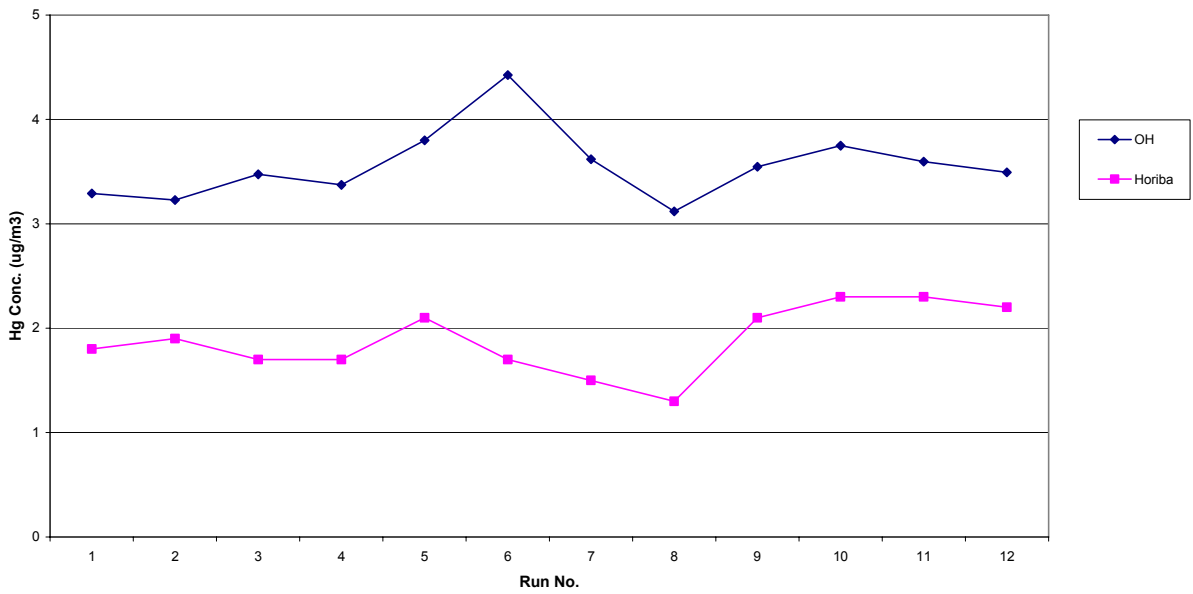


Figure 4-5. Phase 1 RA—OH Versus Horiba

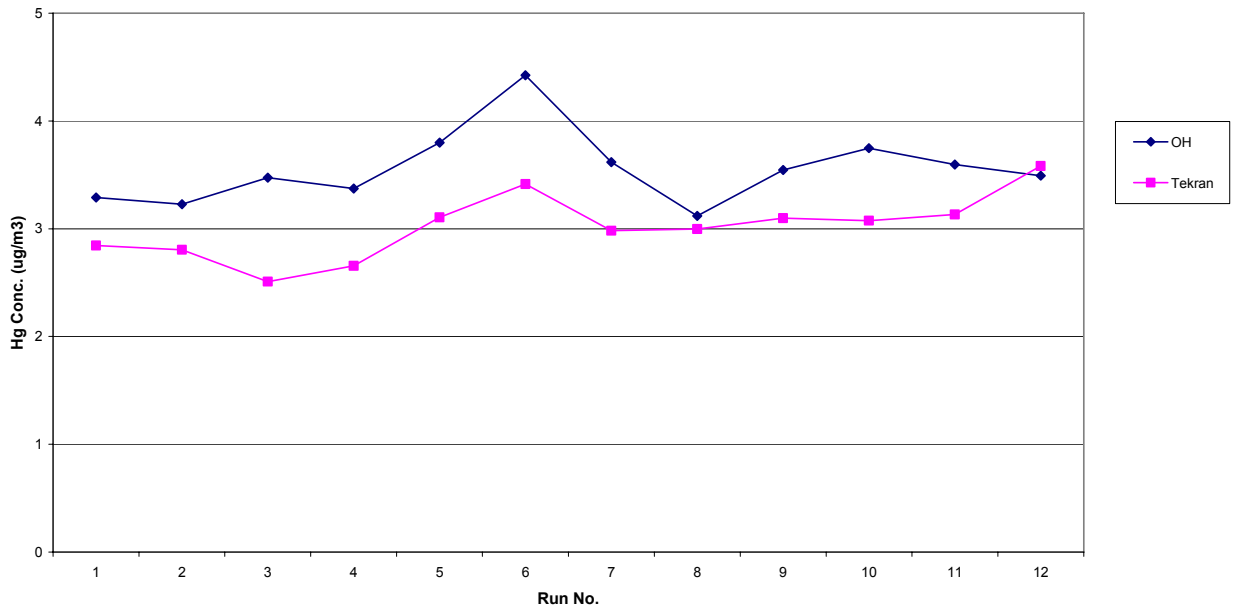


Figure 4-6. Phase 1 RA—OH Versus Tekran

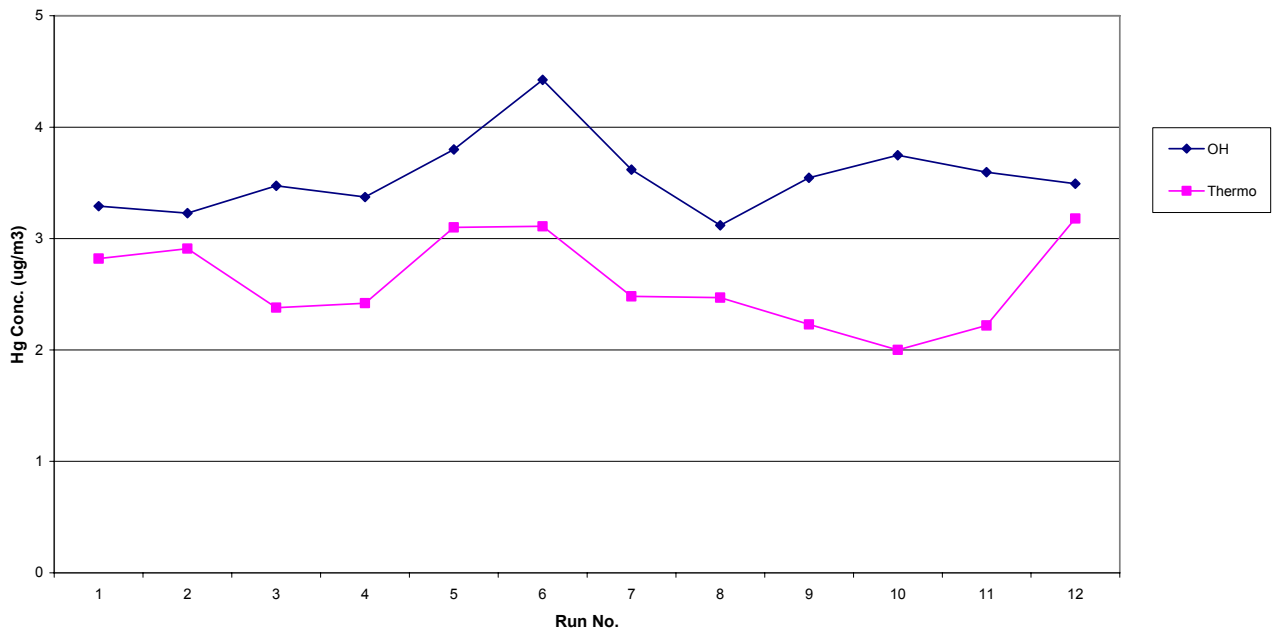


Figure 4-7. Phase 1 RA—OH Versus Thermo

Table 4-27. Phase 1 RA Results for Forney/Genesis

Run number	Use for RA?	Date	Time	CEMS avg. response (µg/dscm)	OH gaseous Hg response (µg/dscm)	Difference (µg/dscm)
1	No	2/22/2005	10:30 - 12:30	N/A	3.284	3.284
2	No	2/22/2005	14:40 - 16:40	N/A	3.216	3.216
3	No	2/23/2005	09:20 - 11:20	N/A	3.455	3.455
4	No	2/23/2005	12:40 - 14:40	N/A	3.348	3.348
5	No	2/23/2005	15:50 - 17:50	N/A	3.771	3.771
6	No	2/24/2005	09:00 - 11:00	1.9	4.402	2.402
7	Yes	2/24/2005	12:05 - 14:05	1.7	3.597	1.797
8	Yes	2/24/2005	15:15 - 17:15	4.0	3.095	-1.005
9	Yes	2/25/2005	08:40 - 10:40	2.3	3.513	1.213
10	Yes	2/25/2005	11:45 - 13:45	1.5	3.721	2.121
11	Yes	2/25/2005	14:50 - 16:50	1.6	3.570	1.970
12	No	2/26/2005	09:30 - 11:30	2.0	3.468	1.368
Arithmetic Mean ^a (µg/dscm)				2.2	3.5	1.3
Bias Adjustment Factor ^b						1.6
Standard Deviation ^c						1.3
Confidence Coefficient ^d						1.6
Relative Accuracy ^e using 5 runs (% of RM)						81.9%

^a Arithmetic Mean = $1/n \sum d_i$.

^b BAF = $1 + |1/n \sum d_i| / \text{Hg CEMS (avg)}$

^c Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$.

^d Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.776$.

^e Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$.

N/A indicates instrument not available for data collection

Table 4-28. Phase 1 RA Results for Horiba (All 12 Runs)

Run number	Use for RA?	Date	Time	CEMS avg. response (µg/dscm)	OH gaseous response (µg/dscm)	Difference (µg/dscm)
1	Yes	2/22/2005	10:30 - 12:30	1.8	3.284	1.484
2	Yes	2/22/2005	14:40 - 16:40	1.9	3.216	1.316
3	No	2/23/2005	09:20 - 11:20	1.7	3.455	1.755
4 ^{a, b}	Yes	2/23/2005	12:40 - 14:40	1.7	3.348	1.648
5	Yes	2/23/2005	15:50 - 17:50	2.1	3.771	1.671
6	No	2/24/2005	09:00 - 11:00	1.7	4.402	2.702
7 ^b	Yes	2/24/2005	12:05 - 14:05	1.5	3.597	2.097
8	Yes	2/24/2005	15:15 - 17:15	1.3	3.095	1.795
9	Yes	2/25/2005	08:40 - 10:40	2.1	3.513	1.413
10	Yes	2/25/2005	11:45 - 13:45	2.3	3.721	1.421
11	Yes	2/25/2005	14:50 - 16:50	2.3	3.570	1.270
12	No	2/26/2005	09:30 - 11:30	2.2	3.468	1.268
Relative Accuracy Using Avg. Run 4 OH						
Arithmetic Mean ^c (µg/dscm)				1.9	3.5	1.6
BAF						1.8
Standard Deviation ^e						0.3
Confidence Coefficient ^f						0.2
Relative Accuracy ^g (% of RM)						51.9%
Relative Accuracy Using Run 4 OH						
Arithmetic Mean (µg/dscm)				1.9	3.4	1.5
BAF						1.8
Standard Deviation						0.3
Confidence Coefficient						0.2
Relative Accuracy (% of RM)						51.0%
Relative Accuracy Using Run 4 OH Dup						
Arithmetic Mean (µg/dscm)				1.9	3.5	1.6
BAF						1.9
Standard Deviation						0.3
Confidence Coefficient						0.2
Relative Accuracy (% of RM)						52.9%

^a Run 4 OH result was 2.941 µg/dscm, Run 4 Dup OH result was 3.755 (Avg. of 3.348).

^b Data from half of run was lost.

^c Arithmetic Mean = $1/n \sum d_i$

^d BAF = $1 + |1/n \sum d_i| / \text{Hg CEMS (avg)}$

^e Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^f Confidence Coefficient = $t_{0.975} * \text{Std Dev} / n^{1/2}$, where $t_{0.975} = 2.306$

^g Relative Accuracy =

$([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

Table 4-29. Phase 1 RA Results for Tekran (All 12 Runs)

Run number	Use for RA?	Date	Time	CEMS avg. response (µg/dscm)	OH gaseous response (µg/dscm)	Difference (µg/dscm)
1	Yes	2/22/2005	10:30 - 12:30	2.844	3.284	0.440
2	Yes	2/22/2005	14:40 - 16:40	2.805	3.216	0.411
3	No	2/23/2005	09:20 - 11:20	2.510	3.455	0.945
4 ^a	Yes	2/23/2005	12:40 - 14:40	2.657	3.348	0.691
5	Yes	2/23/2005	15:50 - 17:50	3.106	3.771	0.665
6	No	2/24/2005	09:00 - 11:00	3.414	4.402	0.988
7	Yes	2/24/2005	12:05 - 14:05	2.982	3.597	0.615
8	Yes	2/24/2005	15:15 - 17:15	2.997	3.095	0.098
9	Yes	2/25/2005	08:40 - 10:40	3.099	3.513	0.414
10	Yes	2/25/2005	11:45 - 13:45	3.076	3.721	0.645
11	Yes	2/25/2005	14:50 - 16:50	3.132	3.570	0.438
12	No	2/26/2005	09:30 - 11:30	3.583	3.468	-0.115
Relative Accuracy Using Avg. Run 4 OH						
Arithmetic Mean ^b (µg/dscm)				2.97	3.5	0.5
BAF ^c						1.2
Standard Deviation ^d						0.2
Confidence Coefficient ^e						0.1
Relative Accuracy ^f (% of RM)						18.4%
Relative Accuracy Using Run 4 OH						
Arithmetic Mean (µg/dscm)				2.97	3.4	0.4
BAF ^c						1.2
Standard Deviation						0.2
Confidence Coefficient						0.1
Relative Accuracy (% of RM)						17.2%
Relative Accuracy Using Run 4 OH Dup						
Arithmetic Mean (µg/dscm)				2.97	3.5	0.6
BAF ^c						1.2
Standard Deviation						0.3
Confidence Coefficient						0.2
Relative Accuracy (% of RM)						21.3%

^a Run 4 OH result was 2.941 µg/dscm, Run 4 Dup OH result was 3.755 (Avg. of 3.348).

^b Arithmetic Mean = $1/n \sum d_i$

^c BAF = $1 + |1/n \sum d_i| / \text{Hg CEMS (avg)}$

^d Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^e Confidence Coefficient = $t_{0.975} * \text{Std Dev} / n^{1/2}$, where $t_{0.975} = 2.306$

^f Relative Accuracy =

$([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100.$

Table 4-30. Phase 1 Initial RA Results for Thermo (All 12 Runs)

Run number	Use for RA?	Date	Time	CEMS avg. response (µg/dscm)	OH gaseous response (µg/dscm)	Difference (µg/dscm)
1	Yes	2/22/2005	10:30 - 12:30	2.82	3.284	0.464
2	Yes	2/22/2005	14:40 - 16:40	2.91	3.216	0.306
3	No	2/23/2005	09:20 - 11:20	2.38	3.455	1.075
4 ^a	Yes	2/23/2005	12:40 - 14:40	2.42	3.348	0.928
5	Yes	2/23/2005	15:50 - 17:50	3.10	3.771	0.671
6	No	2/24/2005	09:00 - 11:00	3.11	4.402	1.292
7	Yes	2/24/2005	12:05 - 14:05	2.48	3.597	1.117
8	Yes	2/24/2005	15:15 - 17:15	2.47	3.095	0.625
9	Yes	2/25/2005	08:40 - 10:40	2.23	3.513	1.283
10 ^b	Yes	2/25/2005	11:45 - 13:45	2.00	3.721	1.721
11 ^c	Yes	2/25/2005	14:50 - 16:50	2.22	3.570	1.350
12	No	2/26/2005	09:30 - 11:30	3.18	3.468	0.288
Relative Accuracy Using Avg. Run 4 OH						
Arithmetic Mean ^d (µg/dscm)				2.52	3.5	1.0
BAF ^c						1.4
Standard Deviation ^e						0.5
Confidence Coefficient ^f						0.4
Relative Accuracy ^g (% of RM)						37.5%
Relative Accuracy Using Run 4 OH						
Arithmetic Mean (µg/dscm)				2.52	3.4	0.9
BAF ^c						1.4
Standard Deviation						0.5
Confidence Coefficient						0.4
Relative Accuracy (% of RM)						37.2%
Relative Accuracy Using Run 4 OH Dup						
Arithmetic Mean (µg/dscm)				2.52	3.5	1.0
BAF ^c						1.4
Standard Deviation						0.5
Confidence Coefficient						0.4
Relative Accuracy (% of RM)						38.7%

^a Run 4 OH result was 2.941 µg/dscm, Run 4 Dup OH result was 3.755 (Avg. of 3.348)

^b Data from first 1-1/2 minutes was lost.*

^c Results provided by Thermo software due to 4-20 mA output failure.*

^d Arithmetic Mean = $1/n \sum d_i$

^e BAF = $1 + [1/n \sum d_i] / \text{Hg CEMS (avg)}$

^f Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^g Confidence Coefficient = $t_{0.975} * \text{Std Dev} / n^{1/2}$, where $t_{0.975} = 2.306$

^h Relative Accuracy =

$([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

Table 4-31. Phase 1 RA Results for Appendix K Method

Run number	Use for Best 9	Date	Time	Appx. K avg. result (µg/dscm)	OH gaseous response (µg/dscm)	Difference (µg/dscm)
1	Yes	2/22/2005	10:30 - 12:30	2.611	3.284	0.673
2	Yes	2/22/2005	14:40 - 16:40	2.606	3.216	0.610
3	No	2/23/2005	09:20 - 11:20	2.485	3.455	0.971
4 ^a	Yes	2/23/2005	12:40 - 14:40	2.457	3.348	0.891
5	Yes	2/23/2005	15:50 - 17:50	2.789	3.771	0.982
6	No	2/24/2005	09:00 - 11:00	2.955	4.402	1.447
7	Yes	2/24/2005	12:05 - 14:05	2.743	3.597	0.854
8	Yes	2/24/2005	15:15 - 17:15	2.865	3.095	0.230
9	No	2/25/2005	08:40 - 10:40	2.698	3.513	0.815
10	Yes	2/25/2005	11:45 - 13:45	2.633	3.721	1.089
11	Yes	2/25/2005	14:50 - 16:50	2.814	3.570	0.755
12	No	2/26/2005	09:30 - 11:30	3.127	3.468	0.341
Relative Accuracy Using Avg. Run 4 OH						
Arithmetic Mean ^b (µg/dscm)				2.69	3.5	0.8
BAF ^c						1.3
Standard Deviation ^d						0.3
Confidence Coefficient ^e						0.2
Relative Accuracy ^f (% of RM)						27.7%
Relative Accuracy Using Run 4 OH						
Arithmetic Mean (µg/dscm)				2.69	3.4	0.7
BAF ^c						1.3
Standard Deviation						0.3
Confidence Coefficient						0.2
Relative Accuracy (% of RM)						27.0%
Relative Accuracy Using Run 4 OH Dup						
Arithmetic Mean (µg/dscm)				2.69	3.5	0.8
BAF ^c						1.3
Standard Deviation						0.3
Confidence Coefficient						0.2
Relative Accuracy (% of RM)						29.9%

^a Run 4 OH result was 2.941 µg/dscm, Run 4 Dup OH result was 3.755 (Avg. of 3.348)

^b Arithmetic Mean = $1/n \sum d_i$

^c BAF = $1 + |1/n \sum d_i| / \text{Hg CEMS (avg)}$

^d Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^e Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.306$

^f Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

4.1.3 Additional Testing

4.1.3.1 Initial Screening of Sorbent Trap Data With Hg CEMS

EPA Method 324 sorbent trap data from samples collected per Part 75 Section K on 12/16/04 are compared with Hg CEMS results in Table 4-32.

Table 4-32. Comparison of Sorbent Trap and Hg CEMS Data (12/16/04)

Run No.	Sample ID	Start time	End time	Sorbent trap Hg conc. ($\mu\text{g}/\text{m}^3$)	Avg. sorbent trap Hg conc. ($\mu\text{g}/\text{m}^3$)	Horiba avg. Hg conc. ($\mu\text{g}/\text{m}^3$)	Tekran avg. Hg conc. ($\mu\text{g}/\text{m}^3$)
1	Trap #1	9:24	11:18	3.0	3.0	3.0	2.695
	Trap #2	9:24	11:18	3.1			
2	Trap #3	11:38	13:31	3.4	3.4	3.8	3.325
	Trap #4	11:38	13:31	3.4			

4.1.3.2 Dynamic Spiking Data

Dynamic spiking and data collection were performed on the Tekran Hg CEMS as a preliminary evaluation of the instrumental reference method concept. Elemental Hg spiking was performed at the probe tip at three levels. These data are presented below in Table 4-33 and Figure 4-7.

Table 4-33. Tekran Elemental Mercury Sample Spikes

	Pre-test	Pre- and post-test	Post-test
Average Background Hg:	2.523	2.625	2.659
<u>1.32 $\mu\text{g}/\text{m}^3$ Spike</u>			
Instrument Reading:	3.803		
Recovered Hg:	1.280	1.178	1.144
Recovery %:	97.0%	89.2%	86.6%
<u>2.64 $\mu\text{g}/\text{m}^3$ Spike</u>			
Instrument Reading:	5.458		
Recovered Hg:	2.935	2.833	2.799
Recovery %:	111.2%	107.3%	106.0%
<u>3.95 $\mu\text{g}/\text{m}^3$ Spike</u>			
Instrument Reading:	7.644		
Recovered Hg:	5.121	5.019	4.984
Recovery %:	129.6%	127.1%	126.2%

% Recovery = (Instrm Rdg – Background/Amount Spiked).

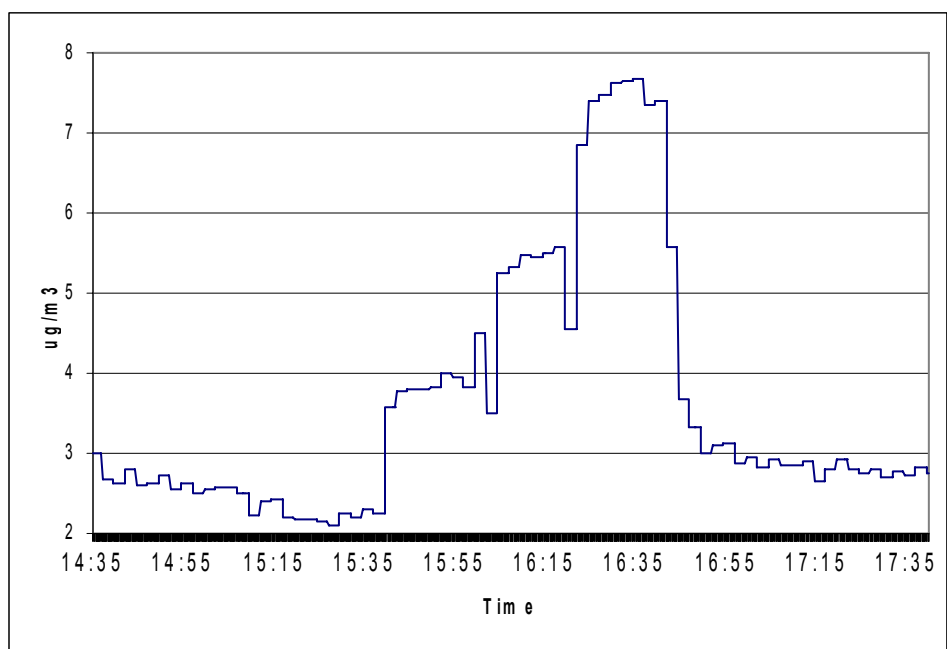


Figure 4-8. Tekran Elemental Mercury Spiking

4.2 Phase 2 Certification Test Results

4.2.1 Certification (excluding RATA)

Certification tests for Phase 2 were conducted on three different occasions through the late spring and summer of 2005. The first set of certification tests was performed during the period between May 13 through 21, 2005, the second set of certification tests was performed between June 22 and July 1, 2005 and the third set of certification tests was performed between July 6 and 15, 2005. Certification tests were conducted as specified in PS-12A and Part 75. Certification tests were performed on the Durag and Opsis in May shortly after their installation, and on the four Durag, Opsis, Tekran, and Thermo systems during June and July.

