September 2003

Environmental Technology Verification Report

PS ANALYTICAL, LTD.
SIR GALAHAD II MERCURY CONTINUOUS EMISSION MONITOR

Prepared by
Battelle

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ETV ETV ETV

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ETV Advanced Monitoring Systems Center

PS Analytical, Ltd.
Sir Galahad II Mercury Continuous Emission Monitor

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of seven environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AMS	Advanced Monitoring Systems
CO	carbon monoxide
CO_2	carbon dioxide
CEM	continuous emission monitor
cm	centimeter
CVAA	cold vapor atomic absorption
dscf	dry standard cubic foot
dscm	dry standard cubic meter
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ETTP	East Tennessee Technology Park
ETV	Environmental Technology Verification
FIU-HCET	Florida International University, Hemispheric Center for Environmental Technology
Hg^o	elemental mercury
Hg_{OX}	oxidized mercury
Hg_T	total vapor-phase mercury
hr	hour
µg	microgram
mL	milliliter
m^3	cubic meter
mg	milligram
min	minute
NIST	National Institute of Standards and Technology
O_2	oxygen
OH	Ontario Hydro
ORD	Office of Research and Development
PE	performance evaluation
QA	quality assurance
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
RA	relative accuracy
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RSD	relative standard deviation
SEI	Shaw Environmental, Inc.
STL	Severn Trent Laboratories
TSA	technical systems audit
TSCAI	Toxic Substances Control Act Incinerator

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA’s National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of continuous emission monitors (CEMs) for mercury, including the PS Analytical, Ltd., Sir Galahad II (SG-II) mercury CEM.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the SG-II mercury CEM. Following is a description of the SG-II mercury CEM, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The SG-II is an automated continuous emission monitor for elemental mercury (Hg^o) and total vapor-phase mercury (Hg_T) in combustion flue gases and other gas streams. The SG-II consists of a Model S235C400 mercury speciation module; an enclosed cabinet housing the SG-II amalgamation atomic fluorescence mercury detector (PSA 10.525); a stream selector module (PSA S235S100); a personal computer, monitor, and keyboard; and a mercury calibration source (PSA 10.533). The speciation module converts oxidized mercury in the sample gas to Hg^o by means of a proprietary aqueous reagent, allowing separate detection of Hg^o and Hg_T. The speciation module is approximately 75 centimeters (cm) wide x 45 cm deep x 90 cm high (30 inches wide x 18 inches deep x 36 inches high), and can be mounted on the stack being sampled, or on a wall or supporting frame. The cabinet enclosing the other modules is approximately 75 cm wide x 75 cm deep x 180 cm high (30 inches wide x 30 inches deep x 72 inches high) and is mounted on wheels. The speciation module and detector cabinet of the SG-II are shown in Figure 2-1.

Figure 2-1. PS Analytical, Ltd., SG-II CEM

A heated Teflon diaphragm pump draws a filtered sample flow of approximately five liters per minute from the gas source into the speciation module, which contacts the gas stream with the aqueous reagents in two bubblers. Two separate gas streams are thus produced, one of which has been scrubbed of oxidized mercury and therefore contains only Hg^o. In the other gas stream, oxidized mercury is reduced to Hg^o, producing an Hg^o concentration equivalent to the original sum of oxidized mercury and Hg^o. These two gas streams flow to the stream selector module. Mercury in the selected gas stream is collected by passage through a preconcentration trap and subsequently thermally desorbed into the SG-II detector, which has a detection limit of as little as 0.1 picograms of mercury. In this verification test, a sample flow of 0.5 liter/minute was passed through the preconcentration trap for 1 to 2 minutes. The resulting detection limit for vapor-phase mercury is approximately 0.001 microgram per cubic meter ($\mu g/m^3$), with a linear dynamic range of up to 2,500 $\mu g/m^3$. The PSA 10.533 mercury source provides a calibration gas and blank stream that can be substituted for the sample stream on a scheduled or as-needed basis. This allows system bias checking for the entire sampling system.

The SG-II uses Windows®-based operating software for calibrating and operating the instrument and recording and displaying data. The duration, flow rate, and sequencing of the Hg^o and Hg_T measurements are controlled by the software, as are the operation of the SG-II detector, the graphical display of data, and the scheduling of internal calibration checks. The software checks for alarm outputs from the various modules and can warn of any malfunctions of the system.

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Field Demonstration of Mercury Continuous Emission Monitors at the TSCA Incinerator*.(1) The purpose of the verification test was to evaluate the performance of mercury CEMs at a full-scale field location, over a substantial period of continuous operation. The mercury CEMs were challenged by stack gases generated from the thermal treatment of a variety of actual wastes in the Toxic Substances Control Act Incinerator (TSCAI) at the East Tennessee Technology Park (ETTP) in Oak Ridge, Tennessee. CEM responses were compared with reference mercury measurements of total (Hg_T), oxidized (Hg_{OX}), and elemental (Hg°) mercury. Mercury standard gases were used to challenge the CEMs to assess stability in long-term operation, and the instruments were operated for several weeks by TSCAI staff to assess operational aspects of their use.

The performance of the SG-II was verified while monitoring emissions from the TSCAI that were generated from treating actual waste. The reference method for establishing the quantitative performance of the tested technologies was the Ontario Hydro (OH) method.(2)

The SG-II performance parameters addressed included

- Relative accuracy (RA) with respect to reference method results
- Correlation with reference method results
- Precision
- Sampling system bias
- Relative calibration and zero drift
- Response time
- Data completeness
- Operational factors.

Relative accuracy, correlation with the reference method, and precision (i.e., repeatability at stable test conditions) were assessed for total and elemental mercury in the stack gas emissions. Sampling system bias, calibration and zero drift, and response time were assessed for Hg^o only, using commercial compressed gas standards of Hg^o. The data completeness, reliability, and maintainability of the CEMs over the course of the verification test were assessed during several weeks of continuous operation.

This verification test was conducted jointly by the ETV AMS Center and the DOE. Under DOE funding, Shaw Environmental, Inc. (SEI), under subcontract to Bechtel Jacobs Company LLC, and the Hemispheric Center for Environmental Technology at Florida International University (FIU-HCET) directed the field test. Reference method analyses were conducted by Severn Trent Laboratories, and data analysis was conducted by the University of Tennessee. Funding for these activities was provided by DOE's Transuranic and Mixed Waste Focus Area; the Characterization, Monitoring and Sensor Technology Crosscutting Program; and FIU-HCET.

3.2 Facility Description

The TSCAI is designed and permitted for receiving, sorting, storing, preparing, and thermally destroying low-level radioactive and Resource Conservation and Recovery Act (RCRA) mixed waste contaminated with polychlorinated biphenyls. This waste is treated in a rotary kiln incinerator with a secondary combustion chamber and off-gas treatment system for cleaning combustion effluent gases. The TSCAI includes various support buildings, an unloading and storage area, a tank farm, an incinerator area, concrete collection sumps, and carbon adsorbers. A schematic of the TSCAI is shown in Figure 3-1, and photographs of the facility are shown in Figures 3-2 and 3-3.

The TSCAI treats a wide range of waste categories, including oils, solvents and chemicals, aqueous liquids, solids, and sludges. Solid and non-pumpable sludge material is typically received and stored in metal containers and repackaged into combustible containers prior to feeding. A hydraulic ram feeds containerized solids and sludges to the rotary kiln. Aqueous waste is injected into the kiln through a lance. High heat-of-combustion liquids are burned in either the rotary kiln or a secondary combustion chamber with gas burners. Both solids and waste liquids are permitted for treatment in the primary combustion chamber, but only organic liquids may be treated in the secondary combustion chamber. The typical temperature in the primary combustion chamber is approximately 870°C (1,600°F), and in the secondary combustion chamber is greater than 1,200°C (2,200°F).

Ash residue from the wet ash removal system is collected and handled through hazardous and radioactive waste storage facilities. Selected residues are sent to a commercial landfill. Kiln off-gas flows to the secondary combustion chamber. The off-gas from the secondary combustion chamber then passes through a four-stage treatment system that includes a quench chamber and scrubber treatment system for cooling, removing particulate matter, and neutralizing acidic by-products. An induced-draft fan forces flue gases through the stack. Liquid waste generated by the scrubber systems is treated by the Central Neutralization Facility, an adjacent on-site waste water treatment plant. Solid waste, such as scrubber sludge, is collected in drums for off-site disposal.

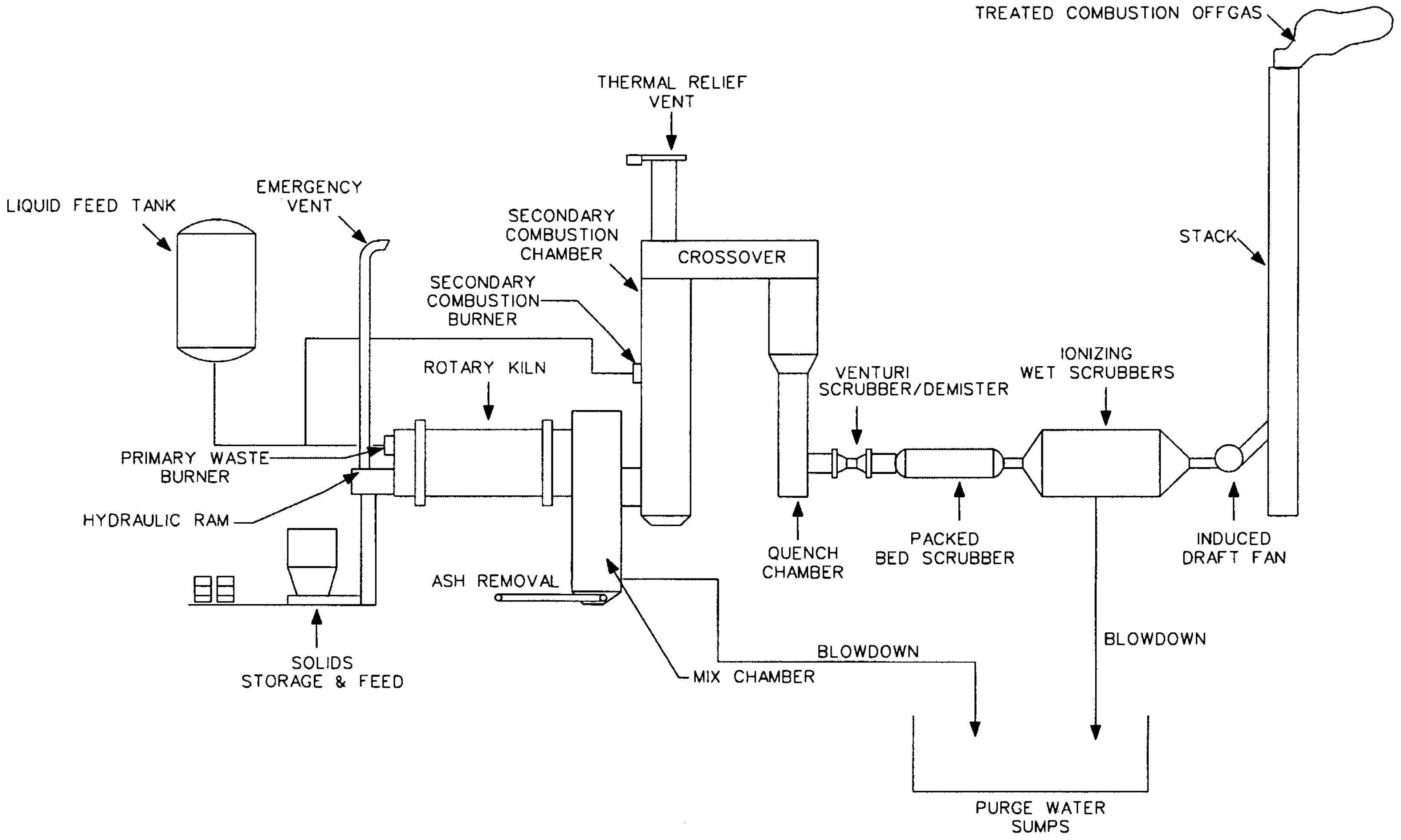

Figure 3-1. Schematic of the TSCAI and Off-Gas Cleaning System

Figure 3-2. Overview of TSCAI Test Location. The incinerator stack is at left, with waste feed area behind the stack. The trailers housing the mercury CEMs for this test were located in the foreground at the base of the stack.