The results for each Hg CEMS are provided in this section. The certification tests for each instrument included a 7-day calibration error test, a linearity check, a system integrity test (which checks converter efficiency), a measurement error test, and zero/upscale drift tests. The span was defined at 10 $\mu\text{g}/\text{m}^3$ for each CEMS, and values used to assess CEMS performance are summarized based on that span, as shown in Table 4-34 below.

Table 4-34. Summary of Phase 2 CEMS Certification Criteria and Performance (Excluding RATA)

Test	Criteria	Criteria Met? (Y/N)			
		Durag	Opsis	Tekran	Thermo
7 Day Calibration Error Test	Error must be $\leq 5\%$ of span; or $\leq 1 \mu\text{g}/\text{m}^3$ (alternative specification when span is defined at $10 \mu\text{g}/\text{m}^3$).	Y	Y	Y	N
Linearity Test	Error must be $\leq 10\%$ of reference gas tag value or $\leq 1 \mu\text{g}/\text{m}^3$, whichever is least restrictive.	N	N	Y ^a	N
System Integrity Test	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y ^c	Y ^b	Y ^c	N
Cycle Time Test	Cycle times must be ≤ 15 minutes.	Y	Y	Y	Y
Measurement Error Test	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y ^a	N	Y ^a	N
Zero and Upscale Drift Test	Error must be $\leq 5\%$ of span (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y	N	Y ^c	N

^a Passed the first of two tests performed in July.

^b Passed the test performed in June.

^c Passed the test performed in May.

4.2.1.1 Durag

The Durag 7-day calibration error test, linearity check, system integrity test (which tests converter efficiency), measurement error test, and zero/upscale drift test results are presented in Tables 4-35 through 4-40. Testing and test dates are discussed below.

4.2.1.1.1 7-Day Calibration Error Test

The Durag system was challenged with three separate 7-day calibration error tests. Results from the three calibration error tests are summarized in Table 4-35. The instrument met the performance criteria for all three separate tests. The first test was conducted between the dates of May 13 and May 20, 2005. The reference gas used during the May 7-day calibration error test was from the Tekran 3310 Hg calibration source. The purpose of using the Tekran 3310 was due to a limited supply of available reference gases during the test period and an effort to conserve the gases for the remaining duration of the study.

The second 7-day calibration error test was conducted between the dates of June 22 and June 29, 2005. The reference gas used during the June 7-day calibration error test varied between the Tekran 3310 Hg calibration source and the $5.8 \mu\text{g}/\text{m}^3$ cylinder gas source. The difference between sources was due to the availability of the source concentration at the available time to perform the test.

A third 7-day calibration error test was conducted between the dates of July 6 and July 15, 2005. The reference gas used during the July test was from the $2.2 \mu\text{g}/\text{m}^3$ cylinder gas source. The 7-day calibration error test during the month of July was conducted within the same time frame as the RATA. This test information was collected and provided to make the test data complete. The information may also be useful in determining the instrument integrity.

Table 4-35. Durag 7-Day Calibration Error Test—Phase 2

Gas Source: Tekran 3310 Concentration: 2.5 µg/m ³							
Date	Time	CEMS Reading		Error		Criteria met?	
		Zero	Reference	Zero	Reference	Zero	Reference
05/13/05	16:32	0.0	2.2	0.00	0.26	Yes	Yes
05/14/05	16:36	0.0	2.4	0.00	0.06	Yes	Yes
05/15/05	11:09	0.0	2.9	0.00	0.44	Yes	Yes
05/16/05	10:52	0.0	2.1	0.00	0.36	Yes	Yes
05/17/05	10:44	0.0	2.4	0.00	0.06	Yes	Yes
05/18/05	9:36	0.0	2.1	0.00	0.36	Yes	Yes
05/19/05	9:03	0.0	2.7	0.00	0.24	Yes	Yes
05/20/05	8:40	0.0	2.5	0.00	0.04	Yes	Yes
7-Day Cal Error Result (5/13 - 5/20): Met criteria.							
Gas Source: Tekran 3310 and Cylinder Concentration: 4.9 and 5.8* µg/m ³							
Date	Time	CEMS Reading		Error		Criteria met?	
		Zero	Reference	Zero	Reference	Zero	Reference
* 06/22/05	16:33	0.1	5.6	0.10	0.20	Yes	Yes
* 06/23/05	9:23	0.1	5.7	0.10	0.10	Yes	Yes
06/24/05	15:43	0.0	5.3	0.00	0.39	Yes	Yes
* 06/25/05	10:46	0.1	5.8	0.10	0.00	Yes	Yes
* 06/26/05	10:52	0.1	5.3	0.10	0.50	Yes	Yes
06/27/05	9:07	0.2	4.8	0.20	0.11	Yes	Yes
* 06/28/05	7:17	0.1	5.9	0.10	0.10	Yes	Yes
* 06/29/05	14:17	0.1	5.6	0.10	0.20	Yes	Yes
7-Day Cal Error Result (6/22 - 6/29): Met criteria.							
Gas Source: Cylinder Concentration: 2.2 µg/m ³							
Date	Time	CEMS Reading		Error		Criteria met?	
		Zero	Reference	Zero	Reference	Zero	Reference
07/06/05	16:59	0.0	2.2	0.00	0.00	Yes	Yes
07/07/05	14:06	0.0	2.2	0.00	0.00	Yes	Yes
07/08/05	13:48	0.0	2.0	0.00	0.20	Yes	Yes
07/09/05	11:54	0.0	2.4	0.00	0.20	Yes	Yes
07/10/05	11:41	0.1	2.5	0.10	0.30	Yes	Yes
07/11/05	12:04	0.1	2.5	0.10	0.30	Yes	Yes
07/12/05	12:10	0.1	2.6	0.10	0.40	Yes	Yes
07/13/05	9:10	0.0	1.7	0.00	0.50	Yes	Yes
07/14/05	12:06	0.0	2.2	0.00	0.00	Yes	Yes
07/15/05	10:43	0.0	2.5	0.00	0.30	Yes	Yes
7 Day Cal Error Result (7/06 - 7/15): Met criteria.							

4.2.1.1.2 Linearity Test

The Durag system was challenged with two separate linearity tests. Results of the linearity tests are summarized in Table 4-36. The instrument did not meet the Part 75 criteria during either of the two tests. The first test was conducted on May 16, 2005. The reference gas used during the May measurement error test was from the Tekran 3310 mercury calibration source. The Tekran 3310 source was used due to a limited supply of available cylinder gases during the test period and an effort to conserve the cylinder gases for the remaining duration of the study. During the May linearity test, the average of the three high-level gas concentrations measured by the instrument was 0.1 µg/m³ above the allowable alternative criteria of ±1.0 µg/m³.

The second linearity test was conducted on July 13, 2005. The reference gas concentrations used during the July test were from the gas cylinder sources. The July test was performed after the RATA, primarily due to the limited time available to conduct the test prior to the RATA. The Durag system did not meet the test criteria during the July linearity test since the average of the three high-level gas concentrations measured by the instrument was 0.3 $\mu\text{g}/\text{m}^3$ above the allowable alternative criteria of $\pm 1.0 \mu\text{g}/\text{m}^3$.

An observation for both Durag linearity tests was that from cycle to cycle, the instrument showed an upward measurement trend.

Table 4-36. Durag Linearity Test—Phase 2

			From Tekran 3310
Low-Level Gas Concentration:			2.5 $\mu\text{g}/\text{m}^3$
Mid-Level Gas Concentration:			6.1
High-Level Gas Concentration:			9.8
Test Date:			5/16/2005
Cycle	Time	Gas type	CEMS Reading
1	15:21	Low	2.0
1	15:36	Mid	6.2
1	15:51	High	10.5
2	16:51	Low	2.8
2	17:01	Mid	6.7
2	17:17	High	11.2
3	17:34	Low	2.8
3	17:51	Mid	6.7
3	18:07	High	11.1
Gas	Low	Mid	High
Average	2.5	6.5	10.9
% Error	3.19%	6.44%	11.32%
Linear Error	0.1	0.4	1.1
Criteria met?	Yes	Yes	No
5/16/05 Linearity Result: Criteria not met.			
			From Cylinders
Low-Level Gas Concentration:			2.2 $\mu\text{g}/\text{m}^3$
Mid-Level Gas Concentration:			5.1
High-Level Gas Concentration:			10.4
Test Date:			07/13/05
Cycle	Time	Gas type	CEMS reading
1	9:18	Low	1.7
1	9:55	Mid	4.8
1	10:10	High	10.9
2	10:26	Low	2.7
2	10:48	Mid	5.4
2	11:01	High	11.9
3	11:27	Low	3.1
3	11:42	Mid	6.0
3	11:52	High	12.3
	9:10	Zero	0
Gas	Low	Mid	High
Average	2.5	5.4	11.7
% Error	13.6%	5.9%	12.5%
Linear Error	0.3	0.3	1.3
Criteria met?	Yes	Yes	No
7/13/05 Linearity Result: Criteria not met.			

4.2.1.1.3 System Integrity Test

During the May and June certification test periods, system integrity tests were performed on the Durag system. Results of this system integrity testing are summarized in Table 4-37. The Durag system met the performance criteria for the first system integrity test performed on May 20, 2005, but failed to meet the criteria for the second system integrity test conducted on June 28, 2005. A likely cause of the June system integrity test results was the degrading cuvet UV light filter in the analyzer that was diagnosed three days earlier.

Throughout the entire duration that the Durag system was operating on-site, weekly system integrity tests were performed. The results of all of the weekly system integrity tests are provided in Volume 3, Appendix H. The Durag system met the criteria on two of the 16 weekly system integrity tests performed.

Table 4-37. Durag System Integrity Test—Phase 2

Mid-Level Oxidized Hg Concentration:				From Hovacal	
High-Level Oxidized Hg Concentration:				4.7	
Test Date:				7.6	
				05/20/05	
Time	Gas type	CEMS reading (wet)	Error	Criteria met?	
13:13	Zero	0.5	0.5	Yes	
12:42	Mid	4.6	0.1	Yes	
12:13	High	8.6	1.0	Yes	
5/20/05 Converter Test Result: Criteria not met.					
Mid-Level Oxidized Hg Concentration:				From Hovacal	
High-Level Oxidized Hg Concentration:				4.7	
Test Date:				7.5	
				6/28/2005	
Time	Gas type	CEMS reading (wet)	Error	Criteria met?	
15:14	Zero	0.1	0.1	Yes	
15:40	Mid	3.0	1.7	No	
16:01	High	4.4	3.1	No	
6/28/05 Test Result: Criteria not met.					

4.2.1.1.4 Cycle Time Test

The Durag system was challenged with two complete cycle time tests which are summarized in Table 4-38. The instrument met the performance criteria for both tests. The first test was conducted on May 19, 2005, and the second test was conducted on July 14, 2005, after the RATA. Another cycle time test was attempted on the Durag system on June 26, 2005, but the system-automated 2-hour back-flush event interrupted the test results. Limited time availability prevented the test being repeated in June prior to the RATA that followed the next week.

Table 4-38. Durag Cycle Time—Phase 2

Date: 05/19/05		
Time	CEM reading	Comments
16:44	7.7	Pretest stable stack measurement
17:06	0	Zero and stable
17:06:30		Release CEM back to stack gas
17:13:00	5.9	Reach 95% of stable range
17:21:30	6.2	Stack gas measurement stable
6:30 min		Tolerance< 00:15:00
17:28	6.1	Pretest stable stack measurement
17:35	9.9	High level (10.4) reference Gas and stable
17:37:00		Release CEM back to stack gas
17:45:02	6.8	Reach 95% of stable range
17:52:00	6.6	Stack gas measurement stable
8:02 min		Tolerance< 00:15:00
Cycle time Test Results: Criteria met.		
Date: 07/14/05		
Time	CEM reading	Comments
12:19	3.2	Pretest stable stack measurement
12:28	11.0	Zero and stable
12:29:00		Release CEM back to stack gas
12:39:00	3.1	Reach 95% of stable range
12:44:00	3.1	Stack gas measurement stable
10:00 min		Tolerance< 00:15:00
12:53	3.0	Pretest stable stack measurement
13:02	0	High level (9.85) reference Gas and stable
13:04:00		Release CEM back to stack gas
13:13:00	2.8	Reach 95% of stable range
13:19:00	2.8	Stack gas measurement stable
9:00 min		Tolerance< 00:15:00
Cycle time Test Results: Criteria met.		

4.2.1.1.5 Measurement Error Test

The Durag system was challenged with two separate measurement error tests. Results of measurement error testing are summarized in Table 4-39. The first test was conducted on May 16, 2005. The reference gas used during the May measurement error test was from the Tekran 3310 Hg calibration source. The Tekran 3310 source was used due to a limited supply of available cylinder gases during the test period and an effort to conserve the gases for the remaining duration of the study.

The second measurement test was conducted on July 13, 2005. The reference gas concentrations used during the July measurement error test were from the reference gas cylinder. The July test was performed after the RATA primarily due limited time available to conduct the test prior to the RATA.

The Durag system did not meet the performance criteria for the high level gas for the first test (off by 0.2 $\mu\text{g}/\text{m}^3$), but did meet them for the second test.

Table 4-39. Durag Measurement Error Test—Phase 2

				From Tekran 3310
Low-Level Gas Concentration:				2.5
Mid-Level Gas Concentration:				6.1
High-Level Gas Concentration:				9.8
Test Date:				05/16/05
Gas Type	Time	CEMS Reading	Error	Criteria met?
Zero	15:06	0.0	0	Yes
Low	15:21	2.0	0.5	Yes
Mid	15:36	6.2	0.1	Yes
High	15:51	10.5	0.7	No
5/17/05 Measurement Error Result: Criteria not met.				
				From Cylinders
Low-Level Gas Concentration:				2.2
Mid-Level Gas Concentration:				5.1
High-Level Gas Concentration:				10.4
Test Date:				7/13/2005
Gas Type	Time	CEMS Reading	Error	Criteria met?
Zero	9:10	0.0	0	Yes
Low	9:18	1.7	0.5	Yes
Mid	9:55	4.8	0.3	Yes
High	10:10	10.9	0.5	Yes
7/13/05 Measurement Error Result: Met criteria.				

4.2.1.1.6 Zero/Upscale Drift Test

The Durag system was challenged with three separate zero/upscale drift tests results of which are summarized in Table 4-40. The instrument met the performance criteria for all three separate tests. The first zero/upscale drift test was conducted between the dates of May 13 and May 20, 2005. The reference gas used during the test period was from the Tekran 3310 Hg calibration source. The purpose of using the Tekran 3310 was due to a limited supply of available reference cylinder gases during the test period and an effort to conserve the gases for the remaining duration of the study.

The second zero/upscale drift test was conducted between the dates of June 22 and June 29, 2005. The reference gas used during the June zero/upscale drift test varied between the Tekran 3310 Hg calibration source and the 5.8 $\mu\text{g}/\text{m}^3$ concentration gas cylinder. The difference between gas sources was due to the availability of the gas cylinder at the available time to perform the test.

Table 4-40. Durag Zero/Upscale Drift Tests—Phase 2

Gas Source: Tekran 3310 Reference Gas Concentration: 2.5							
CEMS Reading				Drift		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
05/13/05	16:32	0.0	2.2	0.00	0.26	Yes	Yes
05/14/05	16:36	0.0	2.4	0.00	0.06	Yes	Yes
05/15/05	11:09	0.0	2.9	0.00	0.44	Yes	Yes
05/16/05	10:52	0.0	2.1	0.00	0.36	Yes	Yes
05/17/05	10:44	0.0	2.4	0.00	0.06	Yes	Yes
05/18/05	9:36	0.0	2.1	0.00	0.36	Yes	Yes
05/19/05	9:03	0.0	2.7	0.00	0.24	Yes	Yes
05/20/05	8:40	0.0	2.5	0.00	0.04	Yes	Yes
5/13 - 5/20 Zero Drift Result: Criteria met. 5/13 - 5/20 Upscale Drift Result: Criteria met.							
Gas Source: Tekran 3310 and Cylinder* Reference Gas: 4.9 and 5.8*							
CEMS Reading				Drift		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
* 06/22/05	16:33	0.1	5.6	0.10	0.20	Yes	Yes
* 06/23/05	9:23	0.1	5.7	0.10	0.10	Yes	Yes
06/24/05	15:43	0.0	5.3	0.00	0.39	Yes	Yes
* 06/25/05	10:46	0.1	5.8	0.10	0.00	Yes	Yes
* 06/26/05	10:52	0.1	5.3	0.10	0.50	Yes	Yes
06/27/05	9:07	0.2	4.8	0.20	0.11	Yes	Yes
* 06/28/05	7:17	0.1	5.9	0.10	0.10	Yes	Yes
* 06/29/05	14:17	0.1	5.6	0.10	0.20	Yes	Yes
6/22 - 6/29 Zero Drift Result: Criteria met. 6/22 - 6/29 Upscale Drift Result: Criteria met.							
Gas Source: Cylinder Reference Gas Concentration: 2.2							
CEMS Reading				Drift		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
07/06/05	16:59	0.0	2.2	0.00	0.00	Yes	Yes
07/07/05	14:06	0.0	2.2	0.00	0.00	Yes	Yes
07/08/05	13:48	0.0	2.0	0.00	0.20	Yes	Yes
07/09/05	11:54	0.0	2.4	0.00	0.20	Yes	Yes
07/10/05	11:41	0.1	2.5	0.10	0.30	Yes	Yes
07/11/05	12:04	0.1	2.5	0.10	0.30	Yes	Yes
07/12/05	12:10	0.1	2.6	0.10	0.40	Yes	Yes
07/13/05	9:10	0.0	1.7	0.00	0.50	Yes	Yes
7/6 - 7/13 Zero Drift Result: Criteria met. 7/6 - 7/13 Upscale Drift Result: Criteria met.							

A third zero/upscale drift test was conducted between the dates of July 6 and July 13, 2005. The reference gas used during the July zero/upscale drift test was from the 2.2 ug/m³ concentration reference gas cylinder. The July zero/upscale drift test was conducted within the same time frame as the RATA. This test information was collected and provided to make the test data complete. The information may also be useful in determining the instrument integrity.

4.2.1.2 Opsis

The Opsis 7-day calibration error test, linearity check, system integrity test (which checks converter efficiency), measurement error test, and zero/upscale drift test results are presented in Tables 4-41 through 4-46. Testing and test dates are discussed below.

4.2.1.2.1 7-Day Calibration Error Test

The Opsis system was challenged with three separate 7-day calibration error tests. Results of the calibration error testing are summarized in Table 4-41. The instrument met the performance criteria for three 7-day test periods.

The first test was performed between the dates of May 14 and May 21, 2005. The reference gas used during the May 7-day calibration error test was a 2.46 µg/m³ concentration from the Tekran 3310 Hg calibration source. The Tekran 3310 was used due to the limited supply of available cylinder gases during the test period. On the eighth day of the testing, the Opsis system measured 0.8 µg/m³ lower than the 1.0 µg/m³ tolerance limit specified by Part 75. This eighth day measurement was conducted after the gold trap was damaged by the trace nitric acid used in the oxidized mercury solution for the system integrity test.

The second 7-day calibration error test was conducted between June 23 and July 1, 2005. The reference gas used during this 7-day calibration error test varied between the Tekran 3310 Hg calibration source and the 5.8 µg/m³ concentration reference cylinder gas source. The difference between sources was due to the availability of the source concentration at the available time to perform the test.

Table 4-41. Opsis 7-Day Calibration Error Test—Phase 2

Gas Source: Tekran 3310 Reference Gas Concentration: 2.5								
CEMS Reading				Error		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
05/14/05	14:23	0.4	2.3	0.4	0.2	Yes	Yes	
05/15/05	10:37	0.0	2.3	0.0	0.2	Yes	Yes	
05/16/05	10:25	0.1	2.0	0.1	0.6	Yes	Yes	
05/17/05	9:40	0.2	1.9	0.2	0.7	Yes	Yes	
05/18/05	8:58	0.0	2.0	0.0	0.5	Yes	Yes	
05/19/05	15:38	0.7	2.2	0.7	0.3	Yes	Yes	
05/20/05	9:58	0.0	2.7	0.0	0.5	Yes	Yes	
05/21/05	5:09	0.3	0.7	0.3	1.8	Yes	No	
7-Day Cal Error Result (5/14 - 5/20): Criteria met.								
Gas Source: Tekran 3310 and Cylinder* Reference Gas Concentration: 4.9 and 5.8*								
CEMS Reading				Error		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
* 06/22/05	13:32	0.2	7.5	0.2	1.7	Yes	No	
* 06/23/05	9:59	0.2	5.2	0.2	0.6	Yes	Yes	
* 06/24/05	16:19	0.3	6.4	0.3	0.6	Yes	Yes	
* 06/25/05	10:58	0.0	6.5	0.0	0.7	Yes	Yes	
* 06/26/05	10:52	0.1	6.0	0.1	0.2	Yes	Yes	
06/27/05	8:58	0.1	4.6	0.1	0.3	Yes	Yes	
* 06/28/05	7:19	0.3	4.9	0.3	0.9	Yes	Yes	
* 06/29/05	14:19	0.1	5.4	0.1	0.4	Yes	Yes	
06/30/05	9:26	0.4	5.5	0.4	0.6	Yes	Yes	
07/01/05	8:10	0.2	4.5	0.2	0.4	Yes	Yes	
7-Day Cal Error Result (6/23 - 7/01): Criteria met.								
Gas Source: Cylinder Reference Gas Concentration: 2.2								
CEMS Reading				Error		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
07/06/05	14:26	0.0	1.9	0.0	0.3	Yes	Yes	
07/07/05	10:00	0.1	2.1	0.1	0.1	Yes	Yes	
07/08/05	10:24	0.0	1.8	0.0	0.4	Yes	Yes	
07/09/05	11:38	0.1	2.3	0.1	0.1	Yes	Yes	
07/10/05	11:30	0.0	2.1	0.0	0.1	Yes	Yes	
07/11/05	11:44	0.0	2.0	0.0	0.2	Yes	Yes	
07/12/05	12:28	0.3	1.5	0.3	0.7	Yes	Yes	
07/13/05	12:47	0.2	1.6	0.2	0.6	Yes	Yes	
07/14/05	9:01	0.1	1.8	0.1	0.4	Yes	Yes	
7 Day Cal Error Result (7/06 - 7/14): Criteria met.								

A third 7-day calibration error test was conducted between the dates of July 6 and July 14, 2005. The reference gas used during the July 7-day calibration error test was from the 2.2 µg/m³ concentration cylinder gas source. The 7-day calibration error test during the month of July was conducted within the same time frame as the RATA.