Figure 3-3. Side View of TSCAI Stack. Sampling platforms are at the left and CEM trailers are at the lower right.

The off-gas treatment system of the TSCAI produces a scrubbed, wet gas flow. The TSCAI stack receives this water-saturated flue gas and vents it to the atmosphere. The stack is 100 feet high and its inside diameter is 54 inches, with a gas velocity of approximately 20 feet per second. The stack is equipped with several sample ports for flue gas sampling; a continuous emission monitoring system for measuring carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2); continuous sampling systems for radionuclides and metals; and two access platforms that surround the full circumference of the stack at about 30 feet and 50 feet above ground level. The combustion gas velocity is also monitored by means of the induced-draft fan current and pressure drop across the fan.

The combustion process and off-gas cleaning systems are monitored by instrumentation for process control and data collection. Operational parameters are automatically monitored and logged by the incinerator Supervisory Control and Data Acquisition system.

Stack gas characteristics at the CEM sampling locations used in this test are summarized in Table 3-1. Additional detail on the TSCAI configuration and operations are available in the test/QA plan,(1) and in recent publications describing this test.(3-5)

Table 3-1. TSCAI Stack Gas Characteristics[a]

Parameter	Range	Units
Temperature	83.7 – 86.0 (182.6 – 186.8)	°C (°F)
Static Pressure	- 0.25	inches H_2O
Flow Rate	6,065 – 9,100	dry standard cubic feet (dscf) per minute (min)
	14,920 – 23,450	actual cubic feet per minute
Velocity	15.78 – 19.73	feet per second
O_2	8.4 –11.6	%
CO_2	4.3 – 7.0	%
CO	0 – 10.3	parts per million by volume
Moisture	47.1 – 52.2	%
Particulate Matter Loading	0.0012 – 0.0079	grain/dscf @ 7% O_2
	2.68 – 18.2	mg/dry standard cubic meters (dscm) @ 7% O_2

[a] Values shown are actual conditions during OH reference method periods.

3.3 Test Design

3.3.1 Equipment Setup

The SG-II was housed in the TSCAI Test Bed Mobile Laboratory Trailer located near the base of the TSCAI stack. A dedicated data acquisition system was placed inside the trailer for logging signals from the SG-II and other CEMs undergoing verification. The data logger was also connected to the facility Supervisory Control and Data Acquisition system through an Ethernet link to collect and log process parameters on the SG-II data logger.

At the lower of the two platforms on the TSCAI stack (i.e., about 30 feet above ground level), one sampling port was dedicated to a probe that extracts stack gas to be analyzed for CO, CO_2, and O_2 by the facility CEMs. Other ports at this level were used for the SG-II and other CEMs being tested.

For the SG-II, the vendor-supplied extractive sampling probe was connected to the CEM by means of a 1/4-inch outside diameter (0.156-inch inside diameter), heated PFA Teflon sample line. A vendor representative oversaw installation of the SG-II. The source sample was withdrawn from the TSCAI stack through a Teflon-lined probe and then passed through a heated fiberglass filter located outside the stack in a heater box maintained at 200°C (390°F). This filter was periodically cleaned with a reverse pulse of air. A pump drew the sample gas through the 130-foot PFA Teflon sample line maintained at 200°C (390°F) to a sample splitter that provides separate flows for determination of Hg° and total vapor-phase mercury (Hg_T). The total sample flow through the probe, filter, and Teflon line was approximately five liters per minute. Like all CEMs in this verification test, the SG-II sampled at a single (fixed) point in the stack. This CEM provided alternating batch measurements of Hg° and Hg_T at approximately five-minute intervals. Oxidized mercury (Hg_{OX}) can be determined by the difference between successive readings of Hg_T and Hg°. The SG-II does not determine particle-phase mercury. Verification of the performance of the SG-II was based on comparison with the corresponding results from the OH reference method.

3.3.2 Test Schedule

In this verification test, the CEMs undergoing testing sampled the TSCAI stack gas continuously for nearly two months in the fall of 2002, while the TSCAI operated normally in destroying a variety of waste materials. Stack sampling with the OH reference method was conducted in the first week and the last week of the test, and between those two periods the CEMs operated continuously for approximately five weeks. Table 3-2 summarizes the schedule of verification testing at the TSCAI facility. Shown in this table are the activities conducted during various periods, and the performance parameters addressed by those activities.

Table 3-2. Mercury CEM Verification Test Schedule

Time Period (2002)	Activity	Performance Parameters
August 5 – 7	Installation and shakedown	—
August 8 – 11	OH method sampling; daily challenge with mercury standard gases	RA, correlation, precision; sampling system bias, calibration drift, zero drift, response time
August 12 – September 15	Routine monitoring, with scheduled challenges with mercury standard gases	Calibration drift, zero drift
September 16 – 19	OH method sampling; daily challenge with mercury standard gases	RA, correlation, precision; sampling system bias, calibration drift, zero drift, response time

The TSCAI was operated continuously during the first and last weeks of the test and was not shut down overnight. Such continuous round-the-clock operation is the standard mode of operation for the TSCAI. During the OH reference method sampling runs, the TSCAI burned aqueous, solid, or a combination of aqueous and solid waste. The waste was characterized by chemical analysis before the test began, and some measure of control of the stack mercury concentration was achieved by varying the feed rate of aqueous waste and/or mixing solid and aqueous waste materials.

After installation at the TSCAI in early August 2002, the CEMs went through a shakedown period in which all CEMs sampled the facility stack gas. Sampling of the stack gas then continued for the duration of the verification test, including during the performance of 10 OH reference method sampling runs with dual OH trains on August 8 through 11. During this period, the CEMs also were challenged with zero gas and with commercially prepared compressed gas standards of Hg^o. Vendor representatives oversaw installation and shakedown of the CEMs and operated the CEMs through the first week of testing. Following this first OH sampling period, vendor representatives trained site personnel on routine operation, maintenance, and calibration checks of each of the mercury CEMs. The CEMs then operated for five weeks with only routine attention and maintenance from TSCAI staff. During this period, the staff recorded the maintenance and repair needs of each CEM and made observations on the ease of use of each CEM. Finally, a second four-day period of OH method sampling with dual trains was conducted on September 16 through 19, in which eight OH sampling runs were conducted. The zero gas and mercury standard challenges were carried out by vendor representatives through this period as well.

The OH reference method results are presented in Section 4.2, along with evaluations of the quality of these reference results. The commercial mercury gas standards are described in Section 3.4.2, and the CEM results on those standards are reported in Section 6.

3.3.3 Reference Method Sampling

OH method sampling at the TSCAI was conducted at the upper platform on the stack (50 feet above ground) by staff of SEI, who prepared the trains, conducted sampling at the TSCAI stack using dual OH trains, and then recovered the resulting samples in a laboratory facility near the TSCAI site. The dual OH sampling trains sampled isokinetically at separate ports located 90° apart on the stack circumference and traversed the stack at points determined by EPA Method 1. The two trains were interchanged from port to port at the halfway point in the OH sampling period, so that the trains completed full and identical traverses of the stack during each OH run. Severn Trent Laboratories supplied the chemical reagents used in the OH sampling train impingers and performed the mercury analyses on the OH method samples. Containers for collecting and storing samples were labeled for tracking by Severn Trent Laboratories and subsequently supplied to the SEI field sampling team. Request for Analysis/Chain of Custody forms accompanied the samples from the time of collection by the field sampling team through analysis by the laboratory. Modified QA procedures for the OH method were followed, as described in Section 4.3.1. In addition, two blank OH trains (one in each week for OH method sampling) were spiked with known quantities of mercury to assess recovery in sample analysis. The results of those mercury spikes are reported in Section 4.3.2.

Tables 3-3 and 3-4 summarize the schedule of OH sampling in the initial and final weeks of the verification test, respectively, indicating the run number, date, and start and stop times of each OH run. These tables also show the type of waste burned in each OH run. In most runs, the total sampling period was made up of two separate periods of time, as necessitated by the port change procedure noted above. In a few OH runs, other factors such as disturbances in the waste feed required a stoppage in OH sampling; for those runs the total OH sampling period consists of three or more segments, rather than two. A few OH runs of one hour duration were conducted in the initial week of OH sampling (Table 3-3). However, it was recognized that this sample duration allowed only a few measurements to be made within the OH sample period, by those CEMs that provided sequential batch analyses, as opposed to continuous analysis. Consequently, all OH periods in the final week (Table 3-4) were of two hours duration.

Note that the first 10 OH sampling runs (Table 3-3) were numbered 7 through 16, and the last eight (Table 3-4) were numbered 18 through 25. The numbers 1 through 6 were assigned to OH trains used in pre-test trial runs, and other numbers were assigned to trains used as field blanks or as field spike trains. Each OH run number applies to two trains, designated A and B, which were used in parallel sampling, as described above, or used for separate QA purposes. For example, OH train 17A was spiked with known amounts of mercury, as described in Section 4.3.2, and train 17B was used as a blank. Similarly, train 28A was spiked and train 28B was a blank.

Table 3-3. Schedule of OH Method Sampling Runs in Initial Sampling Period (August 8 – 11, 2002)

Run Number	Date	Start Time	Stop Time	Waste Feed Type
7	8/8/02	09:10	09:28	Solids
		09:43	10:25	
		10:55	11:55	
8	8/8/02	14:40	15:40	Solids
		16:10	17:10	
9	8/9/02	10:50	11:50	Aqueous
		12:15	13:15	
10	8/9/02	14:35	15:35	Aqueous
		16:10	17:10	
11	8/10/02	9:35	10:05	Aqueous
		10:25	10:55	
12	8/10/02	12:15	12:45	Aqueous
		13:10	13:40	
13	8/10/02	15:00	15:30	Aqueous
		15:50	16:20	
14	8/11/02	08:20	08:50	Aqueous and Solids
		09:10	09:40	
15	8/11/02	10:40	10:52	Aqueous and Solids
		11:05	11:23	
		11:45	12:15	
16	8/11/02	13:45	14:15	Solids
		15:00	15:30	

Table 3-4. Schedule of OH Method Sampling Runs in Final Sampling Period (September 16 – 19, 2002)

Run Number	Date	Start Time	Stop Time	Waste Feed Type
18	9/16/02	11:10 13:05	12:10 14:05	Aqueous
19	9/16/02	15:20 16:50	16:20 17:50	Aqueous
20	9/17/02	9:25 11:10	10:25 12:10	Aqueous and Solids
21	9/17/02	13:15 14:35	14:15 15:35	Aqueous and Solids
22	9/18/02	8:35 9:55 12:35	9:35 10:37 12:53	Aqueous
23	9/18/02	14:36 16:36	15:36 17:36	Aqueous
24	9/19/02	8:25 10:56 11:22 11:59	9:20 11:01 11:44 12:37	Aqueous and Solids
25	9/19/02	13:34 15:46	14:34 16:46	Aqueous and Solids

To ensure that the OH reference method and CEM data sets were indeed parallel and comparable for each sampling period, the CEM vendors were notified of the start and stop times of each OH period so that average analyte concentrations corresponding directly to the reference method sampling period could be reported. The CEM vendors were given at least 15 minutes notice prior to initiation of each OH method sampling run.

All OH trains were prepared, recovered, and analyzed in the same manner, with one exception. The particulate filters from trains designated “A” and used for sampling at the TSCAI stack were weighed before and after sampling to determine particulate matter loading in the flue gas, whereas those from the trains designated “B” were not. The particulate loadings determined from the A trains ranged from 0.0012 to 0.0079 grain/dscf (2.68 to 18.2 mg/dscm). Particulate mercury was determined from the filter catch and probe rinse of both the A and B trains in all samples, but was never found at significant levels (i.e., maximum values of particulate Hg were less than 0.003 µg/dscm). Given this negligible amount of particulate mercury, the total vapor-phase mercury (Hg_T) determined by the OH method can be considered as the total mercury content of the stack gas.