4.2.1.2.2 *Linearity Test*

The Opsis system was challenged with three separate linearity tests. Linearity test results are summarized in Table 4-42. The Opsis instrument did not meet the Part 75 performance criteria during any of the three linearity tests conducted. The first test was conducted on May 20, 2005. The reference gas used during the May linearity test was from the Tekran 3310 Hg calibration source. The purpose of using the Tekran 3310 was due to a limited supply of available cylinder gases during the test period and an effort to conserve the gases for the remaining duration of the study. The Opsis system did not meet the criteria for the zero concentration or the low-, mid-, or high-level Hg concentrations during the May test. The May linearity test was discontinued after the linear error of mid-level concentration measured $2.8 \mu\text{g}/\text{m}^3$ below the $\pm 1.0 \mu\text{g}/\text{m}^3$ test criteria.

An investigation by Opsis representatives in June concluded that the analyzer gold trap was damaged, perhaps by the nitric acid in the oxidized mercury solution used during the system integrity test conducted immediately prior to the measurement error test.

A second linearity test was conducted on the Opsis system on June 29, 2005. The reference gas used during the June linearity test was from the Tekran 3310 Hg calibration source. The linear error measured for the high-level Hg concentration was $0.4 \mu\text{g}/\text{m}^3$ beyond the $\pm 1.0 \mu\text{g}/\text{m}^3$ test criteria.

A third linearity test was conducted on the Opsis system on July 14, 2005. The reference gas concentrations used during the July linearity error test were from the gas cylinder sources. The July test was performed after the RATA to confirm the results of the linearity test performed prior to the RATA. The linear error from the mid-level and high-level Hg concentration were $0.7 \mu\text{g}/\text{m}^3$ and $2.4 \mu\text{g}/\text{m}^3$, respectively, beyond the test criteria.

Table 4-42. Opsis Linearity Test—Phase 2

Low-Level Gas Concentration:		2.5		
Mid-Level Gas Concentration:		6.1		
High-Level Gas Concentration:		9.8		
Test Date:		05/20/05		
Cycle	Time	Gas type	CEMS reading	
1	21:51	Low	1.7	
1	22:16	Mid *	2.3	
Level	Average	% Error	Linear error	Criteria met?
Low	1.7	0.32	0.78	Yes
Mid	2.3	0.62	3.81	No
5/20/05 Linearity Result: Incomplete.				
* Test aborted; inadequate mid level performance.				
Low-Level Gas Concentration:		2.455		
Mid-Level Gas Concentration:		6.138		
High-Level Gas Concentration:		9.821		
Test Date:		6/29/2005		
Cycle	Time	Gas type	CEMS reading	
1	18:31	Low	2.0	
1	18:48	Mid	5.0	
1	19:03	High	7.9	
2	19:18	Low	2.4	
2	19:33	Mid	5.4	
2	19:48	High	8.7	
3	20:00	Low	2.2	
3	20:11	Mid	5.2	
3	20:23	High	8.8	
Level	Average	% Error	Linear error	Criteria met?
Low	2.21	10.18%	0.250	Yes
Mid	5.22	15.00%	0.921	Yes
High	8.45	13.99%	1.374	No
6/29/05 Linearity Result: Criteria not met.				
Reference Gas Sources		From Cylinders		
Low-Level Gas Concentration:		2.2		
Mid-Level Gas Concentration:		5.1		
High-Level Gas Concentration:		10.4		
Test Date:		7/14/2005		
Cycle	Time	Gas type	CEMS reading	
1	9:01	Low	1.8	
1	9:18	Mid	3.2	
1	9:33	High	6.5	
2	9:48	Low	2.0	
2	10:08	Mid	3.4	
2	10:26	High	7.2	
3	10:47	Low	2.0	
3	11:03	Mid	3.6	
3	11:23	High	7.3	
Level	Average	% Error	Linear error	Criteria met?
Low	1.89	13.9%	0.305	Yes
Mid	3.39	33.6%	1.715	No
High	6.99	32.8%	3.412	No
7/14/05 Linearity Result: Criteria not met.				

4.2.1.2.3 System Integrity Test

System integrity tests were performed on the Opsis system on two separate occasions. Results of those tests are summarized in Table 4-43. The first system integrity test was performed on the Opsis system on May 20, 2005. The Opsis system did not meet the test criteria during this test, and the test was discontinued after the mid-level concentration measurements were recorded. The system consistently measured abnormally low stack gas values after conducting the system integrity test. All certification tests performed after the system integrity test did not meet the test criteria.

MRI was requested by the on-site Opsis representative to refrain from conducting further system integrity tests on the Opsis system until an investigation could be performed to determine the cause of the low measurements obtained. An investigation by Opsis representatives in June concluded that the analyzer gold trap was damaged and the cause was suspected to be the nitric acid in the oxidized mercury solution used in the system integrity test.

A second system integrity test was performed on June 28, 2005. New zero and oxidized mercury solutions were prepared for the HovaCal that did not include nitric acid. The solutions were prepared with 0.001N HCl. The Opsis system met the system integrity test criteria using the modified solutions. These modified solutions were made up weekly for the Opsis system integrity tests during the remainder of the test program. The results of weekly system integrity tests are provided in Volume 3, Appendix H. The Opsis met the criteria on two of the 11 weekly system integrity tests performed.

Table 4-43. Opsis System Integrity Test—Phase 2

Mid-Level Oxidized Mercury Concentration:		From Hovacal			
High-Level Oxidized Mercury Concentration:		2.9			
Test Date: 05/20/05		*			
Time	Gas type	CEMS reading	Error	Criteria met?	
4:50	Zero	0.47	0.46	Yes	
19:19	Mid	1.40	1.70	No	
	High *				
5/20/05 Conv. Test Result: Criteria not met.					
*Test discontinued.					
Mid-Level Oxidized Mercury Concentration:		From Hovacal			
High-Level Oxidized Mercury Concentration:		3.3			
Test Date: 6/28/2005		5.3			
Time	Gas type	CEMS reading	Error	Criteria met?	
17:58	Zero	0	0.0	Yes	
18:19	Mid	3.7	0.4	Yes	
18:41	High	5.8	0.5	Yes	
6/28/05 Test Result: Criteria met.					

4.2.1.2.4 Cycle Time Test

The Opsis system was challenged with one complete cycle time test. An effort was made to perform a cycle time test during the month of May, but the Opsis system was not operating properly resulting in cycle times up to 1 hour. The first complete cycle test was conducted on June 27, 2005. The Opsis instrument met the performance criteria during the June cycle time test and the results are shown in Table 4-44.

Table 4-44. Opsis Cycle Time—Phase 2

Note: No test in May due to slow response time.		
Date: 06/27/05		
Time	CEM reading	Comments
14:20	1.2	Pretest stable stack measurement
14:28	0	Zero and stable
14:45:08		Release CEM back to stack gas
14:53:08	1.1	Reach 95% of stable range
15:00:00	2.55	Stack gas measurement stable
0:08:00		Tolerance < 00:15:00
	2.7	Pretest stable stack measurement
17:23	9.6	High level (9.85) reference Gas and stable
17:25:38		Release CEM back to stack gas
17:38:08	2.7	Reach 95% of stable range
17:40:38	2.6	Stack gas measurement stable
	0:12:30	Tolerance < 00:15:00
6/27/05 Cycle time Test Results: Criteria met.		

4.2.1.2.5 Measurement Error Test

The Opsis system was challenged with three separate measurement error tests. Results of measurement error testing are summarized in Table 4-45. The Opsis instrument did not meet the performance criteria during any of the three tests conducted. The first test was conducted on May 20, 2005. The reference gas used during the May measurement error test was from the Tekran 3310 Hg calibration source. The purpose of using the Tekran 3310 was due to a limited supply of available cylinder gases during the test period and an effort to conserve the cylinder gases for the remaining duration of the study. The Opsis system did not meet the criteria for the zero concentration point nor any of the mercury concentrations attempted during the May test. The test was aborted after the mid-level mercury concentration was 4.3 $\mu\text{g}/\text{m}^3$ below the 0.5 $\mu\text{g}/\text{m}^3$ tolerance limit.

An investigation by Opsis representatives in June concluded that the analyzer gold trap may have been damaged by the nitric acid in the oxidized mercury solution used during the system integrity test conducted prior to the measurement error test.

The second Opsis measurement error test was conducted on June 29, 2005. The reference gas used during the June measurement error test was from the Tekran 3310 Hg calibration source. The mid-level Hg result was 0.4 $\mu\text{g}/\text{m}^3$ beyond and high-level Hg result was 0.6 $\mu\text{g}/\text{m}^3$ beyond the 0.5 $\mu\text{g}/\text{m}^3$ tolerance limit. No explanation is available as to why the instrument did not meet the test criteria.

Table 4-45. Opsis Measurement Error Test—Phase 2

From Tekran 3310				
Low-Level Gas Concentration:		2.5		
Mid-Level Gas Concentration:		6.1		
High-Level Gas Concentration:		9.8		
Test Date: 05/20/05				
Test aborted; system unable to measure adequate mid-levels				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	20:58	0.6	0.6	No
Low	21:51	1.7	1.0	No
Mid	22:15	2.3	4.3	No
High			10.5	No
5/20/05 Measurement Error Result: Criteria not met.				
From Tekran 3310				
Low-Level Gas Concentration:		2.455		
Mid-Level Gas Concentration:		6.138		
High-Level Gas Concentration:		9.821		
Test Date: 6/29/2005				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	20:43	0.2	0.2	Yes
Low	20:00	2.2	0.2	Yes
Mid	20:11	5.2	0.9	No
High	20:23	8.8	1.1	No
6/29/05 Measurement Error Result: Criteria not met.				
From Cylinders				
Low-Level Gas Concentration:		2.2		
Mid-Level Gas Concentration:		5.1		
High-Level Gas Concentration:		10.4		
Test Date: 7/14/2005				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	8:43	0.1	0.1	Yes
Low	9:01	1.8	0.4	Yes
Mid	9:18	3.2	1.9	No
High	9:33	6.5	3.9	No
7/14/05 Measurement Error Result: Criteria not met.				

A third measurement error test was conducted on July 14, 2005. The reference gas concentrations used during the July measurement error test were from the gas cylinder sources. The July test was performed after the RATA primarily due limited time available to conduct the test prior to the RATA. The Opsis system did not meet the performance criteria since the mid-level Hg result was 1.4 $\mu\text{g}/\text{m}^3$ beyond and high-level Hg result was 3.4 $\mu\text{g}/\text{m}^3$ beyond the 0.5 $\mu\text{g}/\text{m}^3$ test criterion.

4.2.1.2.6 Zero/Upscale Drift Test

The Opsis system was challenged with three separate zero/upscale drift tests. Results of those tests are summarized in Table 4-46. The instrument did not meet the performance criteria for all three test periods. This test does not have the alternate $\leq 1 \mu\text{g}/\text{m}^3$ criteria for a $10 \mu\text{g}/\text{m}^3$ like the 7-day calibration error test. The first

zero/upscale drift test was performed between May 14 and May 21, 2005. The reference gas used during the May zero/upscale drift test was a 2.46 µg/m³ concentration from the Tekran 3310 Hg calibration source. The purpose of using the Tekran 3310 was due to the limited supply of available cylinder gases during the test period. On the sixth day, the Opsis system measured 0.2 µg/m³ beyond the 0.5 µg/m³ test tolerance for the zero gas and on the fourth day, the system did not meet the upscale gas test criteria both because PS 12A does not have the alternative criteria allowance when the span is defined at 10 ug/m³. The eighth day measurement which was made after the gold trap was damaged also did not meet the criteria.

Table 4-46. Opsis Zero/Upscale Drift Tests—Phase 2

Gas Source: Tekran 3310 Reference Gas Concentration: 2.5								
		CEMS reading		Drift		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
05/14/05	14:23	0.4	2.3	0.4	0.2	Yes	Yes	
05/15/05	10:37	0.0	2.3	0.0	0.2	Yes	Yes	
05/16/05	10:25	0.1	2.0	0.1	0.5	Yes	Yes	
05/17/05	9:40	0.2	1.9	0.2	0.6	Yes	No	
05/18/05	8:58	0.0	2.0	0.0	0.5	Yes	Yes	
05/19/05	15:38	0.7	2.2	0.7	0.3	No	Yes	
05/20/05	9:58	0.0	2.7	0.0	0.2	Yes	Yes	
05/21/05	5:09	0.3	0.7	0.3	1.8	Yes	No	
5/14 - 5/21 Zero Drift Result: Criteria not met.								
5/14 - 5/21 Upscale Drift Result: Criteria not met.								
Gas Source: Tekran 3100 and Cylinder* Reference Gas Concentration: 4.9 (Tekran) and 5.8*								
		CEMS reading		Drift		Result		
Date	Time	Zero	Audit	Zero	Audit	Zero criteria met	Span criteria met?	
* 06/23/05	9:59	0.2	5.2	0.2	0.6	Yes	No	
* 06/24/05	16:19	0.3	6.4	0.3	0.6	Yes	No	
* 06/25/05	10:58	0.0	6.5	0.0	0.7	Yes	No	
* 06/26/05	10:52	0.1	6.0	0.1	0.2	Yes	Yes	
06/27/05	8:58	0.1	4.6	0.1	0.3	Yes	Yes	
* 06/28/05	7:19	0.3	4.9	0.3	0.9	Yes	No	
* 06/29/05	14:19	0.1	5.4	0.1	0.4	Yes	Yes	
06/30/05	9:26	0.4	5.5	0.4	0.6	Yes	No	
6/23 - 6/30 Zero Drift Result: Criteria met.								
6/23 - 6/30 Upscale Drift Result: Criteria not met.								
Gas Source: Cylinder Reference Gas Concentration: 2.2								
		CEMS reading		Drift		Result		
Date	Time	Zero	Audit	Zero	Audit	Zero criteria met?	Span criteria met?	
07/06/05	14:26	0.0	1.9	0.0	0.3	Yes	Yes	
07/07/05	10:00	0.1	2.1	0.1	0.1	Yes	Yes	
07/08/05	10:24	0.0	1.8	0.0	0.4	Yes	Yes	
07/09/05	11:38	0.1	2.3	0.1	0.1	Yes	Yes	
07/10/05	11:30	0.0	2.1	0.0	0.1	Yes	Yes	
07/11/05	11:44	0.0	2.0	0.0	0.2	Yes	Yes	
07/12/05	12:28	0.3	1.5	0.3	0.7	Yes	No	
07/13/05	12:47	0.2	1.6	0.2	0.6	Yes	No	
7/06 - 7/13 Zero Drift Result: Criteria met.								
7/06 - 7/13 Upscale Drift Result: Criteria not met.								

The second 7-day calibration error test was conducted between the dates of June 23 and June 30, 2005. The reference gas used during the June 7-day calibration error test varied between the Tekran 3310 Hg gas source and the 5.8 $\mu\text{g}/\text{m}^3$ concentration gas cylinder. Two sources were used due to the availability of the source concentration at the time available to perform the test. The system did not meet the upscale drift criteria because PS 12A does not have the alternative criteria allowance when the span is defined at 10 $\mu\text{g}/\text{m}^3$.

A third 7-day calibration error test was conducted between July 6 and July 13, 2005. The reference gas used during the July 7-day calibration error test was from the 2.2 $\mu\text{g}/\text{m}^3$ gas cylinder. The 7-day calibration error test during the month of July was conducted within the same time frame as the RATA. On the fourth day of the test, the system measured 0.1 $\mu\text{g}/\text{m}^3$ beyond the 0.5 $\mu\text{g}/\text{m}^3$ tolerance limit (5% of span) specified by PS 12A.

4.2.1.3 Tekran

The Tekran 7-day calibration error test, linearity check, system integrity test (which checks converter efficiency), measurement error test, and zero/upscale drift test results are presented in Tables 4-47 through 4-52. The Tekran system was located at the stack sampling platform and was configured with a 50-ft heated line (190°C) to the analysis system in the CEMS shelter on this platform. All reported concentrations are corrected to 20°C. Testing and test dates are discussed below.

4.2.1.3.1 7-Day Calibration Error Test

The Tekran system was challenged with two complete 7-day calibration error tests. Those test results are summarized in Table 4-47. The instrument met the performance criteria for both tests. The first test was performed between May 13 and May 20, 2005. The reference gas used during the May 7-day calibration error test varied between the Tekran 3310 Hg calibration source, and two gas cylinders with concentrations of 1.9 $\mu\text{g}/\text{m}^3$ and 2.2 $\mu\text{g}/\text{m}^3$. The purpose of using the Tekran 3310 was due to the limited supply of available cylinder gases during the test period; the purpose of using gas cylinder sources was to provide an external reference gas source.

Table 4-47. Tekran 7-Day Calibration Error Test—Phase 2

Gas Source: Tekran 3310 and Cylinders Reference Gas Concentration: 2.5, 1.9* and 2.1** µg/m ³							
		CEMS reading		Error		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met	Span criteria met?
05/13/05	13:28	0.0	2.2	0.00	0.28	Yes	Yes
05/14/05	8:42	0.0	2.3	0.00	0.19	Yes	Yes
* 05/15/05	9:49	0.0	1.9	0.00	0.01	Yes	Yes
05/15/05	12:11	0.0	2.1	0.00	0.31	Yes	Yes
* 05/16/05	11:59	0.0	2.0	0.00	0.11	Yes	Yes
05/16/05	13:54	0.0	2.0	0.00	0.44	Yes	Yes
05/17/05	11:28	0.0	2.0	0.00	0.44	Yes	Yes
* 05/17/05	13:55	0.0	1.9	0.00	0.01	Yes	Yes
* 05/18/05	12:15	0.0	2.0	0.00	0.13	Yes	Yes
05/18/05	15:42	0.0	1.9	0.00	0.52	Yes	Yes
** 05/19/05	10:09	0.0	2.1	0.00	0.01	Yes	Yes
** 05/20/05	15:57	0.0	2.1	0.00	0.03	Yes	Yes
7-Day Cal Error Result (5/13 - 5/20): Met criteria.							
Gas Source: Tekran 3310 and Cylinder Reference Gas Concentration: 2.5 and 2.2* µg/m ³							
		CEMS Reading		Error		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
* 07/06/05	17:34	0.0	1.957	0.00	0.40	Yes	Yes
* 07/07/05	9:03	0.0	2.014	0.00	0.35	Yes	Yes
07/08/05	9:34	0.0	2.071	0.00	0.56	Yes	Yes
07/09/05	8:58	0.0	1.957	0.00	0.68	Yes	Yes
07/10/05	8:54	0.0	1.923	0.00	0.71	Yes	Yes
07/11/05	8:54	0.0	1.923	0.00	0.71	Yes	Yes
07/12/05	8:49	0.0	2.008	0.00	0.63	Yes	Yes
* 07/13/05	9:15	0.1	2.423	0.09	0.06	Yes	Yes
* 07/14/05	9:32	0.0	2.389	0.00	0.03	Yes	Yes
* 07/15/05	10:19	0.0	2.454	0.00	0.09	Yes	Yes
7-Day Cal Error Result (7/6 - 7/15): Criteria met.							

An effort made to conduct a 7-day calibration error test during the month of June was interrupted by a system dilution orifice blockage on June 24. The June 25 daily measurement was not made since the system was not back in operation until June 26. The primary purpose of the July 7-day calibration error test was to repeat the interrupted June test.

The second Tekran 7-day calibration error test was conducted between July 6 and July 15, 2005 which also overlapped with the RATA. The reference gas used during the July test varied between the Tekran 3310 Hg calibration source and the 2.2 $\mu\text{g}/\text{m}^3$ cylinder gas source. Two different reference gases were used in an effort to conserve the cylinder gases thereby ensuring that there would be enough gases to complete the certification tests on all of the Hg CEMS.

4.2.1.3.2 Linearity Test

The results of the two linearity tests completed on the Tekran system are shown in Table 4-48. No effort was made to conduct a linearity test on the Tekran system during the month of May. An automated linearity test using reference gases generated by the Tekran 3310 Hg calibration source was attempted on July 1, 2005 but was interrupted when on-site operators unintentionally terminated the test to conduct a daily calibration error test. Another automated linearity test was completed on July 8, 2005 using the Tekran 3310 Hg calibration source and the test criteria were met.

A second linearity test was completed on July 13, 2005. The reference gas concentrations used during the July 13 test were from the gas cylinder sources. The July test was performed after the RATA primarily due to the fact that no low concentration cylinder gas was available in June to conduct a test independent of the Tekran 3310 Hg calibration source. The Tekran system did not meet the test criteria during the July 13 linearity test since the average of the three high-level gas concentrations measured by the instrument was 0.2 $\mu\text{g}/\text{m}^3$ beyond the allowable test criteria of $\pm 1.0 \mu\text{g}/\text{m}^3$.

Table 4-48. Tekran Linearity Test—Phase 2

			From Tekran 3310
Low-Level Gas Concentration:		2.5	
Mid-Level Gas Concentration:		6.1	
High-Level Gas Concentration:		9.8	
Test Date: 07/08/05			
Cycle	Time	Gas type	CEMS reading
1	1:43	Low	2.613
1	4:53	Mid	6.655
1	2:10	High	10.507
2	2:25	Low	2.692
2	2:43	Mid	6.63
2	2:57	High	10.147
3	3:12	Low	2.729
3	3:25	Mid	6.636
3	3:42	High	10.531
		1:30:00	Zero
Gas	Low	Mid	High
Average	2.678	6.640	10.395
% Error	1.63%	0.79%	1.39%
Linear Error	0.043	0.052	0.146
Criteria met?	Yes	Yes	Yes
7/8/05 Linearity Result: Met criteria.			
			From Cylinders
Low-Level Gas Concentration:		2.2	
Mid-Level Gas Concentration:		5.1	
High-Level Gas Concentration:		10.4	
Test Date: 07/13/05			
Cycle	Time	Gas type	CEMS reading
1	9:30	Low	2.423
1	9:55	Mid	4.42
1	10:19	High	9.198
2	10:31	Low	2.503
2	10:43	Mid	4.539
2	11:01	High	9.152
3	11:20	Low	2.509
3	11:42	Mid	4.585
3	11:57	High	9.17
		9:15:00	Zero
Gas	Low	Mid	High
Average	2.478	4.515	9.173
% Error	12.65%	11.48%	11.79%
Linear Error	0.278	0.585	1.227
Criteria met?	Yes	Yes	No
7/13/05 Linearity Result: Criteria not met.			

4.2.1.3.3 System Integrity Test

During the May and June certification test periods, two system integrity tests were performed on the Tekran system as shown in Table 4-49. The Tekran system met the test criteria during first system integrity test performed on May 19, 2005 but did not meet the test criteria during the second system integrity test conducted on June 28, 2002. On June 28, the result for the mid-level gas was 0.2 µg/m³ beyond the 0.5 µg/m³ test criteria and the result for the high-level gas was 0.7 µg/m³ beyond the 0.5 µg/m³ test criteria.

The Tekran system not meeting the test criteria during the June 28 test could have been due to a failure of the dilution eductor heater that occurred on the same day. The heater failure likely occurred due to an operator maintenance error installing the heater on June 26.

Results of the weekly system integrity tests are provided in Volume 3, Appendix H. The Tekran met the criteria for 11 of the 22 tests performed.

Table 4-49. Tekran System Integrity Test—Phase 2

				From Hovacal	
Mid-Level Oxidized Mercury Concentration:				3.5	
High-Level Oxidized Mercury Concentration:				5.6	
Test Date: 05/19/05					
Time	Gas type	CEMS reading	Error	Criteria met?	
15:09	Zero	0.125	0.13	Yes	
16:05	Mid	3.510	0.03	Yes	
16:33	High	5.785	0.22	Yes	
5/19/05 Test Result: Met criteria.					
				From Hovacal	
Mid-Level Oxidized Mercury Concentration:				3.3	
High-Level Oxidized Mercury Concentration:				5.3	
Test Date: 6/28/2005					
Time	Gas type	CEMS reading	Error	Criteria met?	
11:28	Zero	0.205	0.19	Yes	
11:52	Mid	2.821	0.70	No	
12:14	High	4.454	1.19	No	
6/28/05 Test Result: Criteria not met.					