3.3.4 Verification Procedures

This section describes the test procedures that were used to verify mercury CEM performance on each of the performance parameters listed in Section 3.1. Table 3-5 lists the quantitative performance parameters and summarizes the types of data that were used to verify each of those parameters.

Table 3-5. Data Used for SG-II Performance Evaluation

Performance Parameter	Objective	Comparison Based On
Relative Accuracy	Determine degree of quantitative agreement with reference method	Reference method results
Correlation with Reference Method	Determine degree of correlation with reference method	Reference method results
Precision	Determine repeatability of successive measurements at relatively stable mercury levels	Repetitive measurements under stable facility conditions
Sampling System Bias	Determine effect of the CEM's sample interface on response to zero gas and Hg^o standard	Response to zero gas and Hg^o standards at analyzer vs. through sample interface
Relative Calibration/Zero Drift	Determine relative response to zero gas and span gas over successive days	Zero gas and Hg^o standards
Response Time	Estimate rise and fall times of the CEMs	CEM results at start/stop of Hg addition

3.3.4.1 Relative Accuracy

The RA of the SG-II was verified using the OH reference method data. The Hg_T and Hg° readings of the SG-II during each OH sampling interval were averaged and compared with the average of the results from the paired OH trains (see Section 4.2.1). The RA equation stated in Section 5.1 was applied to the averaged CEM data, using the OH data as the reference values. To optimize the comparability of the CEM and OH data, the OH sampling was coordinated with the CEM operations as noted in Section 3.3.3.

3.3.4.2 Correlation with Reference Method

The correlation of SG-II results with the OH results was based on the same data used to assess RA. No additional test procedures were needed to verify the correlation.

3.3.4.3 Precision

Precision is the degree of variability of successive CEM readings under conditions of stable mercury concentration. In this test, the TSCAI stack gas mercury concentrations resulted entirely from the waste feed material being burned (i.e., no mercury was spiked into the flue gas). Consequently, mercury concentrations in the TSCAI stack would be most stable when a waste material of uniform mercury content was being fed into the incinerator at a uniform rate. For this verification test, an aqueous waste was stockpiled in quantities sufficient for all the testing and was characterized to document its mercury content. The aqueous feed rate data from the TSCAI were then reviewed for the periods of each OH run in which only aqueous waste was burned (see Tables 3-3 and 3-4). On the basis of the feed rate data, two OH runs (Runs 9 and 12, Table 3-3) were selected as having relatively uniform feed rates. The variability of the responses of each CEM during these two OH runs was then calculated to assess the variability of the CEM response.

As described in Section 5.3, the assessment of precision is based on comparing the variability of CEM readings to that of the aqueous feed rate, with variability expressed as a percent relative standard deviation (RSD). This approach does not assume that the waste feed rate is the sole factor affecting the variability of stack mercury concentrations, nor that the waste feed is perfectly uniform in mercury content. This approach does provide a consistent basis for reporting CEM variability in measuring mercury in the TSCAI stack gas.

3.3.4.4 Sampling System Bias

Sampling system bias was assessed using the commercial Hg^o gas standards described in Section 3.4.2. To assess sampling system bias, a mercury gas standard was supplied at the analyzer portion of the CEM, and separately at the stack gas sampling point of the CEM. Any difference in the CEM responses in the two cases was attributed to the effect on the mercury level of the sampling system components, i.e., the probe, filter, mercury conversion system, and transport lines.

3.3.4.5 Relative Calibration and Zero Drift

Zero drift and calibration drift also were assessed using zero gas and the commercial Hg^o gas standards described in Section 3.4.2, respectively. Although the mercury standards were not suitable for use as absolute standards, they did exhibit stable concentrations and so were useful for assessing CEM relative calibration drift (see Section 3.4.2). These gases were supplied to the CEMs on numerous occasions throughout the study; and the range, mean, and standard deviation of the CEM readings were calculated as indicators of the drift of the instruments over the course of the test. Both low (approximately 8 $\mu g/m^3$) and high (40 to 60 $\mu g/m^3$) mercury standards were used for this evaluation. Zero gas (nitrogen) was used for a similar assessment of the drift in CEM zero readings. The Hg° standards and zero gas were supplied to the analyzer portion of each CEM for this assessment, with the exception of one CEM which was designed to accept standard and zero gases only at its stack gas inlet.

3.3.4.6 Response Time

Mercury CEM response time also was verified using zero gas and the commercial Hg^{o} standards. Response time was determined as the time required for the CEM to reach 95% of its final value, after switching between zero gas and a mercury gas standard, or between different standards. This procedure was used to assess both rise time and fall time. Because the SG-II is a batch (i.e., noncontinuous) analyzer, time response is reported as the percentage response to a step change that is achieved in each measurement cycle.

3.3.4.7 Data Completeness

Data completeness was determined as the percentage of data that each CEM produced, relative to the total possible data return. This parameter was evaluated both in terms of the percentage of OH sampling runs for which each CEM produced data and in terms of the overall fraction of the two-month test period in which the CEM was operating and producing data.

3.3.4.8 Operational Factors

Throughout the field period of testing the mercury CEMs at the TSCAI (August 8 – September 19, 2002), the CEM vendors and TSCAI staff operating the CEMs recorded the repair, routine maintenance, and expendable needs of each CEM and noted operational issues such as the ease of use and calibration of the instruments. These observations are summarized for the SG-II in Section 6.7.

3.4 Materials and Equipment

3.4.1 High Purity Gases

The high purity gas used for zeroing the CEMs during testing was commercial, ultra-high purity (i.e., minimum 99.999% purity) nitrogen. Argon of ultra-high or industrial grade purity also was obtained for those CEMs requiring it.

3.4.2 Mercury Standard Gases

Ten compressed gas standards of Hg^{o} in nitrogen were obtained from Spectra Gases (Alpha, New Jersey) for use in assessing drift and sampling system bias of the CEMs. These cylinders were received in March 2002 and stored outdoors at the TSCAI site until the start of the verification test. When used during the verification test, each mercury standard was placed inside the instrument trailer near the CEMs for ease of access and to maintain the cylinders at room temperature.