4.2.1.3.4 Cycle Time Test

The Tekran system was challenged with one complete cycle time test on July 14, 2005 and met the test criteria during the test as shown in Table 4-50. Two other cycle time tests were attempted on June 30, 2005 but were aborted. The first attempt was aborted due to an operator error while the second was aborted due to unstable stack concentrations during the test period. Limited time availability prevented another attempt of the cycle time test in June prior to the RATA that followed the next week.

Table 4-50. Tekran Cycle Time Test—Phase 2

Date:	07/14/05	
	CEM	
Time	reading	Comments
12:10	1.97	Pretest stable stack measurement
13:02	0	Zero and stable
13:04:10		Release CEM back to stack gas
13:09:00	2.036	Reach 95% of stable range
13:19:00	2.059	Stack gas measurement stable
0:04:50		Tolerance< 00:15:00
12:10	2.02	Pretest stable stack measurement
12:28	9.073	High level (9.85) cylinder Gas and stable
12:29:10		Release CEM back to stack gas
12:37:00	1.951	Reach 95% of stable range
12:44:00	1.928	Stack gas measurement stable
0:07:50		Tolerance< 00:15:00
7/14/05 Cycle time Test Results: Met criteria.		

4.2.1.3.5 Measurement Error Test

No effort was made to conduct a measurement error test on the Tekran system during the month of May. An automated measurement error test using the Tekran 3310 Hg calibration source was attempted on July 1, 2005, but was interrupted by on-site operators unintentionally terminating the test to conduct a daily calibration error test. Another automated measurement error test was completed on July 8, 2005 using the Tekran 3310 Hg calibration source and the instrument met the test criteria.

The second measurement error test was conducted on July 13, 2005. The reference gas concentrations used during the July measurement error test were from the reference gas cylinder sources. The July test was performed after the RATA primarily due to the lack of available low concentration reference gas in June to conduct a test independent of the Tekran 3310 Hg calibration source. The Tekran system did not meet the test criteria during the July 13 test. The result for the high-level gas was 0.7 µg/m³ beyond the 0.5 µg/m³ test criteria limit. The results of all of the completed measurement error tests are shown in Table 4-51.

Table 4-51. Tekran Measurement Error Test—Phase 2

From Tekran 3310		From Tekran 3310		
Low-Level Gas Concentration:		2.5		
Mid-Level Gas Concentration:		6.1		
High-Level Gas Concentration:		9.8		
Test Date: 7/8/2005				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	1:30	0.0	0.0	Yes
Low	1:43	2.613	0.0	Yes
Mid	4:53	6.655	0.1	Yes
High	2:10	10.507	0.0	Yes
7/08/05 Measurement Error Result: Met criteria.				
From Tekran 3310		From Cylinders		
Low-Level Gas Concentration:		2.2		
Mid-Level Gas Concentration:		5.1		
High-Level Gas Concentration:		10.4		
Test Date: 7/13/2005				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	9:15	0.1	0.1	Yes
Low	9:30	2.423	0.2	Yes
Mid	9:55	4.420	0.7	No
High	10:19	9.198	1.2	No
7/13/05 Measurement Error Result: Criteria not met.				

4.2.1.3.6 Zero/Upscale Drift Test

Results of the Tekran zero/upscale drift testing are shown in Table 4-52. The Tekran system was challenged with two separate drift tests. The instrument met the test method criteria for the first test. The first zero/upscale drift test was conducted between May 13 and May 17, 2005. The reference gas used during the May zero/upscale drift test varied between the Tekran 3310 Hg calibration source, and the 1.9 µg/m³ and the 2.1 µg/m³ Hg concentration gas cylinder sources. The difference between Hg sources was due to the availability of the source concentration at the available time to perform the test.

A second zero/upscale drift test was conducted between July 8 and July 15, 2005. The reference gas used during the July zero/upscale drift test also varied between the Tekran 3310 Hg calibration source and the 2.2 µg/m³ Hg concentration gas cylinder. The difference between sources was due to the availability of the source concentration at the available time to perform the test. On the first four days of the test, the system measured less than 0.5 µg/m³ tolerance limit (5% of span) specified by PS 12A which does not have an alternative criteria for spans at 10 µg/m³.

Table 4-52. Tekran Zero/Upscale Drift Tests—Phase 2

Reference Gas Source: Tekran 3310 and Cylinder Reference Gas Concentration: 2.5, 1.9*, 2.1**							
Date	Time	CEMS Reading		Drift		Result	
		Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
05/13/05	13:28	0.0	2.2	0.00	0.28	Yes	Yes
05/14/05	8:42	0.0	2.3	0.00	0.19	Yes	Yes
* 05/15/05	9:49	0.0	1.9	0.00	0.01	Yes	Yes
05/15/05	12:11	0.0	2.1	0.00	0.31	Yes	Yes
* 05/16/05	11:59	0.0	2.0	0.00	0.11	Yes	Yes
05/16/05	13:54	0.0	2.0	0.00	0.44	Yes	Yes
05/17/05	11:28	0.0	2.0	0.00	0.44	Yes	Yes
* 05/17/05	13:55	0.0	1.9	0.00	0.01	Yes	Yes
5/13 - 5/17 Zero Drift Result: Met criteria. 5/13 - 5/17 Upscale Drift Result: Met criteria.							
Reference Gas Source: Tekran 3310 and Cylinder Low-Level Gas Concentration: 2.5, 2.2*							
Date	Time	CEMS Reading		Drift		Result	
		Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
07/08/05	9:34	0.0	2.071	0.00	0.56	Yes	No
07/09/05	8:58	0.0	1.957	0.00	0.68	Yes	No
07/10/05	8:54	0.0	1.923	0.00	0.71	Yes	No
07/11/05	8:54	0.0	1.923	0.00	0.71	Yes	No
07/12/05	8:49	0.0	2.008	0.00	0.63	Yes	No
* 07/13/05	9:15	0.1	2.171	0.09	0.06	Yes	Yes
* 07/14/05	9:32	0.0	2.389	0.00	0.03	Yes	Yes
* 07/15/05	10:19	0.0	2.454	0.00	0.09	Yes	Yes
7/8 - 7/15 Zero Drift Result: Met criteria. 7/8 - 7/15 Upscale Drift Result: Criteria not met.							

4.2.1.4 ThermoElectron

The ThermoElectron 7-day calibration error test, linearity check, system integrity test (which checks converter efficiency), measurement error test, and zero/upscale drift test results are presented in Tables 4-53 through 4-58. The Thermo CEMS system was located at the stack sampling platform and configured with a 50-ft heated line (165°C) to the analysis system in the CEMS shelter on this platform.

4.2.1.4.1 7-Day Calibration Error Test

The Thermo system was challenged with one partial and one complete 7-day calibration error test. The partial test was performed between May 13 and May 20, 2005. The reference gas used during the May 7-day calibration error test was from the Tekran 3310 Hg calibration source. Maintenance to the system by Thermo representatives on the sixth day prevented an opportunity to obtain the sixth of seven

consecutive days of measurements. Although all of the recorded measurements leading to the sixth day as well as the seventh day were within the 1.0 µg/m³ test, the test did not meet the test criteria since 7 consecutive days were not completed.

A complete 7-day calibration error test was conducted on the Thermo system between June 23 and June 30, 2005. The reference gas used during this 7-day calibration error test varied between the Tekran 3310 Hg calibration source and the 5.8 µg/m³ reference gas cylinder. The Thermo system did not meet the test criteria during the test performed in June. During the first five days and last day of testing, the Thermo system measured from 0.2 µg/m³ to 1.7 µg/m³ beyond the 1.0 µg/m³ test criteria limit. The results for both 7-day calibration error tests are shown in Table 4-53.

Plans to repeat the 7-day calibration error test during the period of the RATA were unsuccessful after the Thermo system failed to operate properly and required corrective maintenance in the middle of the fifth RATA test run.

Table 4-53. Thermo 7-Day Calibration Error Test—Phase 2

Gas Source: Tekran 3310 Reference Gas Concentration: 2.5							
		CEMS reading		Error		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
5/14/05	0.70	-0.12	2.81	0.12	0.35	Yes	Yes
5/15/05	0.48	-0.04	2.60	0.04	0.14	Yes	Yes
5/16/05	0.48	-0.38	2.63	0.38	0.17	Yes	Yes
5/17/05	0.44	-0.34	2.40	0.34	0.06	Yes	Yes
5/18/05	0.40	-0.34	2.29	0.34	0.17	Yes	Yes
5/19/05	Maintenance to system prevented daily measurement						
5/20/05	0.65	0.03	2.70	0.03	0.24	Yes	Yes
7 Day Cal Error Result: Incomplete							
Gas Source: Tekran 3310 and Cylinder* Reference Gas Concentration: 4.9 and 5.8*							
		CEMS reading		Error		Result	
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?
* 06/22/05	17:02	0.25	7.76	0.25	1.96	Yes	No
* 06/23/05	11:29	0.28	6.99	0.28	1.19	Yes	No
* 06/24/05	11:33	0.18	7.44	0.18	1.64	Yes	No
* 06/25/05	11:50	0.37	8.32	0.37	2.52	Yes	No
* 06/26/05	11:20	0.22	7.63	0.22	1.83	Yes	No
06/27/05	9:22	0.26	4.52	0.26	0.39	Yes	Yes
* 06/28/05	12:11	0.43	6.59	0.43	0.79	Yes	Yes
* 06/29/05	11:51	0.05	5.89	0.05	0.09	Yes	Yes
* 06/30/05	11:12	0.46	6.11	0.46	0.31	Yes	Yes
* 07/01/05	8:22	0.03	8.48	0.03	2.68	Yes	No
7-Day Cal Error Result (6/22 - 7/01): Criteria not met.							

4.2.1.4.2 Linearity Test

Results of linearity testing of the Thermo system are summarized in Table 4-54. One linearity test was conducted on the Thermo system on June 29, 2005. The reference gas concentrations used were from the Tekran 3310 Hg calibration source. The Thermo system did not meet the test criteria during this linearity test since the average of the three high-level gas concentrations measured by the instrument was 0.1 $\mu\text{g}/\text{m}^3$ beyond the allowable tolerance of $\pm 1.0 \mu\text{g}/\text{m}^3$.

Table 4-54. Thermo Linearity Test—Phase 2

			From Tekran 3310
Low-Level Gas Concentration:			2.5
Mid-Level Gas Concentration:			6.1
High-Level Gas Concentration:			9.8
Test date:		6/29/2005	
Cycle	Time	Gas type	CEMS reading
1	18:33	Low	2.19
1	18:47	Mid	5.26
1	18:58	High	8.81
2	19:18	Low	2.53
2	19:24	Mid	5.38
2	19:44	High	8.75
3	19:49	Low	2.47
3	20:09	Mid	5.29
3	20:19	High	8.53
	20:34	Zero	0.27
Gas	Low	Mid	High
Average	2.40	5.31	8.70
% Error	2.6%	13.5%	11.4%
Linear Error	0.063	0.830	1.12
Criteria met?	Yes	Yes	No
6/29/05 Linearity Result: Criteria not met.			

4.2.1.4.3 System Integrity Test

The results of the weekly system integrity tests on the Thermo system are provided in Table 4-55. System integrity tests were performed on the Thermo during both the May and June, 2005 certification test periods. The Thermo system did not meet the test criteria during either of the two system integrity tests performed. The results for the high-level gas were 0.4 $\mu\text{g}/\text{m}^3$ beyond the allowable test tolerance of $\pm 0.5 \mu\text{g}/\text{m}^3$ for both the May and June tests. Results of the weekly system integrity tests are provided in Volume 3, Appendix H. The Thermo met the criteria for three of the 22 tests performed.

Table 4-55. Thermo System Integrity Test—Phase 2

		From Hovacal		
Mid-Level Oxidized Mercury Concentration:		3.3		
High-Level Oxidized Mercury Concentration:		5.3		
Test Date: 05/19/05				
Time	Gas type	CEMS reading	Error	Criteria met?
12:45	Zero	-0.13	0.13	Yes
12:23	Mid	3.64	0.33	Yes
11:59	High	6.21	0.88	No
5/19/05 Converter Test Result: Criteria not met.				
		From Hovacal		
Mid-Level Oxidized Mercury Concentration:		3.3		
High-Level Oxidized Mercury Concentration:		5.3		
Test Date: 6/29/2005				
Time	Gas Type	CEMS Reading	Error	Criteria met?
14:34	Zero	0.17	0.17	Yes
14:54	Mid	3.72	0.43	Yes
15:09	High	6.18	0.85	No
6/29/05 Test Result: Criteria not met.				

4.2.1.4.4 Cycle Time Test

The Thermo system was challenged with one cycle time test on June 26, 2005. The instrument met the test method criteria during the test. The results of the June 26 cycle time test are shown in Table 4-56.

Table 4-56. Thermo Cycle Time—Phase 2

Date: 06/26/05		
Time	CEM reading	Comments
15:57	2.6	Pretest stable stack measurement
16:12	0.7	Zero and stable
16:14:00		Release CEM back to stack gas
16:19:48	2.45	Reach 95% of stable range
16:24:08	2.55	Stack gas measurement stable
	0:05:48	Tolerance < 00:15:00
Pretest stable stack measurement		
16:39	11.39	High level (9.85) reference Gas and stable
16:38:00		Release CEM back to stack gas
16:49:08	2.82	Reach 95% of stable range
16:58:58	2.64	Stack gas measurement stable
	0:11:08	Tolerance < 00:15:00
6/26/05 Cycle time Test Results: Met criteria.		

4.2.1.4.5 Measurement Error Test

A measurement error test was conducted on the Thermo system using the Tekran 3310 Hg calibration source on June 29, 2005. The Thermo system did not meet the test criteria. The results for both the mid- and high-level Hg gases were beyond the 0.5 µg/m³ test tolerance limit. Results of the measurement error test are shown in Table 4-57.

Table 4-57. Thermo Measurement Error Test—Phase 2

		From Tekran 3310		
Low-Level Gas Concentration:		2.5		
Mid-Level Gas Concentration:		6.1		
High-Level Gas Concentration:		9.8		
Test Date: 6/29/2005				
Gas type	Time	CEMS reading	Error	Criteria met?
Zero	20:34	0.27	0.27	Yes
Low	19:49	2.47	0.01	Yes
Mid	20:09	5.29	0.85	No
High	20:19	8.53	1.29	No
6/29/05 Measurement Error Result: Criteria not met.				

4.2.1.4.6 Zero/Upscale Drift Test

Zero/upscale drift test results for the Thermo system are shown in Table 4-58. The Thermo system underwent one partial and one complete zero/upscale drift test. The Thermo did not meet the test criteria on either of the two tests conducted. The partial test was performed between May 13 and May 20, 2005. The reference gas used during the May zero/upscale drift test was from the Tekran 3310 Hg calibration source. Maintenance to the system by Thermo representatives on the sixth day prevented an opportunity to obtain the sixth of seven consecutive days of measurements. All the recorded measurements leading to the sixth day as well as the seventh day were within the 0.5 µg/m³ test limitation, due to the missed sixth day of comparative test data, the Thermo system did not meet the test method criteria for the May zero/upscale drift test.

A second zero/upscale drift test was conducted between June 23 and June 30, 2005. The reference gas used during the June zero/upscale drift test varied between the Tekran 3310 Hg calibration source and the 5.8 µg/m³ Hg concentration reference gas cylinder source. The difference between sources was due to the availability of the source concentration at the available time to perform the test. The Thermo instrument measured from 0.3 µg/m³ to 2.0 µg/m³ beyond the allowable 0.5 µg/m³ test tolerance on five of eight test dates.

Table 4-58. Thermo Zero/Upscale Drift Tests—Phase 2

Gas Source: Tekran 3310 Reference Gas Concentration: 2.5								
		CEMS reading		Drift		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
05/14/05	16:41	-0.1	2.8	0.12	0.35	Yes	Yes	
05/15/05	11:34	0.0	2.6	0.04	0.14	Yes	Yes	
05/16/05	11:28	-0.4	2.6	0.38	0.17	Yes	Yes	
05/17/05	10:35	-0.3	2.4	0.34	0.06	Yes	Yes	
05/18/05	9:36	-0.3	2.3	0.34	0.17	Yes	Yes	
05/19/05	Maintenance to system prevented daily measurement							
05/20/05	15:38	0.0	2.7	0.03	0.24	Yes	Yes	
Zero Drift Result:		Incomplete						
Upscale Drift Result:		Incomplete						
Gas Source: Tekran 3310 and Cylinder Reference Gas Concentration: 4.9 and 5.8*								
		CEMS reading		Drift		Result		
Date	Time	Zero	Reference	Zero	Reference	Zero criteria met?	Span criteria met?	
* 06/23/05	11:29	0.28	6.99	0.28	1.19	Yes	No	
* 06/24/05	11:33	0.18	7.44	0.18	1.64	Yes	No	
* 06/25/05	11:50	0.37	8.32	0.37	2.52	Yes	No	
* 06/26/05	11:20	0.22	7.63	0.22	1.83	Yes	No	
06/27/05	9:22	0.26	4.52	0.26	0.39	Yes	Yes	
* 06/28/05	12:11	0.43	6.59	0.43	0.79	Yes	No	
* 06/29/05	11:51	0.05	5.89	0.05	0.09	Yes	Yes	
* 06/30/05	11:12	0.46	6.11	0.46	0.31	Yes	Yes	
6/23 - 6/30 Zero Drift Result:		Met criteria.						
6/23 - 6/30 Upscale Drift Result:		Criteria not met.						

4.2.2 Phase 2 RATA Test Results

The data presented in this section are from the RA test conducted during July 7-12, 2005. The testing consisted of 12 test runs comparing four mercury Hg CEMS to the Ontario Hydro (OH) reference method. Overall, emissions as measured by OH displayed a general downward trend from 3 to 1.4 µg/m³ over the course of 12 runs.

The Durag, Opsis, and Tekran instruments collected data for all 12 of the RA tests and the Thermo instrument collected usable data for most of the first 5 RA test runs. Duplicate OH sampling trains were used during all 12 RA test runs. Further details of the Ontario Hydro results and results for each mercury CEMS are presented in the sections that follow.

Mercury analysis results are provided in Appendix E of Volume 3. Mercury CEMS data collected during the RA test are provided in Appendix F of Volume 3.

4.2.2.1 Ontario Hydro Sample Results

Sampling times for the Ontario Hydro sampling method are provided in Table 4-59. All runs had sample collection times of 2 hr according to the method. Samples were collected over a period of several days in order to observe any variation in emission data that would be useful in evaluating CEMS response.

Table 4-59. Phase 2 RA Test Run Times

Run number	Date	Stack sampling intervals (in minutes per 24-hour clock)	Sampling time (min)
1	7/7/2005	10:45 - 12:45	120
2	7/7/2005	14:35 - 16:35	120
3	7/8/2005	10:00 - 12:00	120
4	7/8/2005	13:55 - 15:55	120
5	7/9/2005	9:25 - 11:25	120
6	7/9/2005	13:10 - 15:10	120
7	7/10/2005	9:25 - 11:25	120
8	7/10/2005	12:40 - 14:40	120
9	7/11/2005	09:15 - 11:15	120
10	7/11/2005	14:00 - 16:00	120
11	7/12/2005	9:45 - 11:45	120
12	7/12/2005	13:00 - 15:00	120

Table 4-60 summarizes the sampling conditions of the reference method trains. Ontario Hydro sampling and recovery data are provided in Appendix C of Volume 3 of this report. Method 3B sample collection data and the Orsat analysis results for each sample are also included with Appendix C. Sample traceability data sheets are presented in Appendix B, and sampling equipment calibration results are in Appendix D of Volume 3.

Mercury analysis results are presented in Table 4-61 and were obtained using the Ontario Hydro (OH) method analytical procedures. Data are presented separately for each sample train component.

The reproducibility between run duplicates for the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ fraction of the OH sampling trains was large ($> 10\%$ RD) for 8 of the 12 runs. The analytical laboratory was asked to reanalyze this fraction from each of the trains. This time a different set of 8 runs had large RD ($> 10\%$) values, so the laboratory was contacted. During a conversation with the laboratory, it was discovered that they had did not clear the KMnO_4 samples prior to extracting an aliquot for analysis. Reanalysis results are included in Appendix E of Volume 3 of this report.

Because the highest amount of mercury is found in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers, with much of it located in the brown residue inside the sample bottle, both the first and second $\text{KMnO}_4/\text{H}_2\text{SO}_4$ sample results were considered nonrepresentative of the sample.

Table 4-60. Phase 2 RA Test Stack Sampling Data

	Sampling time (min)	Gas volume (dscm)	Orsat Analysis			Avg. stack temp. (°F)	Iso-kinetic (%)
			Oxygen (%)	CO ₂ (%)	Water (%)		
Run 1	120	2.615	5.6	12.4	16.0	131.1	102.7
Run 1 dup	120	2.589	5.0	13.4	15.2	129.3	103.6
Run 2	120	2.084	5.6	12.4	15.9	130.7	102.6
Run 2 dup	120	2.107	5.2	13.4	15.1	128.9	104.2
Run 3	120	2.027	5.6	12.6	16.3	131.8	101.2
Run 3 dup	120	2.042	4.8	13.4	15.6	130.2	102.7
Run 4	120	2.026	5.4	12.8	15.7	130.7	102.5
Run 4 dup	120	2.059	4.8	13.4	14.9	128.6	103.8
Run 5	120	2.015	5.6	12.6	15.6	130.3	99.7
Run 5 dup	120	2.060	6.4	12.2	15.0	128.9	102.4
Run 6	120	2.031	5.8	12.6	15.2	129.5	97.6
Run 6 dup	120	2.090	6.0	12.6	14.5	127.7	102.3
Run 7	120	2.035	5.6	12.8	15.5	130.1	100.6
Run 7 dup	120	2.042	5.6	12.8	14.9	128.7	102.5
Run 8	120	2.068	5.6	12.6	15.8	130.8	102.5
Run 8 dup	120	2.060	5.6	13.0	15.0	129.0	102.3
Run 9	120	2.011	5.4	12.8	16.0	131.1	100.9
Run 9 dup	120	2.031	5.4	12.8	15.3	129.3	102.5
Run 10	120	2.018	5.4	12.8	15.9	131.0	102.7
Run 10 dup	120	2.001	5.0	13.2	15.4	129.6	102.3
Run 11	120	2.070	5.2	13.2	16.0	130.9	102.4
Run 11 dup	120	2.060	5.2	13.2	15.6	130.0	102.6
Run 12	120	2.147	5.6	12.8	15.8	130.5	103.5
Run 12 dup	120	2.082	5.6	12.8	15.4	129.7	102.4

Table 4-61. Phase 2 RA Test Ontario Hydro Mercury Analysis Results (µg)

Field ID	Particle bound phase			Gaseous phase						Total (µg)
				Ionic	Elemental			Gaseous phase subtotal		
	KCl impingers	HNO ₃ /H ₂ O ₂ impinger	HNO ₃ /H ₂ O ₂ imp. blank corrected amt. ^b		KMnO ₄ /H ₂ SO ₄ impingers ^c	Elemental subtotal				
Run 1	0.011 ^a	0.020	0.031	0.980	0.170	0.160	5.76	5.93	6.90	6.94
Run 1 dup	0.021 ^a	0.030	0.052	1.013	0.164	0.154	6.30	6.46	7.47	7.53
Run 2	< 0.005	< 0.015	< 0.020	0.486	0.072 ^a	0.062	3.91	3.98	4.46	4.47
Run 2 dup	< 0.005	< 0.011	< 0.016	0.636	0.082 ^a	0.072	2.43	2.51	3.13	3.14
Run 3	< 0.005	< 0.018	< 0.023	0.509	0.087 ^a	0.077	3.99	4.08	4.58	4.59
Run 3 dup	< 0.005	< 0.016	< 0.021	0.579	0.106 ^a	0.096	4.05	4.16	4.73	4.74
Run 4	0.013 ^a	0.064	0.077	0.487	0.095 ^a	0.085	3.21	3.31	3.78	3.87
Run 4 dup	< 0.005	0.061	0.061	0.531	0.078 ^a	0.068	3.19	3.27	3.79	3.86
Run 5	< 0.005	0.029	0.029	0.455	0.076 ^a	0.066	3.14	3.22	3.66	3.70
Run 5 dup	< 0.005	0.029	0.029	0.456	0.100 ^a	0.090	3.01	3.11	3.56	3.60
Run 6	< 0.005	0.024	0.024	0.306	0.101 ^a	0.091	3.08	3.18	3.47	3.51
Run 6 dup	< 0.005	0.036	0.036	0.385	0.060 ^a	0.050	2.96	3.02	3.39	3.44
Run 7	< 0.005	0.046	0.046	0.441	0.133 ^a	0.123	3.09	3.22	3.65	3.71
Run 7 dup	< 0.005	< 0.019	< 0.024	0.499	0.120 ^a	0.110	2.23	2.35	2.83	2.84
Run 8	< 0.005	0.023	0.023	0.458	0.123 ^a	0.113	3.12	3.25	3.69	3.73
Run 8 dup	< 0.005	< 0.022	< 0.027	0.637	0.099 ^a	0.089	3.30	3.39	4.02	4.03
Run 9	< 0.005	< 0.021	< 0.026	0.550	0.096 ^a	0.086	4.27	4.37	4.91	4.92
Run 9 dup	< 0.005	< 0.019	< 0.024	0.771	0.071 ^a	0.061	4.15	4.22	4.98	4.99
Run 10	0.006 ^a	0.055	0.061	0.897	0.058 ^a	0.048	4.42	4.48	5.37	5.44
Run 10 dup	< 0.005	0.033	0.033	0.769	0.052 ^{a d}	0.042	3.18	3.23	3.99	4.03
Run 11	0.007 ^a	< 0.016	0.007	0.370	0.113 ^a	0.103	3.40	3.52	3.88	3.89
Run 11 dup	< 0.005	0.019	0.019	0.357	0.081 ^a	0.071	3.69	3.77	4.12	4.15
Run 12	< 0.005	< 0.020	< 0.025	0.337	0.096 ^a	0.086	2.84	2.94	3.27	3.28
Run 12 dup	< 0.005	< 0.020	< 0.025	0.341	0.080 ^a	0.070	2.05	2.13	2.46	2.47
FB-2	0.006	< 0.007		< 0.012	0.032		< 0.016			
FB-4	0.010	< 0.008		< 0.014	0.057		0.019			
SB	< 0.005	< 0.006		< 0.001	0.006		0.003			
Hydroxylamine^e					0.00004		0.00004			

FB = Field Blank Train; SB = Solution Blank plus Filter Blank.

^a The Field Blank Train result exceeded 30% of the measured value, however the contribution does not significantly impact total results.

^b Blank corrections performed per OH method.

^c Results were reanalyzed with no way to correct for solution blank; however, the estimated blank contribution is less than 1% of the mercury total.

^d The Solution Blank exceeded 10% of the measured value; however the contribution does not significantly impact total results.

^e A maximum of approximately 0.2 mL (1-2 drops) in KCl impingers and 0.2 mL in KMnO₄/H₂SO₄ impingers was used during recovery; amount in blank was 0.0002 µg/mL.

NOTE: Bolded sample results are biased low.

A second laboratory (ARCADIS G&M, Inc. in Research Triangle Park, NC) was asked to reanalyze the remaining portion of the original $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples. Upon receipt at ARCADIS, the remaining sample volume in the bottles did not add up correctly. Subsequent conversations with Oxford Laboratory revealed that one 50-mL aliquot was extracted from each sample for preparation and duplicate analysis (i.e., one sample aliquot processed, then analyzed twice). Also, the four $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples which had been spiked were missing an additional 100-mL to 200-mL volume with no corresponding analytical data.

In order to determine the fraction of mercury contained in the KMnO_4 fraction of each train, analytical results from each Oxford aliquot times the aliquot volume was added to the ARCADIS analytical result times the remaining sample volume to obtain a sum total mass. Because the four spiked samples from Oxford were missing an additional 100-mL to 200-mL of sample, the results on those samples are biased low since those missing amounts cannot be added into the total.

Tables 4-62 and 4-63 combine the mercury analysis results with the stack sampling results and provide the mercury emissions on a concentration basis. All test runs used duplicate trains, and precision information is summarized in Table 4-64. The relatively large RD for the elemental fraction on Runs 2, 7, 10, and 12 is most likely the result of not having the complete samples for analysis for those runs. Figure 4-9 shows concentrations of the total gaseous and oxidized fraction of mercury along with scatter points from each train.

The OH sampling was performed isokinetically from a single point at a similar effective sampling location as the Hg CEMS and sorbent trap monitoring system. As specified in Part 75 requirements for mercury monitoring and PS-12A, only the ionic (oxidized) and elemental fractions of the OH results are included in the gaseous phase concentration values used for the RATA calculations. Therefore, the mercury CEMS and the OH results are on a similar basis (i.e., gaseous phase only, concentrations per dry standard volume). The particle-bound fraction, which constituted 1% (or less) of the total mercury, is reported only for informational purposes.

The field blank train $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger results previously shown on Table 4-61 are noteworthy due to the presence of mercury at levels greater than 30% of the field sample values. The cause is not known. Even though the mercury levels in the field blank trains were greater than 30% of the stack samples, it should be noted that this fraction constitutes only about 5% of the total mercury in the train.

Table 4-62. RA Total OH Mercury Concentrations

	Particle-bound subtotal		Gaseous-phase subtotal	
	Mass (µg)	Concentration (µg/dscm)	Mass (µg)	Concentration (µg/dscm)
Run 1	0.031 ^a	0.012	6.90	2.64
Run 1 rep	0.052 ^a	0.020	7.47	2.89
Avg.				2.77
Run 2	<0.020	N/D	4.46 ^b	2.14
Run 2 rep	<0.016	N/D	3.13 ^b	1.49
Avg.				1.82
Run 3	<0.023	N/D	4.58 ^b	2.26
Run 3 rep	<0.021	N/D	4.73 ^b	2.32
Avg.				2.29
Run 4	0.077 ^a	0.038	3.78 ^b	1.87
Run 4 rep	0.061	0.030	3.79 ^b	1.84
Avg.				1.86
Run 5	0.029	0.014	3.66 ^b	1.82
Run 5 rep	0.029	0.014	3.56 ^b	1.73
Avg.				1.78
Run 6	0.024	0.012	3.47 ^b	1.71
Run 6 rep	0.036	0.017	3.39 ^b	1.62
Avg.				1.67
Run 7	0.046	0.023	3.65 ^b	1.79
Run 7 rep	<0.024	N/D	2.83 ^b	1.39
Avg.				1.60
Run 8	0.023	0.011	3.69 ^b	1.79
Run 8 rep	<0.027	N/D	4.02 ^b	1.95
Avg.				1.87
Run 9	<0.026	N/D	4.91 ^b	2.44
Run 9 rep	<0.024	N/D	4.98 ^b	2.45
Avg.				2.45
Run 10	0.061 ^a	0.030	5.37 ^b	2.66
Run 10 rep	0.033	0.016	3.99 ^{b d}	1.99
Avg.				2.33
Run 11	0.007 ^a	0.003	3.88 ^b	1.87
Run 11 rep	0.019	0.009	4.12 ^b	2.00
Avg.				1.94
Run 12	<0.025	N/D	3.27 ^b	1.52
Run 12 rep	<0.025	N/D	2.46 ^b	1.18
Avg.				1.36

^a The field blank train result exceeded 30% of the measured value; these results are not used in the gaseous-phase mercury concentration calculations.

^b The Field Blank Train result exceeded 30% of the measured value, however the contribution does not significantly impact total results.

^c The Solution Blank exceeded 10% of the measured value; however, the contribution does not significantly impact total results.

NOTE: Shaded sample results are biased low.

Table 4-63. Phase 2 RA Gaseous-Phase Mercury From OH Testing

	Elemental portion		Oxidized portion		Total gaseous	% Oxidized ^a (Ionic)
	Mass (µg)	Concentration (µg/dscm)	Mass (µg)	Concentration (µg/dscm)	Concentration (µg/dscm)	
Run 1	5.93	2.27	0.980	0.375	2.64	14.2
Run 1 rep	6.46	2.50	1.013	0.391	2.89	13.6
Avg.		2.38		0.383	2.77	13.9
Run 2	3.98	1.91	0.486	0.233	2.14	10.88
Run 2 rep	2.51	1.19	0.636	0.302	1.49	20.2
Avg.		1.55		0.268	1.82	14.72
Run 3	4.08	2.01	0.509	0.251	2.26	11.1
Run 3 rep	4.16	2.04	0.579	0.284	2.32	12.2
Avg.		2.03		0.267	2.29	11.7
Run 4	3.31	1.63	0.487	0.240	1.87	12.8
Run 4 rep	3.27	1.59	0.531	0.258	1.84	14.0
Avg.		1.61		0.249	1.86	13.4
Run 5	3.22	1.60	0.455	0.226	1.82	12.4
Run 5 rep	3.11	1.51	0.456	0.221	1.73	12.8
Avg.		1.55		0.223	1.78	12.6
Run 6	3.18	1.56	0.306	0.150	1.72	8.77
Run 6 rep	3.02	1.443	0.385	0.184	1.62	11.3
Avg.		1.50		0.167	1.67	10.0
Run 7	3.22	1.58	0.441	0.216	1.79	12.04
Run 7 rep	2.35	1.15	0.499	0.244	1.39	17.5
Avg.		1.37		0.230	1.60	14.4
Run 8	3.25	1.57	0.458	0.221	1.79	12.4
Run 8 rep	3.39	1.65	0.637	0.309	1.96	15.8
Avg.		1.61		0.265	1.87	14.2
Run 9	4.37	2.17	0.550	0.274	2.44	11.2
Run 9 rep	4.22	2.08	0.771	0.380	2.45	15.5
Avg.		2.12		0.327	2.45	13.3
Run 10	4.48	2.22	0.897	0.445	2.66	16.7
Run 10 rep	3.23	1.614	0.769	0.38	2.00	19.2
Avg.		1.92		0.414	2.33	17.8
Run 11	3.52	1.70	0.370	0.179	1.87	9.5
Run 11 rep	3.77	1.83	0.357	0.173	2.00	8.6
Avg.		1.77		0.176	1.94	9.1
Run 12	2.94	1.37	0.337	0.157	1.52	10.3
Run 12 rep	2.130	1.02	0.341	0.164	1.18	13.8
Avg.		1.20		0.160	1.36	11.8

^a % Oxidized = (Oxidized Concentration / Total Concentration) * 100.

NOTE: Runs 2Rep, 7Rep, 10Rep, and 12Rep (shaded) are biased low.

Table 4-64. Phase 2 Paired OH Train Relative Deviation (RD)

Run Avg	Concentration %RD		
	Oxidized (KCl)	Elemental	Gaseous subtotal
Run 1	2%	5%	5%
Run 2	13%	23%	18%
Run 3	6%	1%	1%
Run 4	4%	1%	1%
Run 5	1%	3%	3%
Run 6	10%	4%	3%
Run 7	6%	16%	13%
Run 8	17%	2%	4%
Run 9	16%	2%	0.2%
Run 10	7%	16%	14%
Run 11	2%	4%	3%
Run 12	2%	14%	13%

The PS-12A objective is <10% RD, where $\%RD = 100 * (Abs(a-b)) / (a+b)$.
 Values shown in **bold** for Gaseous Subtotal have a RD $\geq 10\%$.
 Shaded values have RD calculated from samples with low biased results.

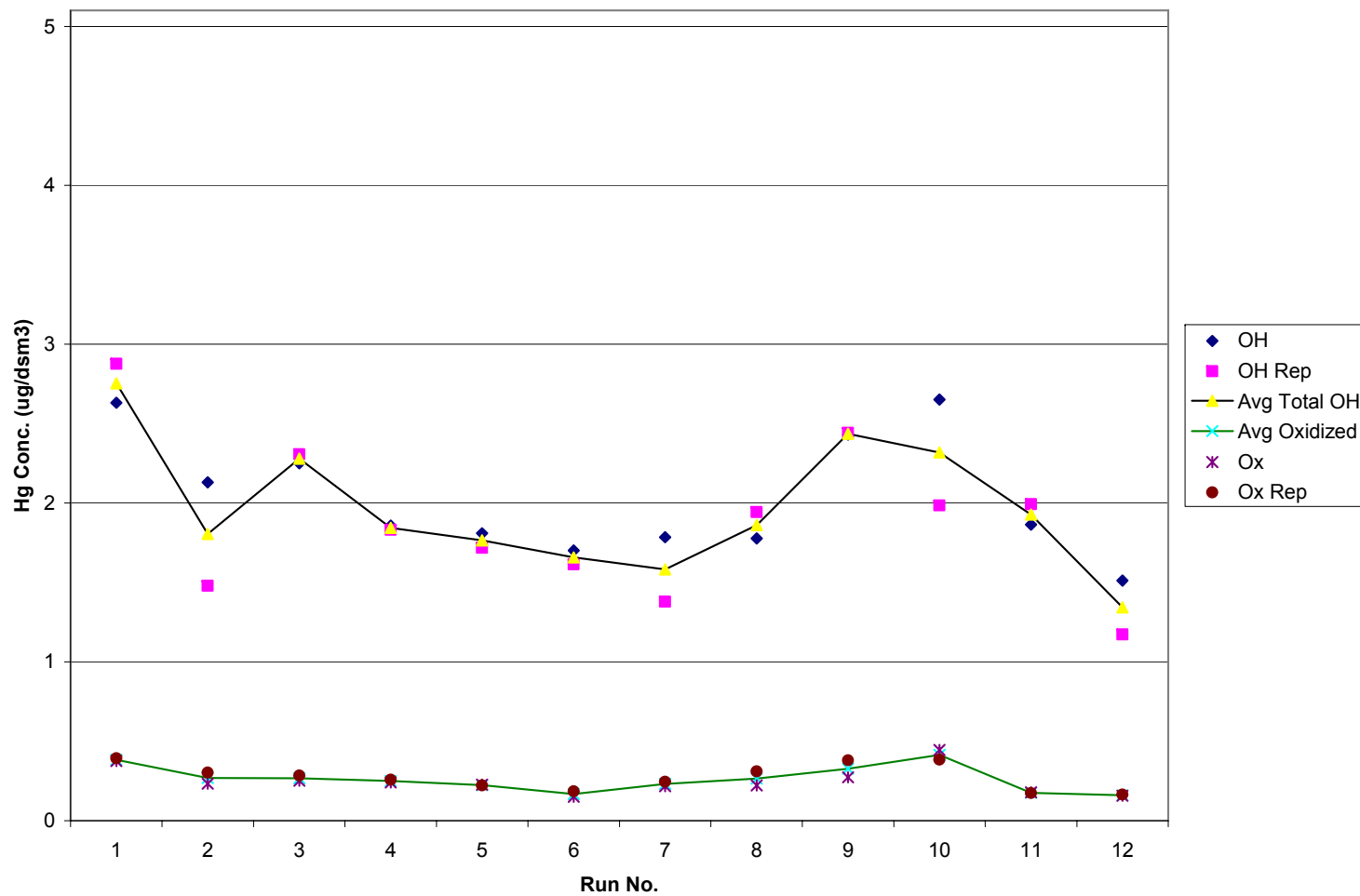


Figure 4-9. Phase 2 OH Gaseous Phase Mercury Concentrations

Results from the remaining field blank samples revealed the presence of mercury in the filter and KMnO_4 impingers at levels near the detection limit. Also, two of the six solution blanks indicated the presence of mercury near the detection limit. As previously indicated at the bottom of Table 4-67, the calculated contribution from hydroxylamine (used in train recovery for the KCl and KMnO_4 impingers) is not expected to have contributed significantly to the remaining impingers. The laboratory method blanks showed no levels of mercury above detection limits.

The estimated contribution from solution blanks was less than 1% of the total amount of mercury found in the samples. Thus, even though mercury was found in the $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution blank samples, it did not appear to have an appreciable effect on the overall result. The $\text{HNO}_3/\text{H}_2\text{O}_2$ samples were blank-corrected using the decision tree shown below in Figure 4-10, as described in Section 13.4.3.1 of the Ontario Hydro Method. The $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples could not be blank corrected since the results are a combination of more than one analysis.

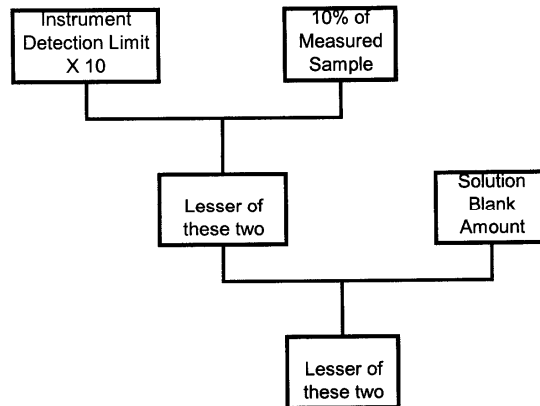


Figure 4-10. Decision Tree for Blank Corrections

Most significantly, the Relative Deviation (RD) for seven of the 12 runs exceeded the 10% RD criteria in PS-12A. The greatest deviation is attributed to the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers. These impingers were reanalyzed, but since the H_2O_2 impinger results contributed $< 5\%$ of the total and were consistent over a narrow concentration range, those impingers were not reanalyzed. A review of other sampling parameters (O_2 , CO_2 , and H_2O) indicates that all parameters for all runs were within 8% of each other. Thus sampling variations do not appear to be contributing to the RD variances for those four runs (3, 4, 6, and 12). The RD calculation (previously called RSD) is Equation K-7 from Part 75 Appendix K (per 75.22) and Equation 12A-1 from PS-12A.

4.2.2.2 CEMS RA Results

Table 4-65 summarizes the relative accuracy calculations for each of the CEMS evaluated. Because four of the runs had a $\text{RD} > 10\%$, and only three could be eliminated

the two runs with the largest RD (Runs 2 and 10) were eliminated first. The remaining two runs had a RD of 13% (Runs 7 and 12). The RA was calculated using first one then the other of these remaining two runs. The run which produced the lowest RA value was included for reporting. Calculations followed the procedures of Part 75, and are provided in Table 4-66 through 4-69. Hg CEMS data are included in Appendix F, and results for each analyzer are briefly discussed below. Emissions appeared to follow a generally decreasing trend from around 3 $\mu\text{g}/\text{m}^3$ to 1.4 $\mu\text{g}/\text{m}^3$ throughout the course of the test. Because mercury was observed in the solution blanks, blank corrections were applied to the OH results. Hg levels measured with the OH method were fairly consistent with all average Hg CEM values.

The reported values in the RA tables are based on the resolution of the analyzer; however the believed resolution is more likely 0.1 $\mu\text{g}/\text{m}^3$.

Table 4-65 and Figure 4-11 show that despite the large RD numbers seen in Runs 2, 7, 10, and 12, the average OH results are consistent with much of the CEMS results.

Table 4-65. Phase 2 Summary of All RA Results for All CEMS

Run number	OH gaseous mercury	CEMS ($\mu\text{g}/\text{dscm}$)			
		Durag	Opsis	Tekran	Thermo
1	2.77	6.07	2.19	2.41	2.19
2	1.82	3.88	2.01	1.93	1.79
3	2.29	3.67	1.77	2.08	1.94
4	1.86	2.59	1.69	1.40	1.47
5	1.78	2.51	1.34	1.37	2.19
6	1.67	1.53	1.50	1.44	-0.32
7	1.60	2.15	1.24	1.55	-0.26
8	1.87	1.79	1.70	1.57	-0.21
9	2.45	2.69	1.28	2.16	-0.20
10	2.33	2.65	1.45	1.92	-0.11
11	1.94	1.56	1.19	1.65	0.38
12	1.36	1.29	1.05	1.31	3.03
Relative Accuracy using best 9 runs		75.7%	36.2%	18.8%	94.5%

NOTE: Data in bold indicates that run was not used to calculate Relative Accuracy.

Note that the RA criteria can be either $\leq 20\%$ RA or $\pm 1 \mu\text{g}/\text{m}^3$. All four CEMS met the mean difference criteria of $\leq 1 \mu\text{g}/\text{m}^3$ (though the Thermo system quit operating accurately during Run 5.) Calculations for Durag produced a relative accuracy of 76% for the best 9 test runs. Opsis relative accuracy was around 36%. Tekran RA results were around 19%. The Thermo RA results were about 95% .

Figures 4-12 through 4-15 show plots of the run-by-run data for each analyzer, and Tables 4-66 through 4-69 show RA results for each analyzer compared with the OH method.