To assess their stability, the mercury gas standards were analyzed using various methods at intervals before, during, and after the verification test. The 10 mercury standards were analyzed by Spectra Gases in March, before shipment to the TSCAI site. In addition, a cold vapor atomic absorption mercury analyzer (Seefelder Messtechnik) on loan from the EPA Office of Research and Development (EPA-ORD) was used to analyze the mercury gas standards at the TSCAI field site. Analysis of all 10 cylinders was conducted with the Seefelder analyzer on August 8 and on nine of the cylinders on October 17, after the field test had been completed. The contents of one cylinder (CC133537) were unintentionally depleted during the verification test, and post-test analysis was not possible. Eight cylinders, including the depleted one, were returned to Spectra Gases, where the seven cylinders with remaining gas were analyzed on November 13.

SEI staff also analyzed the remaining two cylinders (CC133359 and CC133367) using a modified version of EPA Method 101A(6), with sampling performed on November 5 and 6, respectively, for the two cylinders. Finally, the contents of these two cylinders were determined on November 6 using the EPA-ORD Seefelder analyzer. Upon return to Spectra Gases, the gas in these two cylinders was analyzed on November 21 by the vendor. The results of these diverse measurements on each of the cylinders are summarized in Table 3-6. This table lists the cylinder numbers, the various analytical results obtained on each cylinder (Hg^{o} results in µg/m^3), and the percent difference between the initial and final concentrations determined by the gas vendor.

Table 3-6. Results of Elemental Mercury Standard Analyses(a)

			Post-Test				**Difference Between Initial and Final Gas Vendor Certified Analyses (%)**
	March 1	**August 8**	**October 17**	**November 5 & 6**	**November 6**	**November 13 & 21**	
Cylinder Number	**Initial Gas Vendor Certified Analysis (µg/m^3)**	**EPA-ORD Seefelder Analysis (µg/m^3)**	**EPA-ORD Seefelder Analysis (µg/m^3)**	**Method 101A Mini-Train Analysis (µg/m^3)**	**EPA-ORD Seefelder Analysis (µg/m^3)**	**Final Gas Vendor Certified Analysis (µg/m^3)**	
CC133146	14.0	11.3	11.4	NA	NA	12.1	-13.3
CC133172	64.3	44.7	42.4	NA	NA	44.7	-30.4
CC133174	59.6	46.0	45.2	NA	NA	47.5	-20.3
CC133345	11.2	7.9	6.8	NA	NA	5.6	-50.0
CC133357	53.1	37.6	37.1	NA	NA	40.1	-24.6
CC133359	60.6	37.2	34.5	30.6	35.4	44.7	-26.2
CC133367	10.2	6.3	5.4	4.6	5.6	5.6	-45.4
CC133537	15.8	14.9	NA	NA	NA	NA	NA
CC133612	57.8	36.9	34.4	NA	NA	35.4	-38.7
CC133619	59.6	39.9	37.8	NA	NA	40.1	-32.8

(a) All measurements corrected to 1 atmosphere and 20°C.
NA: Not available, analysis not performed.

It is apparent from the last column of Table 3-6 that there was a substantial decrease in all the concentrations determined after the test by Spectra Gases, relative to those determined before the test by Spectra Gases. This finding suggests a decay in the mercury content of all the standards between these March and November analyses by the gas vendor. However, Table 3-6 also shows that all analyses subsequent to the initial analysis by Spectra Gases show better agreement. This observation suggests that any such decay in concentration must have occurred primarily before the August 8 analyses. Unfortunately, no measurements were made between the original March 1, 2002, Spectra Gases analyses and the August 8 analyses made during the first week of CEM testing. Thus, there is no way to determine whether the decrease occurred as a sudden, step-wise drop or a gradual decay over time. However, the important point regarding Table 3-6 is that the data indicate stable mercury concentrations in all cylinders throughout the period of the verification test.

This point is supported by Table 3-7, which shows the mean, standard deviation, and percent RSD of all analyses of each mercury standard from August 8 on. Table 3-7 indicates that the RSD values for six of the standard cylinders were about 4% or less, and the RSD values for the other three cylinders having multiple analyses were less than 17%. These results indicate that the contents of the mercury standard cylinders were stable over the course of the verification test and, consequently, were suitable for assessing the stability of the CEMs themselves.

Table 3-7. Precision of Elemental Mercury Standard Measurements

	August 8 and Later		
Cylinder Number	**Mean ($\mu g/m^3$)**	**Standard Deviation ($\mu g/m^3$)**	**RSD (%)**
CC133146	11.6	0.5	4.0
CC133172	43.9	1.3	3.0
CC133174	46.2	1.2	2.6
CC133345	6.8	1.1	16.8
CC133357	38.3	1.6	4.1
CC133359	36.5	5.2	14.2
CC133367	5.5	0.6	11.4
CC133537	14.9	NA(a)	NA
CC133612	35.6	1.3	3.5
CC133619	39.3	1.2	3.2

(a) Not applicable for one data point.

Spectra Gases conducted a quality review of its production and analytical records to determine the cause of the concentration decay observed.(7) The preliminary conclusion from the review was that an important step had been omitted from the manufacturing process. Spectra Gases tested this hypothesis by manufacturing two separate cylinder batches of three cylinders each. The first batch was made according to procedure, and the second batch was made with the suspect step omitted from the manufacturing process. After the cylinders were prepared, each cylinder was analyzed every seven days over a 49-day period. After 49 days, the concentration of the first batch was stable, but the second batch (with the manufacturing step omitted) exhibited a sharp decay in concentration. This test seemed to validate the theory that an important step had been omitted from the manufacturing process, which led to a decrease in concentration from the initial certified analysis of the gases used in the TSCAI CEM test.

3.4.3 Mercury Spiking Standard

A National Institute of Standards and Technology (NIST)-traceable aqueous mercury standard, with a concentration of 1,000 mg/L of Hg as HgO in dilute nitric acid, was obtained from VWR Scientific (Catalog No. VW4217-1). This solution was Lot No. B2015064 and had an expiration date of August 2003. Dilution of this standard in American Society for Testing and Materials Type II water with added nitric acid was used to prepare the 10 µg/mL and 30 µg/mL spiking solutions for the performance evaluation (PE) audit of the reference method (Section 4.3.2).