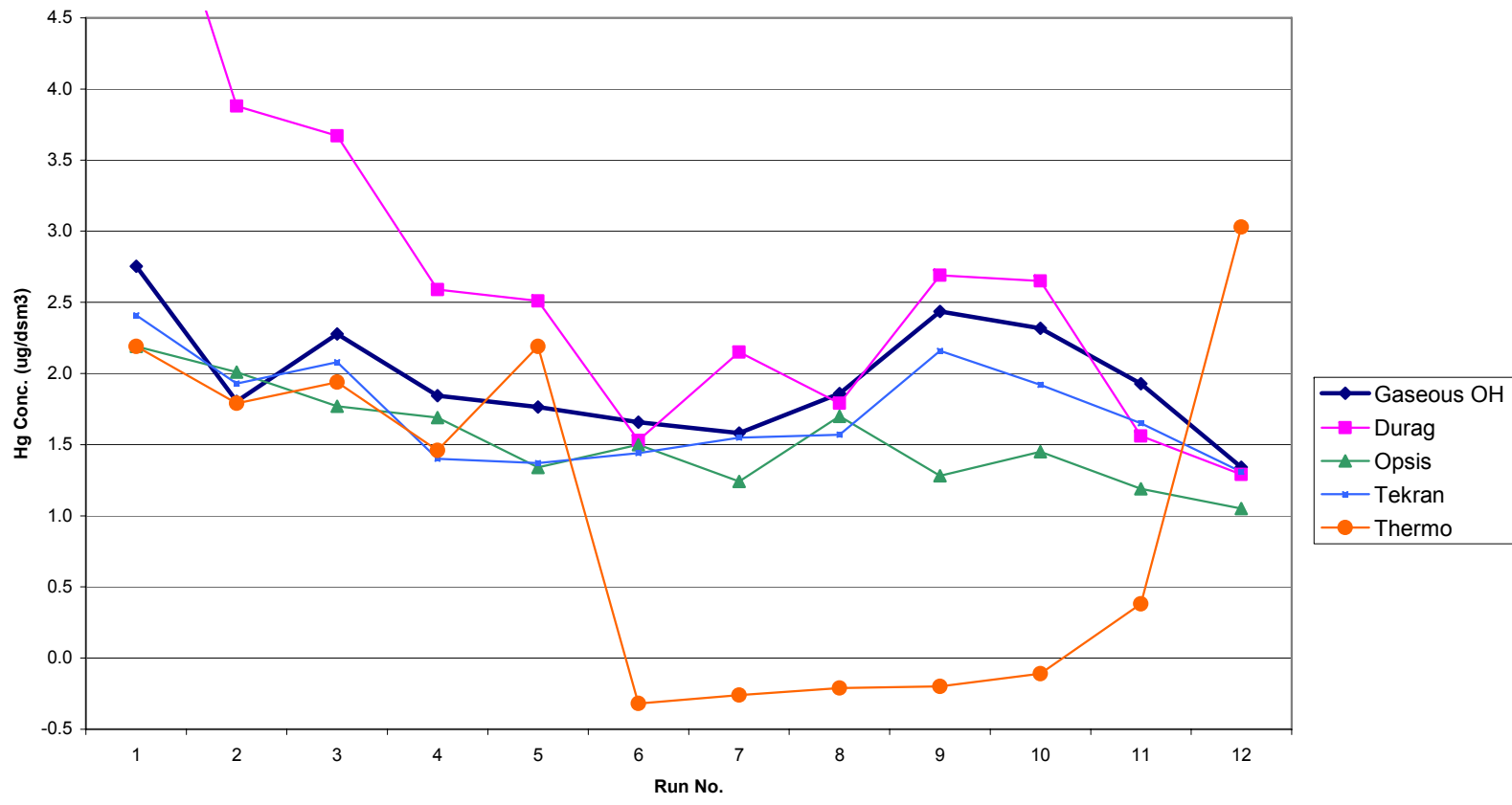


Figure 4-11. Phase 2 Summary of RA Tests

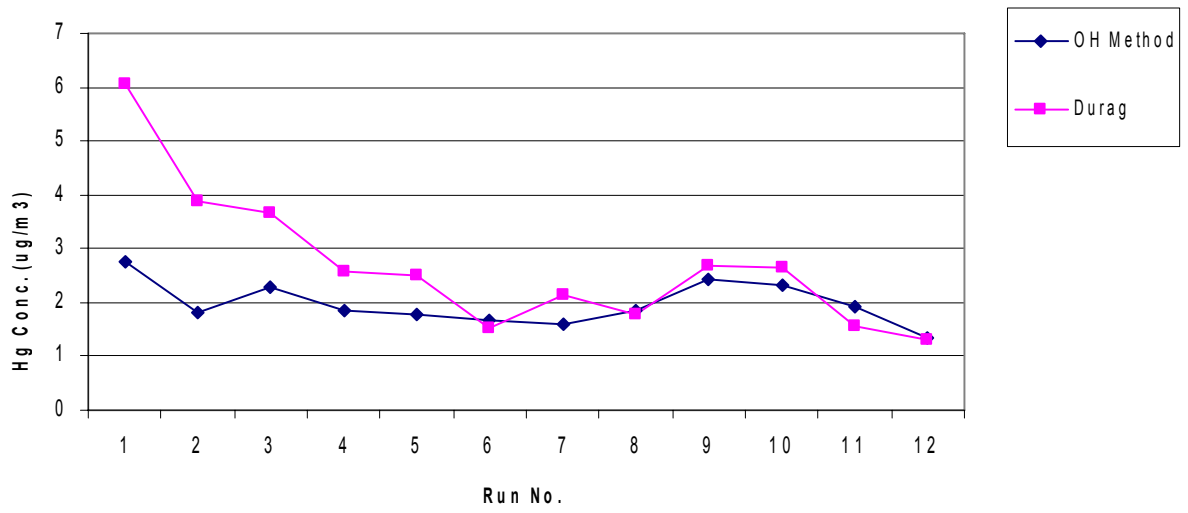


Figure 4-12. Phase 2 RA—OH Versus Durag

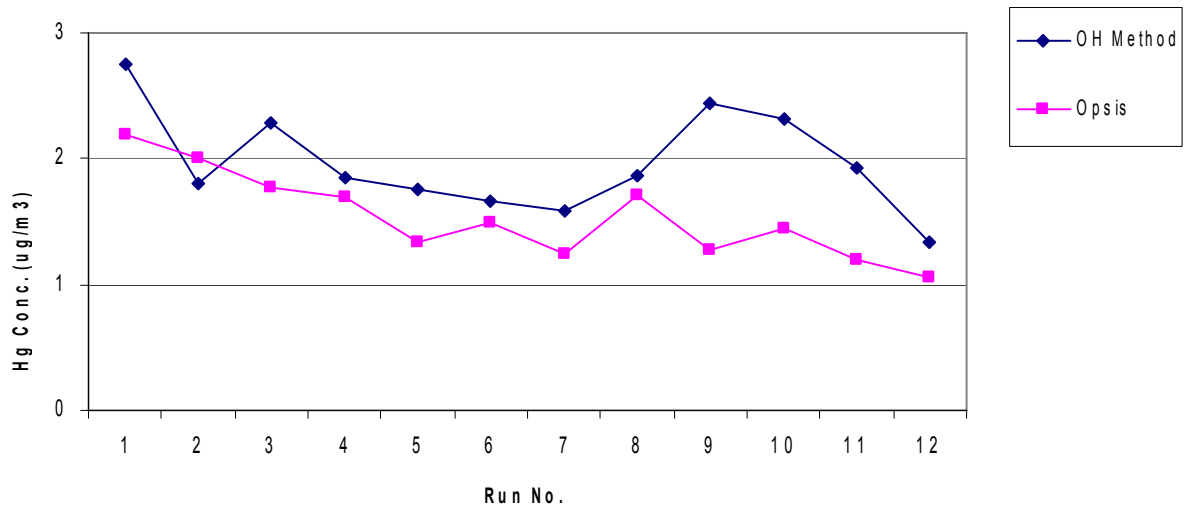


Figure 4-13. Phase 2 RA—OH Versus Opsis

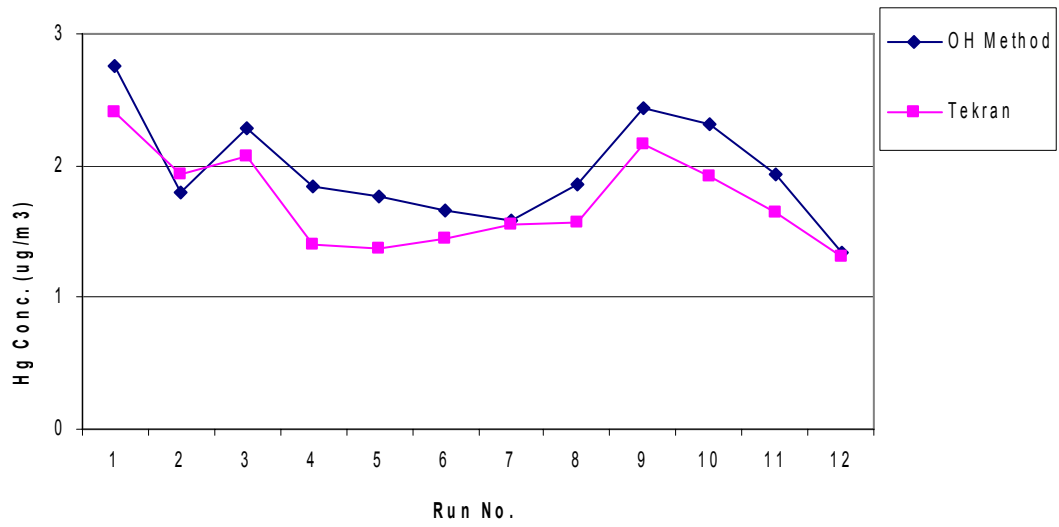


Figure 4-14. Phase 2 RA—OH Versus Tekran

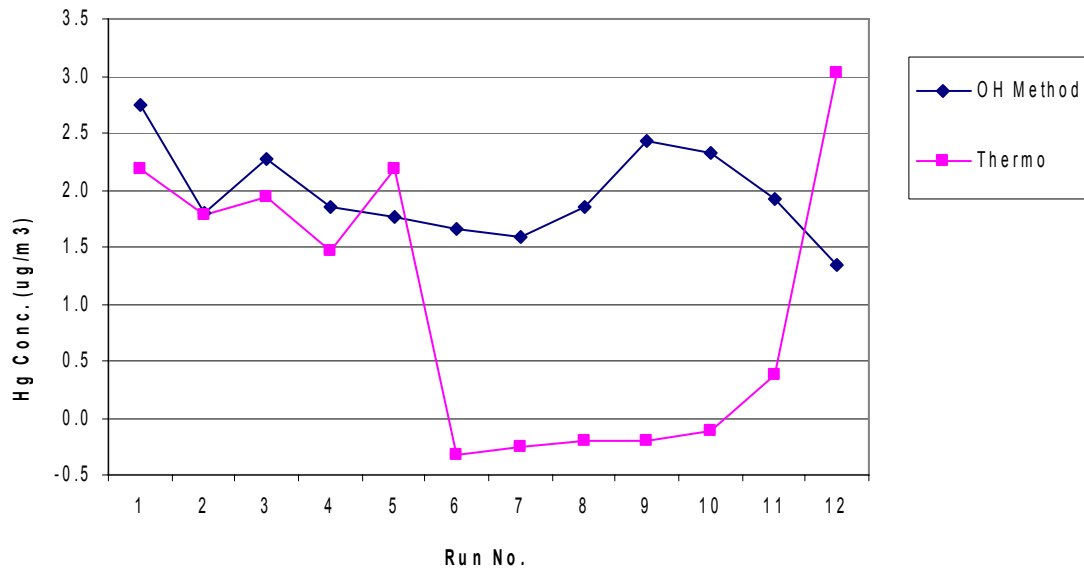


Figure 4-15. Phase 2 RA—OH Versus Thermo

Table 4-66. Phase 2 RA Results for Durag

Run Number	Use	Date	Time	CEMS Avg. Response (ug/dscm)	OH Total Hg Response (ug/dscm)	Difference (d) (ug/dscm)
1	Yes	7/7/2005	10:45 - 12:45	6.07	2.77	-3.30
2	No	7/7/2005	14:35 - 16:35	3.881	1.82	-2.061
3	Yes	7/8/2005	10:00 - 12:00	3.67	2.29	-1.38
4	Yes	7/8/2005	13:55 - 15:55	2.59	1.86	-0.73
5	Yes	7/9/2005	9:25 - 11:25	2.51	1.78	-0.73
6	Yes	7/9/2005	13:10 - 15:10	1.53	1.67	0.14
7	No	7/10/2005	9:25 - 11:25	2.15	1.6	-0.55
8	Yes	7/10/2005	12:40 - 14:40	1.79	1.87	0.08
9	Yes	7/11/2005	09:15 - 11:15	2.69	2.45	-0.24
10	No	7/11/2005	14:00 - 16:00	2.654	2.33	-0.324
11	Yes	7/12/2005	9:45 - 11:45	1.56	1.94	0.38
12	Yes	7/12/2005	13:00 - 15:00	1.29	1.36	0.07
Arithmetic Mean ^a (ug/dscm):				2.63	2.00	-0.63
BAF ^b						1.24
Standard Deviation						1.14
Confidence Coefficient ^d						0.88
Relative Accuracy ^e (% of RM)						75.7%

^a Arithmetic Mean = $1/n \sum d_i$

^b BAF = $1 + |1/n \sum d_i| / \text{HgCEMS}(\text{avg})$

^c Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^d Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.306$

^e Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

Table 4-67. Phase 2 RA Results for Opsis

Run Number	Use	Date	Time	CEMS Avg. Response (ug/dscm)	OH Total Hg Response (ug/dscm)	Difference (d) (ug/dscm)
1	Yes	7/7/2005	10:45 - 12:45	2.19	2.77	0.58
2	No	7/7/2005	14:35 - 16:35	2.007	1.82	-0.187
3	Yes	7/8/2005	10:00 - 12:00	1.77	2.29	0.52
4	Yes	7/8/2005	13:55 - 15:55	1.69	1.86	0.17
5	Yes	7/9/2005	9:25 - 11:25	1.34	1.78	0.44
6	Yes	7/9/2005	13:10 - 15:10	1.50	1.67	0.17
7	Yes	7/10/2005	9:25 - 11:25	1.24	1.60	0.36
8	Yes	7/10/2005	12:40 - 14:40	1.70	1.87	0.17
9	Yes	7/11/2005	09:15 - 11:15	1.28	2.45	1.17
10	No	7/11/2005	14:00 - 16:00	1.449	2.33	0.881
11	Yes	7/12/2005	9:45 - 11:45	1.19	1.94	0.75
12	No	7/12/2005	13:00 - 15:00	1.053	1.36	0.307
Arithmetic Mean ^a (ug/dscm):				1.55	2.03	0.48
BAF ^b						1.31
Standard Deviation ^b						0.33
Confidence Coefficient ^d						0.25
Relative Accuracy ^e (% of RM)						36.2%

^a Arithmetic Mean = $1/n \sum d_i$

^b BAF = $1 + |1/n \sum d_i| / \text{HgCEMS}(\text{avg})$

^c Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^d Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.306$

^e Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

Table 4-68. Phase 2 RA Results for Tekran

Run Number	Use	Date	Time	CEMS Avg. Response (ug/dscm)	OH Total Hg Response (ug/dscm)	Difference (d) (ug/dscm)
1	Yes	7/7/2005	10:45 - 12:45	2.41	2.77	0.36
2	No	7/7/2005	14:35 - 16:35	1.931	1.82	-0.111
3	Yes	7/8/2005	10:00 - 12:00	2.08	2.29	0.21
4	Yes	7/8/2005	13:55 - 15:55	1.40	1.86	0.46
5	Yes	7/9/2005	9:25 - 11:25	1.37	1.78	0.41
6	Yes	7/9/2005	13:10 - 15:10	1.44	1.67	0.23
7	Yes	7/10/2005	9:25 - 11:25	1.55	1.60	0.05
8	Yes	7/10/2005	12:40 - 14:40	1.57	1.87	0.30
9	Yes	7/11/2005	09:15 - 11:15	2.16	2.45	0.29
10	No	7/11/2005	14:00 - 16:00	1.915	2.33	0.415
11	Yes	7/12/2005	9:45 - 11:45	1.65	1.94	0.29
12	No	7/12/2005	13:00 - 15:00	1.307	1.36	0.05
Arithmetic Mean ^a (ug/dscm):				1.7	2.0	0.3
BAF ^b						1.17
Standard Deviation ^c						0.1
Confidence Coefficient ^d						0.1
Relative Accuracy ^e (% of RM)						18.8%

^a Arithmetic Mean = $1/n \sum d_i$

^b BAF = $1 + |1/n \sum d_i| / \text{HgCEMS}(\text{avg})$

^c Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^d Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.306$

^e Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

Table 4-69. Phase 2 RA Results for Thermo

Run Number	Use	Date	Time	CEMS Avg. Response (ug/dscm)	OH Total Hg Response (ug/dscm)	Difference (d) (ug/dscm)
1	Yes	7/7/2005	10:45 - 12:45	2.19	2.77	0.58
2	Yes	7/7/2005	14:35 - 16:35	1.789	1.82	0.03
3	Yes	7/8/2005	10:00 - 12:00	1.94	2.29	0.35
4	Yes	7/8/2005	13:55 - 15:55	1.46	1.86	0.40
5	Yes	7/9/2005	9:25 - 11:25	2.19	1.78	-0.41
6	Yes	7/9/2005	13:10 - 15:10	-0.32	1.67	1.99
7	Yes	7/10/2005	9:25 - 11:25	-0.261	1.6	1.86
8	No	7/10/2005	12:40 - 14:40	-0.21	1.87	2.08
9	No	7/11/2005	09:15 - 11:15	-0.20	2.45	2.65
10	No	7/11/2005	14:00 - 16:00	-0.109	2.33	2.44
11	Yes	7/12/2005	9:45 - 11:45	0.38	1.94	1.57
12	Yes	7/12/2005	13:00 - 15:00	3.03	1.36	-1.67
Arithmetic Mean ^a (ug/dscm):				1.16	2.00	0.84
BAF ^b						1.72
Standard Deviation ^c						1.37
Confidence Coefficient ^d						1.05
Relative Accuracy ^e (% of RM)						94.5%

^a Arithmetic Mean = $1/n \sum d_i$

^b BAF = $1 + |1/n \sum d_i| / \text{HgCEMS}(\text{avg})$

^c Standard Deviation = $[(\sum d_i^2 - (\sum d_i)^2 / n) / (n-1)]^{1/2}$

^d Confidence Coefficient = $t_{0.975} * \text{Standard Deviation} / n^{1/2}$, where $t_{0.975} = 2.306$

^e Relative Accuracy = $([\text{Difference Arithmetic Mean}] + [\text{Confidence Coefficient}]) / \text{RM Arithmetic Mean} * 100$

4.2.3 Additional Testing

4.2.3.1 Instrumental Reference Method Testing

The instrumental reference method (IRM) evaluations were performed towards development of an instrumental alternative to the Ontario Hydro reference method as used to perform Hg CEMS Relative Accuracy Test Audits (RATA). Results of the IRM testing are shown in Table 4-70. The technique of dynamic spiking was employed as an approach to assess matrix interferences and begin determination of appropriate method performance criteria.

Known mass and volumetric feed rates of elemental and oxidized Hg were dynamically introduced at the probe of an Hg CEMS and the resulting recoveries calculated. By holding the sampling rate at a known constant, the resulting diluted concentration was determined. The elemental and oxidized Hg dynamic spikes were

introduced at a volumetric flow that did not dilute the total stack sample flow rate by more than 10%.

The Tekran Hg CEMS was used to perform the IRM test procedures because it is capable of extracting a high volume of stack gas through the probe at a controlled and measured flowrate and it was already appropriately configured for dynamic spiking. The probe allows for introduction of gas at the entrance of the dilution orifice which is downstream of the inertial separator/filter, and the probe tip upstream of the inertial separator/filter. Both of these injection locations were used to perform the IRM test.

Table 4-70. IRM Daily Hg Tests During RATA

Test date	Hg Source	Tekran	
	$\mu\text{g}/\text{m}^3$	Pre-Run	Post-Run
7/6/2005	zero (N ₂) elemental	0.000 *	n/a
	2.2 elemental (cylinder gas)	1.957 *	n/a
	zero (N ₂) ionic	0.444	n/a
	2.6 Ionic	1.974	n/a
7/7/2005	zero (N ₂) elemental	0.000	0.000
	2.2 elemental (cylinder gas)**	2.014	2.019
	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)**	2.313	2.230
	zero (N ₂) ionic	0.097	0.142
2.6 Ionic	1.456	1.451	
7/8/2005	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)	2.071	2.008
	zero (N ₂) ionic	0.114	0.131
	2.6 Ionic	1.797	1.776
7/9/2005	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)	1.957	1.985
	zero (N ₂) ionic	0.108	0.131
	2.6 Ionic	1.752	1.712
7/10/2005	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)	1.923	2.014
	zero (N ₂) ionic	0.142	0.097
	2.6 Ionic	1.741	1.680
7/11/2005	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)	1.923	1.991
	zero (N ₂) ionic	0.108	0.085
	2.6 Ionic	1.763	1.712
7/12/2005	zero (N ₂) elemental	0.000	0.000
	2.455 elemental (3310 gas)	2.008	2.143
	zero (N ₂) ionic	0.114	0.097
	2.6 Ionic	1.786	1.900

* Measured at orifice; all measurements after 7/6/05 were made at the probe.

** Supply of 2.2 $\mu\text{g}/\text{m}^3$ cylinder gas was insufficient to complete test series.

4.2.3.2 Screening of Sorbent Trap Data with Hg CEMS

RMB Associates collected sorbent trap samples per Part 75 Section K during the 6 days of RATA testing. Those data were not available for inclusion in this report.

Section 5.

Quality Assurance/Quality Control

The Quality Assurance/Quality Control (QA/QC) requirements, emission measurement, and data quality objectives for this test project are summarized in this section. The QC procedures and acceptance criteria specified in the EPA methods and the QAPP were used. The procedures included, but were not limited to, (1) sampling equipment calibrations, (2) procedural elements of the methods, such as leak checks, placement of the sampling probe, verification of the integrity of metering systems prior to the start and at the completion of each sampling run, etc., and (3) the use of QC samples and analytical approaches such as reagent blank samples, method blanks, matrix spike samples, duplicate analysis, and surrogate spiking for both manual methods and CEMS. The performance and results of all QC procedures were recorded on appropriate forms, data sheets, field logs, and laboratory notebooks, as appropriate.

This QA/QC section is divided into two parts. The first part, 5.1, provides a summary of the Phase 1 November 2004 through February 2005, and the second part, 5.2, provides a summary of the Phase 2 testing performed March through September 2005.

5.1 Phase 1 Certification Testing

5.1.1 QA/QC Issues

It was discovered very late in the test program that a deviation from the Ontario-Hydro method had occurred during the laboratory analysis. The brown residue found in $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impinger samples was not cleared (see Section 13.3.5 of Ontario Hydro method) prior to extracting an aliquot for analysis. This is a critical step which greatly affects the analytical result. By the time MRI was made aware of this method deviation the samples had already been discarded and it was too late to perform any reanalysis. Omission of this step adversely affects both precision and accuracy. For that reason the elemental mercury from the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impinger samples are considered suspect. More information on this method deviation is provided in Section 5.2.1.

The field blank KCl impinger result was $> 30\%$ of the results for the field samples. This, coupled with extremely low Run 1 KCl impinger results, casts doubt on those sample results. However, since the oxidized mercury captured in the KCl impinger comprises on average $< 10\%$ of the total captured mercury, the impact is minimal. The paired train relative deviation (RD) criterion of $\leq 10\%$ RD was met for 8 of the 12 runs. The RA results for three of the four CEMS evaluated were greater than the 20% criteria and had differences greater than $1 \mu\text{g}/\text{m}^3$ for 9 runs. Two of the four CEMS met the remaining initial certification criteria listed in Table 5-1. Minor variances from the data quality criteria are noted in the remainder of this section.

5.1.2 Ontario Hydro Sampling Equipment Calibration

QC procedures, acceptability limits for sampling equipment calibrations, and calibration results are presented in Table 5-2. Calibration data sheets and equipment condition checklists used during calibration are provided in Appendix C of Volume 2 of this report. Equipment used for sample analysis was calibrated according to the procedures in the approved methods and manufacturers' manuals.

5.1.3 Hg CEMS Emission Measurement and Data Quality Objectives

The QC procedures, acceptability limits, and calibration results are presented in Table 5-2. Detailed information for these results was presented in Section 4 of this report.

5.1.4 Ontario Hydro Emission Measurement and Data Quality Objectives

Specific QC procedures were followed to ensure the continuous generation of useful and valid data. Table 5-3 presents a summary of criteria for assessing overall emission measurement and data quality for the initial RATA test. Section 5.4.1 presents a brief summary of the QA sample results for the RATA. All samples were analyzed within the 28-day holding time; however, shipping and storage temperatures for HNO₃/H₂O₂ and KMnO₄/H₂SO₄ samples could not be verified.

5.1.4.1 QA Sample Results

It was discovered very late in the test program that the laboratory did not perform the Ontario-Hydro method closely. They had not cleared the brown residue found in KMnO₄/H₂SO₄ impinger samples prior to extracting an aliquot for analysis. This is a critical step which greatly affects the analytical result. By the time MRI was made aware of this method deviation, the samples had already been discarded and it was too late to perform any reanalysis. Omission of this step adversely affects both precision and accuracy. For that reason the elemental mercury from the KMnO₄/H₂SO₄ sample fractions are considered suspect. More information on this method deviation is provided in Section 5.2.1.