3.4.4 Sampling Trains

The SEI field sampling team supplied the glassware, probes, heater boxes, meter boxes, and other associated equipment for the OH method sampling. Severn Trent Laboratories supplied the chemical reagents and materials used in the OH sampling train impingers. Multiple trains were prepared each day so that as many as six trains (i.e., three sampling runs with two trains each) could be sampled in a single day, in addition to at least one blank train. The SEI field sampling team recovered samples from OH method trains in a laboratory facility near the TSCAI site. Containers for collecting and storing samples were purchased and labeled for tracking by Severn Trent Laboratories. Samples were packaged and delivered by the field sampling team to Severn Trent Laboratories.

3.4.5 Analysis Equipment

Laboratory equipment for sample recovery and analysis was provided by Severn Trent Laboratories. This included all chemicals and solutions for rinsing train components and recovering impinger samples, as well as cold vapor atomic absorption (CVAA) spectroscopy equipment for mercury determination.

Chapter 4
Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(7) and the test/QA plan for this verification test.(1)

4.1 Facility Calibrations

During this verification test, the TSCAI facility was operated normally to carry out its function of destroying hazardous waste. Consequently, calibration procedures and schedules for the TSCAI monitoring equipment were followed throughout the verification test, as required to maintain RCRA certification of the TSCAI. These procedures, which included both weekly and monthly calibrations, took precedence over the conduct of the verification test. Included in these activities were calibrations of the O_2 and CO_2 CEMs on the incinerator stack. Records of all such calibrations are maintained in the operation files of the TSCAI.

Measurements that factored into the verification test results were also the subject of PE audits, as described in Section 4.3.2. Those audits included checks of the facility O_2 and CO_2 CEMs.

4.2 Ontario Hydro Sampling and Analysis

The preparation, sampling, and recovery of samples from the OH trains adhered to all aspects of the OH method,(2) with minor modifications as described in Section 4.3.1. The preparation and recovery of trains was carried out by SEI staff in a laboratory on the ETTP site; trains were sealed for transport between the preparation/recovery laboratory and the TSCAI. Blank trains were prepared in both the initial and final weeks of OH sampling, taken to the sampling location on the TSCAI stack, and recovered along with the sampled trains. Reagent blanks were collected as specified in the OH method. OH trains and resulting samples were numbered uniquely, and samples were transferred to the analysis laboratory (STL) within about 24 hours of collection, using chain-of-custody forms prepared before the field period. As described in Section 4.3.1, trial OH sampling by SEI and OH sample analysis by STL were both subjected to a pre-test evaluation before the field verification took place.

Because of the importance of the OH data in this verification, the following sections present key data quality results from the OH data.

4.2.1 Ontario Hydro Reproducibility

The results of the OH flue gas sampling are shown in Tables 4-1 and 4-2, for the initial (August 8 – 11) and final (September 16 – 19) weeks of OH method sampling, respectively. Each table indicates the OH run number, and lists the Hg^o, Hg_{OX}, and Hg_T results from the paired OH trains (designated A and B) in each run. Also shown are the mean values of the paired train results, and the relative percent difference (RPD) of each pair of results (RPD = difference between A and B results divided by sum of A and B results expressed as a percentage). All mercury results are in µg/dscm, adjusted to 20°C (68°F) at 7% flue gas O_2 content. Particulate mercury is not shown in Tables 4-1 and 4-2. Particulate mercury was determined from the particulate filters in both OH trains for each run, but was always less than 0.003 µg/dscm. Thus, particulate mercury was a negligible fraction of the total mercury in the TSCAI stack.

Inspection of Tables 4-1 and 4-2 shows that Hg^o composed most of the total mercury value, consistent with the extent of scrubbing of the TSCAI flue gas. The total mercury level was controlled to some extent by the choice of waste feed material and the waste feed rate entering the TSCAI. Total mercury was less than 1.7 µg/dscm in the first two OH runs and then was progressively increased throughout the rest of the first 10 OH runs (Table 4-1), peaking at about 200 µg/dscm in OH Run 16. In the eight OH runs conducted during the final week of the test (Table 4-2), total mercury ranged from 22 to 85.4 µg/dscm. All the CEMs tested produced readings of Hg_T that generally paralleled this progression of mercury levels during the two weeks of OH method sampling. Hg_{OX} was typically about 1% of the total mercury, and in 17 of the 18 OH runs, the Hg_{OX} results from both OH trains were less than 2 µg/dscm. The one exception was the Hg_{OX} level of about 15 µg/dscm observed with the peak mercury levels in OH Run 16, when Hg_{OX} was about 7% of Hg_T.

Tables 4-1 and 4-2 show generally close agreement between the A and B train results for all three mercury fractions. The reproducibility of OH results is an important indicator of the quality of the OH reference data for this verification test. Consequently, that reproducibility was quantified by the RPD values for each A and B pair, by linear regression of the A and B train results, including the correlation of the A and B results, and by calculation of the mean RSD of the paired OH results for Hg^o, Hg_{OX}, and Hg_T. Considering the RPD values in Tables 4-1 and 4-2, only one of the 18 RPD values for Hg° exceeds 7%, and the same is true for Hg_T. The RPD values for Hg_{OX} range from 0.5 to 39.4%, with a median of 9.7%. These results indicate close agreement at the low Hg_{OX} concentrations found. Figure 4-1 shows the linear regression of B train results versus A train results, for all three mercury fractions. The data for all three mercury fractions lie closely along the 1-to-1 line shown in this figure. Table 4-3 summarizes the results of the linear regression, correlation, and %RSD analyses for the duplicate OH trains for Hg^o, Hg_{OX}, and Hg_T. The correlation between paired trains is shown in terms of the coefficient of determination (r^2). Table 4-3 shows that the slopes of the paired OH regressions are all close to 1.0, the intercepts are near zero, and the r^2 values are all approximately 0.99. Mean RSD values of about 5.5% were found for the paired results for Hg^o and total mercury. The mean %RSD for Hg_{OX} was higher, due undoubtedly to the low Hg_{OX} levels in the TSCAI flue gas.