Blanks

Results of blank analysis are shown in Table 5-4. Results for 4 of the 5 field blank train components indicated detectable levels of mercury, with the KCl impinger result at greater than 10 times the detection limit. Results from the field blank train analysis showed that mercury levels were > 30% of the field sample results for the KCl impingers and 5 of the 24 filters. These sample results have been flagged.

Table 5-1. Summary of Phase 1 CEMS Certification Criteria

Test	Method of determination	Frequency	Criteria	Criteria met? (Y/N)			
				Forney	Horiba	Tekran	Thermo
7-Day Calibration Error Test	Once per day for 7-day consecutive days	At 24-hr intervals for 7 consecutive days	Error must be $\leq 1 \mu\text{g}/\text{m}^3$ (alternative when span is defined at $10 \mu\text{g}/\text{m}^3$).	N	Y	Y	Y
Linearity Test	At beginning of test program, then quarterly	Once, at beginning of test program	Error must be $\leq 10\%$ or $\leq 1 \mu\text{g}/\text{m}^3$, whichever is least restrictive.	N	N	Y	Y
Cycle Time Test	Once, at beginning of test program	Once, at beginning of test program	Cycle times must be ≤ 15 minutes.	N	N	Y	Y
System Integrity Test	At beginning of test program, then weekly	Once, at beginning of test program	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	Y	Y	Y
Measurement Error Test	Performance of Linearity and Converter Efficiency tests	Once, at beginning of test program	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	N	Y	Y
Zero and Upscale Drift Test	Determines magnitude of drift at 24-hr intervals	7 consecutive days	Error must be $\leq 5\%$ of span (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	Y	N	N
Relative Accuracy ^b (RATA)	One set of 12 test runs, at beginning of test program, and again after 6 months	After initial certification checks	$\leq 1 \mu\text{g}/\text{m}^3$ difference (alternative when average RM indicates Hg concentration is $< 5.0 \mu\text{g}/\text{m}^3$).	N	N	Y ^a	Y ^a

^a Using Run 4 Avg. result.

^b A method deviation from the OH reference method makes all RATA results suspect.

Table 5-2. Phase 1 Calibration, QC Procedures, and Criteria for Ontario Hydro Sampling Equipment

Parameter	Calibration technique	Reference standard	Acceptance limit	Frequency	Criteria met? (yes/no)
Sampling nozzle	Measure 3 diameters to nearest 0.001 in and average measurements	Micrometer	Difference between high and low measurements, ≤ 0.004 in	Prior to sampling	Yes
Dry gas metering system— volume	Compare with calibrated critical orifices, 40 <i>CFR 60</i> , Appendix A, Method 5, Section 5.3	Calibrated critical orifice	Difference between individual calibration factor values and average value, $\leq \pm 0.02$	After test series	Yes
	Use field test data to compute a calibration check value, EPA Method 5, ALT-007	NA	Difference between calibration check value must be $\leq \pm 5\%$ of initial calibration factor	After test series	Yes
Dry gas meter temperature sensors (thermocouples)	Compare to mercury-in-glass thermometer	ASTM thermometer	$\leq \pm 5.4^\circ\text{F}$ difference from reference	Before and after test series	Yes
Gas stream (stack) temperature sensor (thermocouple)	Compare to value generated by dry well monitored with potentiometer thermocouple system	Hart Model 9100A dry well calibration system	Difference of $\leq \pm 1.5\%$ of minimum absolute stack temperature from absolute reference temperature (unsaturated gas streams); $\leq \pm 1^\circ\text{F}$ difference from reference (saturated gas streams)	Before and after test series	Yes
Final impinger outlet temperature sensor (thermocouple)	Compare to mercury-to-glass thermometer	ASTM thermometer	$\leq \pm 2^\circ\text{F}$ difference from reference	Before and after test series	Yes
Filter temperature sensor (thermocouple)	Compare to mercury-to-glass thermometer	ASTM thermometer	$\leq \pm 5.4^\circ\text{F}$ difference from reference	Before and after test series	Yes
Aneroid barometer	Compare to calibrated mercury barometer	Mercury column barometer	$\leq \pm 0.1$ in Hg difference from reference	Before and after test series	Yes
Type S pitot tube	Measure dimensions according to 40 <i>CFR 60</i> , Appendix A, Method 2 for baseline coefficient of 0.84	Micrometer and angle finder	Meets dimensional criteria specified in Method 2, Section 6.1 and Figures 2-2 and 2-3	Before and after test series	Yes

Table 5-3. Phase 1 Test Criteria for Emission Measurement and Data Quality

Test parameters	Matrix	Method of determination	Frequency	Accuracy objective	Precision objective	Criteria met? (Yes/No)
Hg	Ontario Hydro train samples	Analysis of blank train sample components (field blank)	Once to demonstrate system control (no gross contamination)	Hg levels >30% of measured results must be flagged		See Note 1
		Analysis of field reagent solutions (solution blank)	Each time new reagents are prepared	Hg levels >10% of measured results must be flagged		See Note 2
		Duplicate train analyses	Each run		RD must be within 10% of each other	No, see Notes 6 and 7
		Duplicate analysis	Every sample analyzed		Results must be within 10% of each other	No, see Notes 3 and 7
		Triplicate analysis	Every 10 th sample analyzed		Results must be within 10% of each other	No, see Notes 3 and 7
		Matrix spikes	Every 10th sample analyzed	65%-135% recovery	< 40% RPD	Yes
		Spiked lab reagent blanks simulating front-half and back-half train components	Two lab control spikes for each component (or combined components) at 10X the estimated detection limit	65%-135% recovery	< 40% RPD	See Note 4
		Continuing calibration check	Check standard every 10 samples	90% to 110% recovery	NA	Yes; see Note 5
		QC check standard (certified standard, independent of working calibration standards)	After each initial calibration	85% to 115% recovery	NA	Yes
Moisture pressure temperature velocity	Gas stream being measured	Secondary technical review of field test data and equipment calibration records relative to EPA Methods 1-5	Ongoing during testing	Validated by meeting posttest equipment calibration tolerances	NA, but multiple test runs may be used as indication of overall operation variability	Yes
O ₂ and CO ₂ by Orsat	Gas bag samples	Analysis of ambient air	Once prior to bag sample analysis	±0.2 percent by volume for ambient air oxygen	Method 3B criteria	Yes
		Triplicate analysis of bag samples	Each bag sample	NA	Method 3B criteria	Yes

Note 1 Mercury was reported in filter blank results at 0.017 µg. This level was > 30% of sample results for 5 of 24 filter samples. Mercury was also reported in the KCl impinger results at > 30% of all KCl sample values. The reported results have been flagged.

Note 2 Mercury was reported in the HNO₃/H₂O₂ impinger blank result at 0.004 µg. This level was > 10% of sample results for 21 of 24 impinger samples. The reported results have been flagged.

Note 3 Replicate results on approximately 10% of samples submitted were above the ±10% difference criteria. Analytical values for particle-bound samples were near the detection limit and do not significantly impact data quality. The KCl and HNO₃/H₂O₂ impinger samples have been reanalyzed and met the acceptance criteria. The reanalyzed results have been incorporated into this report.

Note 4 Only a single spiked lab reagent blank was performed and showed 98% recovery.

Note 5 A filter sample and a H₂O₂ impinger sample were slightly outside of the acceptance criteria at 86% and 112%, respectively.

Note 6 The RD was not met for 4 of the 12 runs. Runs 3, 6, and 12 had RDs of 13%, 13%, and 15%, respectively. Run 4 had an RD of 12% and variations of the train and train duplicate were used in the Relative Accuracy calculations.

Note 7 A method deviation (omission of clarification step of KMnO₄/H₂SO₄ sample prep) makes all results for this sample fraction suspect.

Table 5-4. Phase 1 RA Blank Analysis Results

Description	Hg result	Detection limit (µg)
Field Blank Train (µg)		
Filter	0.017	0.005
Probe Rinse	< 0.006	0.006
0.1 N KCl (Impingers 1-3)	0.475	0.010
5% HNO ₃ /10% H ₂ O ₂ (Impinger 4)	0.014	0.007
4% KMnO ₄ /10% H ₂ SO ₄ (Impingers 5-7)	0.014	0.020
Field Solution Blanks		
Filter (µg)	< 0.005	0.005
0.1 N HNO ₃ (µg)	< 0.005	0.005
0.1 N KCl (µg)	0.002	0.001
5% HNO ₃ /10% H ₂ O ₂ (µg)	0.004	0.002
4% KMnO ₄ /10% H ₂ SO ₄ (µg)	< 0.001	0.001
10% Hydroxylamine (µg/mL) *	0.0157	0.020
Laboratory Method Blanks (µg)		
Filter	< 0.0010	0.001
0.1 N HNO ₃	< 0.0010	0.001
0.1 N KCl	< 0.0200	0.001
5% HNO ₃ /10% H ₂ O ₂	< 0.0010	0.001
4% KMnO ₄ /10% H ₂ SO ₄	< 0.0200	0.0011

* At 0.0157 µg/mL, estimated maximum amounts in the KCl and KMnO₄ impingers are 0.002 µg and 0.008 µg, respectively.

Results shown in bold have values > 10 times the detection limit.

Results for three of the six solution blanks indicated detectable levels of mercury, with hydroxylamine result at greater than 10 times the detection limit. The blank results for hydroxylamine are shown in units of $\mu\text{g}/\text{mL}$ because the amount used per train component varied. The maximum amounts estimated to have been used in the KCl and KMnO_4 impingers were around 0.2 mL and 0.5 mL, respectively. Therefore, the estimated maximum amounts of mercury contributed to those train components was 0.002 μg and 0.008 μg , respectively.

Replicate Sample Analyses

Percent differences for duplicate and triplicate analysis are shown in Table 5-5. Approximately 10% of the sample replicates had $> 10\%$ difference. These samples were reanalyzed and the revised results were within the acceptance criteria.

Spikes and Audit Sample

Matrix spike results are found in Table 5-6. All of the matrix spikes met the QA criteria of $\pm 10\%$. Also, the audit sample result was within the QC criteria. The blank spike was only performed on the filter portion of the train and analyzed once. However, the percent recovery was within the accuracy objective.

Continuing Calibration Checks

Results of continuing calibration checks are provided in Table 5-7. All of the calibration checks met the $\pm 10\%$ criteria with the exception of two (a filter and a H_2O_2 impinger sample) which were slightly outside those criteria at 86% and 112%, respectively.

Table 5-5. Percent Difference for Phase 1 Mercury Analysis Results

Field ID	Lab ID	Percent Difference (%)				
		Particle bound		Oxidized	Elemental	
		Filter ^a	Probe rinse	KCl lipingers	HNO ₃ /H ₂ O ₂ Impinger	KMnO ₄ /H ₂ SO ₄ Impingers
Run 1	Lab 1	N/A ^a	N/A	8%	0%	1%
Run 1 dup train	Lab 2/3	N/A	N/A	3%	8%	1%
Run 2	Lab 4	N/A	N/A	1%	2%	1%
Run 2 dup train	Lab 5	N/A	9%	5%	10%	7%
Run 3	Lab 7	N/A	0%	2%	3%	1%
Run 3 dup train	Lab 8	N/A	0%	3%	0%	1%
Run 4	Lab 9	N/A	N/A	1%	8%	1%
Run 4 dup train	Lab 10	N/A	N/A	3%	0%	3%
Run 5	Lab 11	N/A	N/A	4%	10%	9%
Run 5 dup train	Lab 12	N/A	7%	3%	10%	6%
Run 6	Lab 13	N/A	N/A	0%	4%	1%
Run 6 dup train	Lab 14/15	N/A	N/A	3%	7%	1%
Run 7	Lab 16	N/A	5%	1%	0%	2%
Run 7 dup train	Lab 17	10%	5%	3%	7%	6%
Run 8	Lab 19	7%	N/A	0%	0%	1%
Run 8 dup train	Lab 20	0%	N/A	1%	0%	2%
Run 9	Lab 21	N/A	8%	3%	0%	2%
Run 9 dup train	Lab 22	N/A	4%	1%	0%	3%
Run 10	Lab 23	N/A	8%	2%	3%	0%
Run 10 dup train	Lab 24	N/A	N/A	2%	0%	0%
Run 11	Lab 25	0%	N/A	3%	0%	2%
Run 11 dup train	Lab 26/27	N/A	6%	1%	7%	2%
Run 12	Lab 28	N/A	0%	2%	8%	1%
Run 12 dup train	Lab 29	N/A	5%	1%	8%	0%
Field Blank	Lab 31	N/A	N/A	0%	0%	N/A
Blank Train	Lab 32	6%	N/A	0%	0%	0%

The QA objective is < 10% Difference [%Diff = (1 - (Analysis 1 / Analysis 2)) * 100; for triplicate analysis, the values with greatest difference are used].

^a An "N/A" indicates that Percent Difference calculation is not applicable due to one or more value below being the detection limit.

Values shown in bold did not initially meet the ≤ 10% Diff. objectives and were reanalyzed; reanalysis results are reported.

Table 5-6. Phase 1 RA Spike and Audit Sample Results

Field ID	Lab ID	Spike recoveries (as % of spiked)															
		Particle bound						Oxidized			Elemental						
		Filter			Probe rinse			KCl imp.			HNO ₃ /H ₂ O ₂ imp.			KMnO ₄ /H ₂ SO ₄ imp.			
	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.		
Matrix Spike																	
Run 2	Lab 6	0.0250	0.0262	105%	0.025	0.025	99.2%	0.250	0.268	107%	0.025	0.024	96.0%	0.250	0.258	103%	
Run 7	Lab 18	0.0250	0.0253	101%	0.025	0.025	100%	0.250	0.241	96.4%	0.025	0.023	92.8%	0.250	0.241	96.6%	
Run 12	Lab 30	0.0250	0.0243	97.2%	0.025	0.025	100%	0.250	0.267	107%	0.025	0.023	90.0%	0.250	0.261	104%	
		RPD: 8%			RPD: 1%			RPD: 10%			RPD: 7%			RPD: 8%			
Blank Spike																	
		0.0200	0.0196	98.0%	Not performed			Not performed			Not performed			Not performed			
Audit (QC Check) Sample																	
		Audit Amount (µg)				Amount Found (µg)				% Rec.							
1020	Lab 34	2.8				2.65%				94.6%							

% Recovery = (Amount Found in Spiked Sample – Average Amount Found in Unspiked Sample) / Amount Spiked x 100.

Values shown in bold do not meet the QA objectives.

Table 5-7. Phase 1 Continuing OH Calibration Check Standards

Spike recoveries (as % of spiked)														
Particle bound						Oxidized			Elemental					
Filter			Probe rinse			KCl imp.			HNO ₃ /H ₂ O ₂ imp.			KMnO ₄ /H ₂ SO ₄ imp.		
Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.
0.005	0.0051	102%	0.005	0.0048	96%	0.250	0.246	98%	0.005	0.005	102%	0.250	0.245	98%
0.005	0.0046	92%	0.005	0.0052	104%	0.250	0.240	96%	0.005	0.005	104%	0.250	0.248	99%
0.005	0.0045	90%	0.005	0.0050	100%	0.250	0.234	94%	0.005	0.005	108%	0.250	0.250	100%
0.005	0.0048	96%	0.005	0.0053	106%	0.250	0.248	99%	0.005	0.005	98.0%	0.250	0.236	94%
0.005	0.0046	92%	0.005	0.0054	108%	0.250	0.228	91%	0.005	0.005	92.0%	0.250	0.252	101%
0.005	0.0046	92%	0.005	0.0053	106%	0.250	0.249	99%	0.005	0.005	94.0%	0.250	0.239	95%
0.005	0.0046	92%	0.005	0.0051	102%	0.250	0.242	97%	0.005	0.005	96.0%	0.250	0.236	94%
0.005	0.0053	106%	0.005	0.0054	108%	0.250	0.248	99%	0.005	0.006	112%	0.250	0.233	93%
0.005	0.0043	86%	0.005	0.0051	102%	0.250	0.243	97%	–	–	–	0.250	0.252	101%
0.005	0.0046	92%	0.005	0.0051	102%	–	–	–	–	–	–	–	–	–
0.005	0.0045	90%	0.005	0.0052	104%	–	–	–	–	–	–	–	–	–

Note: Accuracy objective is 90% to 110% recovery. Values in bold are outside the objective.

5.1.5 Phase 1 Summary

QA audits were carried out for the manual Ontario Hydro Method and the CEMS. Sampling procedures and analytical data were evaluated against the quality objectives presented in the QAPP and the Site Specific Test Plan.

The Ontario Hydro data did not meet the data quality and measurement criteria for this work assignment as described earlier in Section 5.1.1 and 5.1.4.1. The omission of a critical sample preparation step in the laboratory causes concerns regarding the OH data quality.

Two CEMS met the Part 75 data quality and measurement criteria. The remaining two CEMS did not meet all the criteria.

An assessment of the overall quality of the data generated for Phase 1 was conducted and the OH data were found to be suspect. The data assessment included a review of the sample collection preparation and analysis data.

5.2 Phase 2 Certification Testing

5.2.1 QA/QC Issues

Because the Phase 2 Relative Deviation (RD) for $\text{KMnO}_4/\text{H}_2\text{SO}_4$ replicate impinger samples was unexplainably large (seven out of 12 replicate results had an RD larger than 16%, with the highest at 47% RD), these samples were reanalyzed. When the reanalyzed results were also unexplainably large with no reproducibility between the first and second analyses, the contract laboratory was questioned and it was discovered that the brown residue found in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impinger samples had not been clarified prior to extracting an aliquot for analysis. This is a critical step which affects the analytical accuracy and precision.

Because the highest amount of mercury is found in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers, with much of it located in the brown residue on the side of the sample bottle, all $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impinger results had to be considered nonrepresentative of the samples. A second laboratory (ARCADIS G&M, Inc.) was contracted to reanalyze the remaining $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples from Phase 2 sampling (Phase 1 samples had long since been discarded). The four $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples which had been spiked were missing a 100-mL to 200-mL volume with no corresponding analytical data. This is likely because the original laboratory often prepares extra aliquots in case there is some problem with preparation. The laboratory did provide some additional analytical spike data, but it was not sufficient to account for the missing 100-mL to 200-mL volume.

In order to determine the mercury values for the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples, the analytical results for each aliquot (as reported by the original laboratory) was multiplied by the aliquot volume, then summed and added to the ARCADIS labs' analytical result

times the remaining sample volume to obtain a total mass. Because the four spiked samples from the original laboratory were missing an additional 100-mL to 200-mL of sample, those results are biased low since the unknown amount of mercury in those missing volumes cannot be added to the total.

The analytical results from the Phase 1 $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples must be considered suspect and the difficulties discussed above would account for the difficulty in meeting the RD criteria of $\leq 10\%$ RD. Because the Phase 2 $\text{KMnO}_4/\text{H}_2\text{SO}_4$ samples were reanalyzed, these results were mostly salvageable, with the exception of the spiked samples (Runs 2, 7, 10, and 12) which are biased low because a significant volume of the sample was missing prior to reanalysis.

The field blank $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger results for mercury were $> 30\%$ of field sample results. However, since the elemental mercury captured in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger comprises on average $< 3\%$ of the total captured mercury, the impact was minimal.

The RD criterion of $\leq 10\%$ RD was met for 8 of the 12 runs. A review of other sampling parameters (O_2 , CO_2 , and H_2O) were within 8% of each other for all runs and do not appear to have contributed to the RD values. Despite the large RD observed for the OH method results, three CEMS had differences less than $1 \mu\text{g}/\text{m}^3$ as compared to the OH results for all 12 runs.

5.2.2 Hg CEMS Emission Measurement and Data Quality Objectives

The QC procedures, acceptability limits, and calibration results are presented in Table 5-8. Detailed results were presented in Section 4 of this report.

5.2.3 Ontario Hydro Sampling Equipment Calibration

QC procedures, acceptability limits for sampling equipment calibrations, and calibration results are presented in Table 5-9. Calibration data sheets and equipment condition checklists used during calibration are provided in Appendix C of Volume 3 of this report. Equipment used for sample analysis was calibrated according to the procedures in the approved methods and manufacturers' manuals.

Table 5-8. Summary of Phase 2 CEMS Certification Criteria

Test	Method of determination	Frequency	Criteria	Criteria met? (Y/N)			
				Durag	Opsis	Tekran	Thermo
7 Day Calibration Error Test	Once per day for 7 consecutive days	At 24-hr intervals for 7 consecutive days	Error must be $\leq 1 \mu\text{g}/\text{m}^3$ (alternative when span is defined at $10 \mu\text{g}/\text{m}^3$).	Y	Y	Y	N
Linearity Test	At beginning of test program, then quarterly	Once, at beginning of test program	Error must be $\leq 10\%$ or $\leq 1 \mu\text{g}/\text{m}^3$, whichever is least restrictive.	N	N	Y ^a	N
Cycle Time Test	Once, at beginning of test program	Once, at beginning of test program	Cycle times must be ≤ 15 minutes.	Y	Y	Y	Y
System Integrity Test	At beginning of test program, then weekly	Once, at beginning of test program	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm .5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y ^c	Y ^b	Y ^c	N
Measurement Error Test	Performance of Linearity and Converter Efficiency tests	Once, at beginning of test program	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm .5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y ^a	N	Y ^a	N
Zero and Upscale Drift Test	Determine magnitude of drift at 24hr intervals	7 consecutive days	Error must be $\leq 5\%$ of span (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	Y	N	Y ^c	N
Relative Accuracy (RATA) ^d	One set of 12 test runs, at beginning of test program, and again after 6 months	After certification checks	$\leq 20\%$; or, for low emitters with avg conc $< 5 \mu\text{g}/\text{m}^3$, $\leq 1 \mu\text{g}/\text{m}^3$ difference.	Y	Y	Y	N

^a Passed first of two tests in July.

^b Passed the test performed in June.

^c Passed the test performed in May.

^d A method deviation with missing sample volume caused Runs 2, 7, 10, and 12 to be biased low which resulted in larger than acceptable RD values and suspect data for these Reference Method results.

Table 5-9. Phase 2 Calibration, QC Procedures, and Criteria for Ontario Hydro Sampling Equipment

Parameter	Calibration technique	Reference standard	Acceptance limit	Frequency	Criteria met? (yes/no)
Sampling nozzle	Measure 3 diameters to nearest 0.001 in and average measurements	Micrometer	Difference between high and low measurements, ≤ 0.004 in	Prior to sampling	Yes
Dry gas metering system— volume	Compare with calibrated critical orifices, 40 <i>CFR 60</i> , Appendix A, Method 5, Section 5.3	Calibrated critical orifice	Difference between individual calibration factor values and average value, $\leq \pm 0.02$	After test series	Yes
	Use field test data to compute a calibration check value, EPA Method 5, ALT-007	NA	Difference between calibration check value must be $\leq \pm 5\%$ of calibration factor	After test series	Yes
Dry gas meter temperature sensors (thermocouples)	Compare to mercury-in-glass thermometer	ASTM thermometer	$\leq \pm 5.4^\circ\text{F}$ difference from reference	Before and after test series	Yes
Gas stream (stack) temperature sensor (thermocouple)	Compare to value generated by dry well monitored with potentiometer thermocouple system	Hart Model 9100A dry well calibration system	Difference of $\leq \pm 1.5\%$ of minimum absolute stack temperature from absolute reference temperature (unsaturated gas streams); $\leq \pm 1^\circ\text{F}$ difference from reference (saturated gas streams)	Before and after test series	Yes
Final impinger outlet temperature sensor (thermocouple)	Compare to mercury-to-glass thermometer	ASTM thermometer	$\leq \pm 2^\circ\text{F}$ difference from reference	Before and after test series	Yes
Filter temperature sensor (thermocouple)	Compare to mercury-to-glass thermometer	ASTM thermometer	$\leq \pm 5.4^\circ\text{F}$ difference from reference	Before and after test series	Yes
Aneroid barometer	Compare to calibrated mercury barometer	Mercury column barometer	$\leq \pm 0.1$ in Hg difference from reference	Before and after test series	Yes
Type S pitot tube	Measure dimensions according to 40 <i>CFR 60</i> , Appendix A, Method 2 for baseline coefficient of 0.84	Micrometer and angle finder	Meets dimensional criteria specified in Method 2, Section 6.1 and Figures 2-2 and 2-3	Before and after test series	Yes

5.2.4 Ontario Hydro Emission Measurement and Data Quality Objectives

Specific QC procedures were followed to ensure the continuous generation of useful and valid data. Table 5-10 presents a summary of criteria for assessing overall emission measurement and data quality for the RATA test. Section 6.4.1 presents a brief summary of the QA sample results for the RATA. All samples were analyzed within the 28-day holding time; however, shipping and storage temperatures for HNO₃/H₂O₂ and KMnO₄/H₂SO₄ samples could not be verified.

5.2.5 QA Sample Results

It was discovered very late in the test program that the laboratory did not perform the Ontario Hydro method closely. They had not cleared the brown residue found in KMnO₄/H₂SO₄ impinger samples prior to extracting an aliquot for analysis. This is a critical step which greatly affects the analytical result. As soon as MRI was made aware of this method deviation, a second laboratory was contacted to reanalyze the KMnO₄/H₂SO₄ samples. Four of the 12 runs were not completely reanalyzed (see discussion in 5.2.1). Omission of this step adversely affects both precision and accuracy. For that reason, the elemental mercury from the Run 2, 7, 10, and 12 KMnO₄/H₂SO₄ samples are considered biased low and are suspect. More information on this method deviation was provided in Section 5.2.1.

Blanks

Results of blank analysis are shown in Table 5-11. Results for the filter, HNO₃/H₂O₂, and KMnO₄ field blank train components indicated detectable levels of mercury, with the HNO₃/H₂O₂ impinger result at greater than 10 times the detection limit. Results from blank train analysis showed that mercury levels were > 30% of sample results for HNO₃/H₂O₂ impingers for all runs except Run 1. Mercury levels were also > 30% of sample results for 5 of the 24 filters. These sample results have been flagged.

Results for three of the six solution blanks indicated detectable levels of mercury. The blank results for hydroxylamine are shown in units of µg/mL because the amount used per train component varied. The maximum amount estimated to have been used in the KCl and KMnO₄ impingers were around 0.2 mL. Therefore, the estimated maximum amount of mercury contributed to the train components was 0.00004 µg.

Replicate Sample Analyses

Percent differences for duplicate and triplicate analysis are shown in Table 5-12. The Run 11 filter and the Solution Blank HNO₃/H₂O₂ impinger sample replicates had > 10% difference. These samples were not reanalyzed.

Table 5-10. Phase 2 RA Test Criteria for Emission Measurement and Data Quality

Test parameters	Matrix	Method of determination	Frequency	Accuracy objective	Precision objective	Criteria met? (Yes/No)
Hg	Ontario Hydro train samples	Analysis of blank train sample components (field blank)	Once to demonstrate system control (no gross contamination)	Hg levels >30% of measured results must be flagged		Yes, see Note 1
		Analysis of field reagent solutions (solution blank)	Each time new reagents are prepared	Hg levels >10% of measured results must be flagged		Yes, see Note 2
		Duplicate train analyses	Each run		RD must be within 10% of each other for 9 or 12 runs	No, see Notes 3 and 6
		Duplicate analysis	Every sample analyzed		Results must be within 10% of each other	No, see Notes 4 and 6
		Triplicate analysis	Every 10 th sample analyzed		Results must be within 10% of each other	No, see Notes 4 and 6
		Matrix spikes	Every 10th sample analyzed	65%-135% recovery	< 40% RPD	Yes
		Spiked lab reagent blanks simulating front-half and back-half train components	Two lab control spikes for each component (or combined components) at 10X the estimated detection limit	65%-135% recovery	< 40% RPD	See Note 5
		Continuing calibration check	Check standard every 10 samples	90% to 110% recovery	NA	Yes
		QC check standard (certified standard, independent of working calibration standards)	After each calibration	85% to 115% recovery	NA	Yes
Moisture pressure temperature velocity	Gas stream being measured	Secondary technical review of field test data and equipment calibration records relative to EPA Methods 1-5	Ongoing during testing	Validated by meeting posttest equipment calibration tolerances	NA, but multiple test runs may be used as indication of overall operation variability	Yes
O ₂ and CO ₂ by Orsat	Gas bag samples	Analysis of ambient air	Once prior to bag sample analysis	±0.2 percent by volume for ambient air oxygen	Method 3B criteria	Yes
		Triplicate analysis of bag samples	Each bag sample	NA	Method 3B criteria	Yes

Note 1 Mercury was reported in the HNO₃/H₂O₂ impinger results at > 30% of Runs 2-12 sample values. The reported results have been flagged.

Note 2 Mercury was reported in the HNO₃/H₂O₂ impinger blank result at 0.006 µg. This level was > 10% of sample result for one impinger sample from Run 6. The reported result has been flagged.

Note 3 The RD was met for only 4 of the 12 runs.

Note 4 Replicate results for Run 11 filter and field blank train HNO₃/H₂O₂ impinger were > 10% of each other. These samples were not reanalyzed.

Note 5 Recoveries were outside criteria for one HNO₃/H₂O₂ impinger and for two KMnO₄/H₂SO₄ impingers. The RPD was outside criteria for the HNO₃/H₂O₂ and KMnO₄/H₂SO₄ fractions.

Note 6 A method deviation with resultant missing sample volume caused Runs 2, 7, 10, and 12 to be biased low, which resulted in suspect data for these Reference Method results.

Table 5-11. Phase 2 Blank Analysis Results

Description	Hg result	Detection limit (µg)
Field Blank Train-2 (µg)		
Filter	0.006	0.001
Probe Rinse	< .007	0.001
0.1 N KCl (Impingers 1-3)	< .012	0.001
5% HNO ₃ /10% H ₂ O ₂ (Impinger 4)	0.032	0.001
4% KMnO ₄ /10% H ₂ SO ₄ (Impingers 5-7)	< .016	0.0011
Field Blank Train-4 (µg)		
Filter	0.010	0.001
Probe Rinse	< .008	0.001
0.1 N KCl (Impingers 1-3)	< .014	0.001
5% HNO ₃ /10% H ₂ O ₂ (Impinger 4)	0.057	0.001
4% KMnO ₄ /10% H ₂ SO ₄ (Impingers 5-7)	0.019	0.0011
Field Solution Blanks		
Filter (µg)	< .005	0.001
0.1 N HNO ₃ (µg)	< .006	0.001
0.1 N KCl (µg)	< .001	0.001
5% HNO ₃ /10% H ₂ O ₂ (µg)	0.006	0.001
4% KMnO ₄ /10% H ₂ SO ₄ (µg)	0.003	0.0011
10% Hydroxylamine (µg/mL) *	0.0002	0.0008
Laboratory Method Blanks (µg)		
Filter	< .005	0.001
0.1 N HNO ₃	< .001	0.001
0.1 N KCl (low calibration curve)	< .001	0.001
0.1 N KCl (high calibration curve)	< .02	0.019
5% HNO ₃ /10% H ₂ O ₂	< .001	0.001
4% KMnO ₄ /10% H ₂ SO ₄ (low calibration curve)	< .001	0.0011
4% KMnO ₄ /10% H ₂ SO ₄ (high calibration curve)	< .02	0.022

Table 5-12. Percent Difference for Phase 2 Mercury Analysis Results

Field ID	Percent Difference (%)				
	Particle Bound	Probe rinse	Oxidized	HNO ₃ /H ₂ O ₂ impinger	Elemental
	Filter ^a		KCl impingers		KMnO ₄ /H ₂ SO ₄ impingers
Run 1	0%	0%	1%	1%	2%
Run 1 dup train	5%	9%	2%	1%	2%
Run 2	N/A	N/A	3%	9%	1%
Run 2 dup train	N/A	N/A	3%	2%	0%
Run 3	N/A	N/A	3%	3%	1%
Run 3 dup train	N/A	N/A	7%	2%	1%
Run 4	0%	0%	4%	3%	2%
Run 4 dup train	N/A	0%	4%	3%	5%
Run 5	N/A	0%	8%	1%	1%
Run 5 dup train	N/A	4%	1%	2%	7%
Run 6	N/A	4%	2%	2%	3%
Run 6 dup train	N/A	5%	5%	0%	4%
Run 7	N/A	4%	1%	0%	2%
Run 7 dup train	N/A	N/A	6%	1%	3%
Run 8	N/A	8%	2%	3%	3%
Run 8 dup train	N/A	N/A	0%	4%	2%
Run 9	N/A	N/A	0%	4%	0%
Run 9 dup train	N/A	N/A	6%	0%	3%
Run 10	0%	0%	0%	2%	0%
Run 10 dup train	N/A	6%	1%	2%	1%
Run 11	14%	N/A	3%	1%	7%
Run 11 dup train	N/A	5%	8%	2%	3%
Run 12	N/A	N/A	7%	2%	5%
Run 12 dup train	N/A	N/A	8%	1%	3%
Field Solution Blank	N/A	N/A	N/A	20%	0%
Blank Train-1	N/A	N/A	1%	0%	1%
Blank Train-2	0%	N/A	N/A	6%	N/A
Blank Train-3	N/A	N/A	0%	2%	0%
Blank Train-4	0%	N/A	N/A	2%	6%
Blank Train-5	N/A	N/A	1%	2%	1%

^a The Method Blank exceeded 10% of the measured value for all filter results; therefore, results should be considered suspect.

The QA objectives are < 10% Difference [%Diff = (1 - (Analysis 1 / Analysis 2)) * 100; for triplicate analysis, the values with greatest difference are used].

Values shown in bold do not meet the QA objectives.

Table 5-13. Phase 2 RA Spike and Audit Sample Results

Field ID	Lab ID	Spike recoveries (as % of spiked)														
		Particle bound						Oxidized			Elemental					
		Filter			Probe rinse			KCl imp.			HNO ₃ /H ₂ O ₂ imp.			KMnO ₄ /H ₂ SO ₄ imp.		
Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.		
Matrix Spike																
Run 2 Rep	Lab 6	0.0250	0.0245	98.0%	0.025	0.0270	108%	0.250	0.229	91.8%	0.025	0.0236	94.4%	0.250	0.264	105%
Run 7 Rep	Lab 18	0.0250	0.0254	102%	0.025	0.0232	92.8%	0.025	0.024	95.2%	0.025	0.0256	102%	0.250	0.242	96.6%
Run 10 Rep	Lab 26	0.0250	0.0280	112%	0.025	0.0270	108%	0.025	0.027	107%	0.025	0.0249	100%	0.250	0.236	94.2%
Run 12 Rep	Lab 32	0.0250	0.0273	109%	0.025	0.0243	97.2%	0.025	0.023	91.6%	0.025	0.0247	98.8%	0.250	0.258	103%
		RPD: 13%			RPD: 16%			RPD: 16%			RPD: 8%			RPD: 11%		
Blank Spike																
Filter Spike		0.0200	0.0201	100.5%												
Blank Train-1 Spike			< 0.005	none		< 0.007	none	0.996	0.860	86.3%	0.050	0.019	38%	7.968	5.93	74.4%
Blank Train-2 Spike			< 0.005	none		< 0.007	none	0.996	0.897	90.1%	0.050	0.058	115%	7.968	4.05	50.8%
Blank Train-3 Spike			< 0.005	none		< 0.007	none	0.996	0.941	94.4%	0.050	0.113	227%	7.968	2.93	36.8%
								RPD: 9%			RPD: 149%			RPD: 70%		
Audit (QC Check) Sample																
		Audit Amount (ng/mL)				Amount Found (ng/mL)				% Rec.						
1017	Lab 40	2.8				2.82				100.7%						

% Recovery = (Amount Found in Spiked Sample – Average Amount Found in Unspiked Sample) / Amount Spiked x 100.

Note: Results outside of QC criteria are shown in bold.

Spikes and Audit Sample

Matrix spike results are found in Table 5-13. All of the matrix spikes met the QA criteria of $\pm 10\%$. Also, the audit sample result was within the QC criteria. Blank spikes for the $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers are noteworthy due to the erratic recoveries and poor precision (large RPDs). These samples were reanalyzed along with all of the sample $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers.

Continuing Calibration Checks

Results of continuing calibration checks are provided in Table 5-14. All of the calibration checks met the $\pm 10\%$ criteria.

5.2.6 Phase 2 Summary

QA audits were carried out for the manual Ontario Hydro Method and the CEMS. Sampling procedures and analytical data were evaluated against the quality objectives presented in the QAPP and the Site Specific Test Plan.

The Ontario Hydro data met the data quality and measurement criteria for this work assignment as described earlier in Section 5.2.1 and 5.2.4.1. None of the CEMS met all of the draft PS-12A and Part 75 data quality and measurement criteria. The RD criteria of $\leq 10\%$ for four of the 12 OH test runs were not met because of a method deviation by the contract laboratory which resulted in data from Runs 2, 7, 10, and 12 being suspect.

An assessment of the overall quality of the data generated for this work assignment was conducted and the data were found to be acceptable for 8 of the 12 Phase 2 RATA runs. Because of a method deviation, the data from Runs 2, 7, 10, and 12 are biased low and should be considered suspect.

Table 5-14. Phase 2 Continuing OH Calibration Check Standards

Spike recoveries (as % of spiked)														
Particle bound						Oxidized			Elemental					
Filter			Probe rinse			KCl imp.			HNO ₃ /H ₂ O ₂ imp.			KMnO ₄ /H ₂ SO ₄ imp.		
Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.	Spiked (µg)	Found (µg)	% Rec.
0.005	0.0048	96.0%	0.005	0.0050	100%	0.005	0.0052	104%	0.005	0.0046	92.0%	0.250	0.253	101%
0.005	0.0049	98.0%	0.005	0.0052	104%	0.005	0.0047	94.0%	0.005	0.0046	92.0%	0.250	0.255	102%
0.005	0.0049	98.0%	0.005	0.0046	92.0%	0.005	0.0051	102%	0.005	0.0049	98.0%	0.250	0.244	97.6%
0.005	0.0050	100%	0.005	0.0046	92.0%	0.005	0.0048	96.0%	0.005	0.0047	94.0%	0.250	0.252	101%
0.005	0.0054	108%	0.005	0.0052	104%	0.250	0.2592	104%	0.005	0.0047	94.0%	0.250	0.256	102%
0.005	0.0047	94.0%	0.005	0.0048	96%	0.250	0.2595	104%	0.005	0.0055	110%	0.005	0.0048	96.0%
0.005	0.0048	96.0%	0.005	0.0054	108%				0.005	0.0049	98.0%	0.005	0.0047	94.0%
0.005	0.0051	102%	0.005	0.0050	100%				0.005	0.0045	90.0%	0.005	0.0047	94.0%
0.005	0.0050	100%	0.005	0.0055	110%				0.005	0.005	106%	0.005	0.0048	96.0%
			0.005	0.0054	108%				0.005	0.004	86.0%	0.250	0.2518	101%
			0.005	0.0054	108%				0.005	0.005	92.0%	0.250	0.2500	100%
			0.005	0.0050	100%				0.005	0.0054	86.0%	0.250	0.2503	100%
			0.005	0.0052	104%									
			0.005	0.0049	98.0%									
			0.005	0.0048	96.0%									
			0.005	0.0048	96.0%									
			0.005	0.0051	102%									

Section 6.

Hg CEMS Conclusions and Recommendations

6.1 Performance Findings

While all of the Hg CEMS participating in this test program had some difficulty at times meeting the certification criteria and providing continuous data, much was learned as a result of field evaluation which was evidenced by improvements made to the Hg CEMS over the course of this program. Table 6-1 provides an overall summary of the Phase 1 and 2 performance results. The ability of each Hg CEMS to provide continuous data is summarized in the long-term monitoring summary, Figure 6-1.

In general, the Hg CEMS consisted of a sample extraction component (probe), a sample conditioning component (dilution probe—converter—SO₂ neutralizer), and an analytical component (CVAA, CVAF, or UV detection). The analytical component of the systems is well established and did not generally contribute to measurement problems. However, multiple problems were observed with the sample transfer and conditioning of the stack gas. The most commonly observed problems related to either physical plugging of the probe during sample transfer or fouling of the converter. Often it would take some time for this type of problem to be evident. In some cases, more than one attempt was necessary to meet performance criteria and system maintenance was required.

The challenges to the Hg CEMS were more mechanical or physical than chemical. These challenges have provided a test bed for Hg CEMS improvement. Also, many of the challenges to the Hg CEMS are also applicable to non-mercury continuous emissions monitoring systems.

6.2 Conclusions and Recommendations

This test program demonstrated that the source characteristics can have a significant effect on Hg CEMS performance. Regardless of the vendor supplying the Hg CEMS, the CEMS should be appropriately modified for the source. For instance, the source sampled for this demonstration project has a wet emission matrix and thus requires an Hg CEMS with efficient sample transfer and conditioning capabilities in order to function properly.

Because of the extent to which source characteristics influence Hg CEMS performance, it is suggested that:

- Potential purchasers review available Hg CEMS performance testing data obtained from sources similar to their own.
- Potential purchasers ask vendors to provide specific experience, including ongoing improvements that the vendor has made as a result of their experience at similar sources.

Because the source characteristics can greatly affect the performance of the Hg CEMS and because it may take some time for problems to manifest, it is also suggested that:

- An Hg CEMS considered for purchase be operated on-site for six months to demonstrate its capability to perform (reliability and accuracy) under the site-specific conditions before acceptance.
- The above should be part of a performance warranty agreement.

Table 6-1. Summary of CEMS Certification Criteria and Performance

Test	Criteria	Phase 1 Criteria Met? (Y/N)				Phase 2 Criteria Met? (Y/N)			
		Forney	Horiba	Tekran	Thermo	Durag	Opsis	Tekran	Thermo
7 Day Calibration Error Test	Error must be $\leq 1 \mu\text{g}/\text{m}^3$ (span is defined at $10 \mu\text{g}/\text{m}^3$).	N	Y	Y	Y	Y	Y	Y	N
Linearity Test	Error must be $\leq 10\%$ or $\leq 1 \mu\text{g}/\text{m}^3$, whichever is least restrictive.	N	N	Y	Y	N	N	Y ^b	N
Cycle Time Test	Cycle times must be ≤ 15 minutes.	N	N	Y	Y	Y	Y	Y	Y
System Integrity Test (includes Converter Efficiency)	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	Y	Y	Y	Y ^d	Y ^c	Y ^d	N
Measurement Error Test	Error must be $\leq 5\%$ of span from certified gas value (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	N	Y	Y	Y ^b	N	Y ^b	N
Zero and Upscale Drift Test	Error must be $\leq 5\%$ of span (i.e., within $\pm 0.5 \mu\text{g}/\text{m}^3$ of certified gas value).	N	Y	N	N	Y	Y	Y ^d	N
Relative Accuracy (RATA)	$\leq 20\%$; or, for low emitters with avg conc $< 5 \mu\text{g}/\text{m}^3$, difference within $\pm 1.0 \mu\text{g}/\text{m}^3$.	N	N	Y ^a	Y ^a	Y	Y	Y	N

^a Using Run 4 Avg. result

^b Passed the first of two tests performed in July.

^c Passed the test performed in June.

^d Passed the test performed in May.

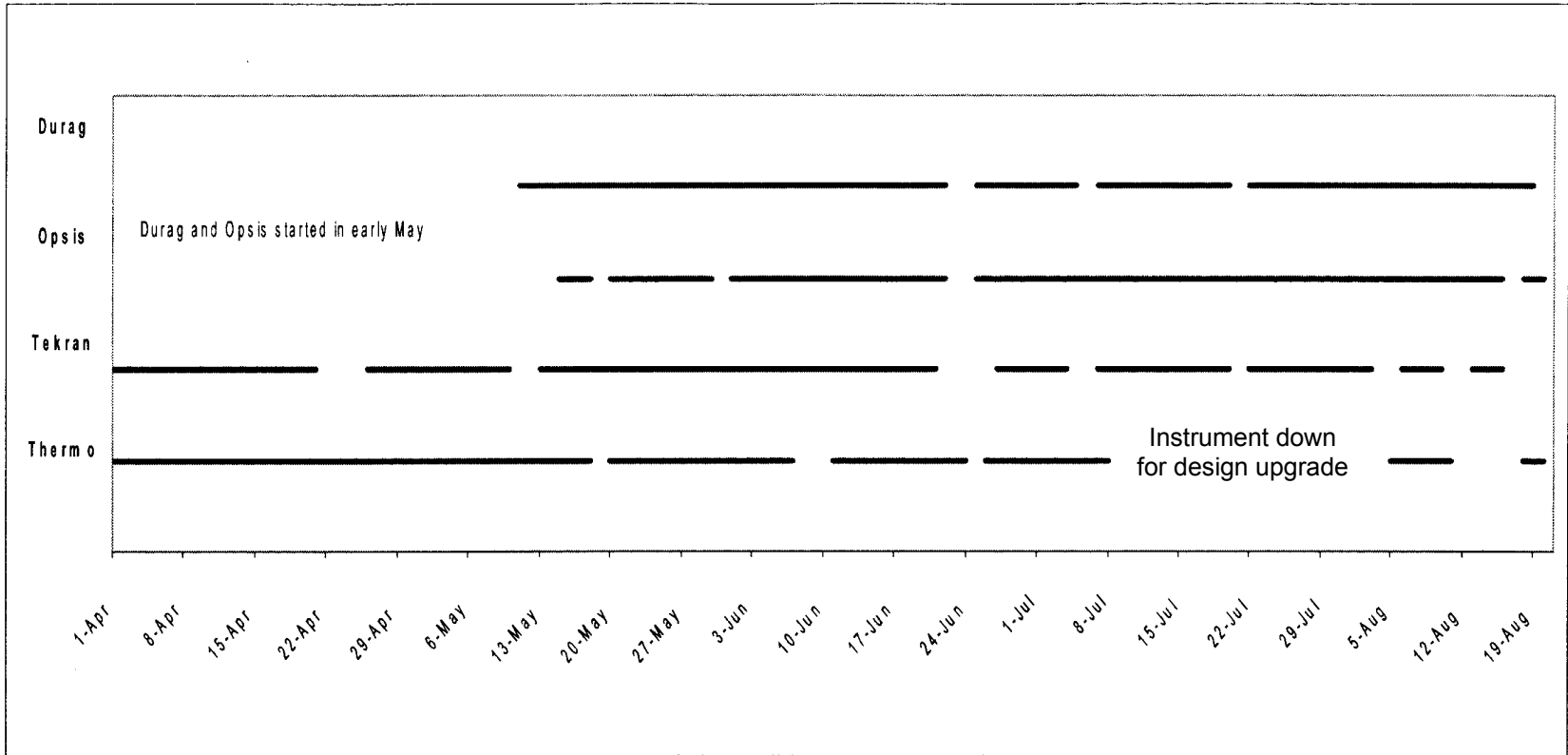


Figure 6-1. Phase 1 and 2 Long-Term Monitoring Periods