Based on the close agreement of the duplicate OH results for all mercury fractions in all sample runs, the mean OH results in each run were used for comparison to the CEM results.

Table 4-1. Ontario Hydro Results from Initial Sampling Period (August 8 – 11, 2002)(μg/dscm)

OH Run Number	Hg^o				Hg_{OX}				Hg_T			
	A[a]	B[a]	Mean	RPD	A	B	Mean	RPD	A	B	Mean	RPD
7	1.46	1.53	1.49	2.4	0.17	0.15	0.16	7.2	1.63	1.68	1.65	1.5
8	0.17	0.19	0.18	6.7	0.17	0.19	0.18	5.1	0.34	0.38	0.36	5.9
9	17.9	18.3	18.1	1.1	0.34	0.42	0.38	10.4	18.2	18.7	18.4	1.3
10	34.7	39.0	36.8	5.9	0.32	0.48	0.40	19.8	35.0	39.5	37.2	6.0
11	48.5	36.0	42.3	14.8	0.34	0.40	0.37	8.1	48.9	36.4	42.6	14.6
12	47.8	47.4	47.6	0.5	0.64	0.45	0.54	17.2	48.5	47.8	48.1	0.7
13	36.9	37.9	37.4	1.3	0.26	0.58	0.42	37.5	37.1	38.4	37.8	1.7
14	38.1	43.3	40.7	6.5	0.44	0.44	0.44	0.5	38.5	43.8	41.1	6.4
15	68.6	66.3	67.5	1.7	0.84	1.93	1.39	39.4	69.4	68.3	68.8	0.8
16	187.5	181.4	184.4	1.7	13.7	15.1	14.4	5.1	201.2	196.5	198.8	1.2

[a] A and B are the paired OH trains used in sampling.

Table 4-2. Ontario Hydro Results from Final Sampling Period (September 16 – 19, 2002) (µg/dscm)

OH Run Number	Hg^o				Hg_{OX}				Hg_T			
	A[a]	B[a]	Mean	RPD	A	B	Mean	RPD	A	B	Mean	RPD
18	74.1	67.7	70.9	4.5	0.45	0.95	0.70	35.9	74.6	68.7	71.6	4.1
19	77.5	76.6	77.0	0.6	0.47	0.49	0.48	2.0	77.9	77.1	77.5	0.6
20	82.3	84.7	83.5	1.4	0.59	0.63	0.61	3.7	82.9	85.4	84.1	1.4
21	50.3	54.1	52.2	3.7	0.30	0.36	0.33	9.0	50.6	54.4	52.5	3.7
22	21.7	23.9	22.8	4.7	0.22	0.32	0.27	18.5	22.0	24.2	23.1	4.9
23	30.5	35.1	32.8	7.0	0.45	0.32	0.39	16.6	30.9	35.4	33.1	6.7
24	23.4	23.0	23.2	0.9	0.26	0.27	0.27	1.6	23.6	23.2	23.4	0.9
25	55.3	63.1	59.2	6.6	1.04	0.59	0.82	28.2	56.3	63.6	60.0	6.1

[a] A and B are the paired OH trains used in sampling.

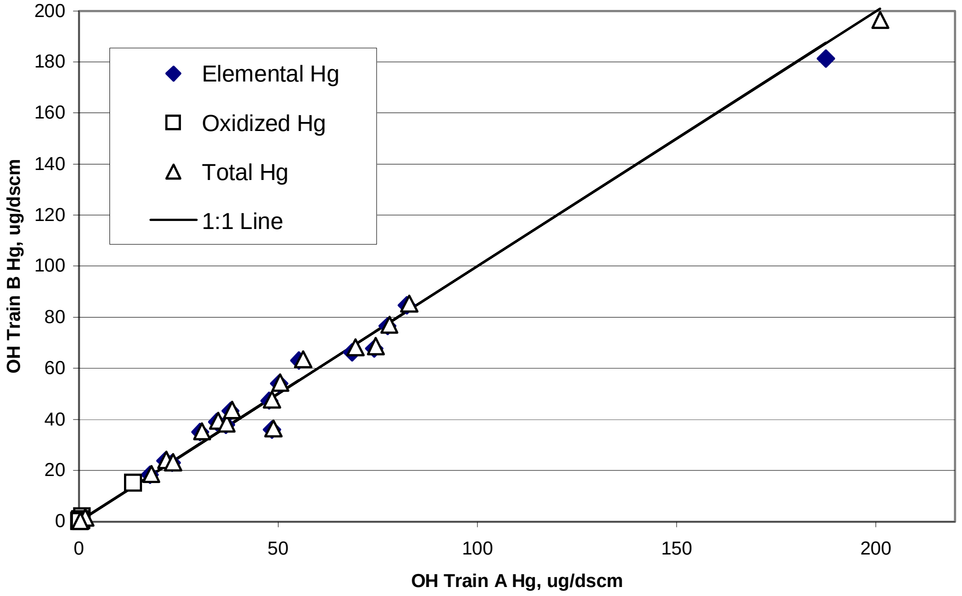

Figure 4-1. Plot of Ontario Hydro Train B Results vs. Train A Results

Table 4-3. Results of Linear Regression, Correlation, and Percent Relative Standard Deviation of Paired Ontario Hydro Train Results (n = 18)

Analyte	Slope (CI)[a]	Intercept (CI) µg/m^3	r^2	%RSD
Hg^o	0.959 (0.027)	2.19 (1.73)	0.988	5.55
Hg$_{OX}$	1.104 (0.025)	0.053 (0.082)	0.992	20.9
Hg$_T$	0.969 (0.025)	1.93 (1.65)	0.990	5.36

[a] (CI) = 98% confidence interval shown in parentheses.

4.2.2 Ontario Hydro Blank and Spike Results

None of the OH reagent blanks showed any detectable mercury. Also, OH sampling trains were prepared and taken to the sampling location at the TSCAI stack on two occasions, and then returned for sample recovery without exposure to stack gas. These blank OH trains provide additional assurance of the quality of the train preparation and recovery steps. Four sample fractions were analyzed from these blank trains: the particulate filter and probe rinse; impingers 1-3 (KCl); impinger 4 (H_2O_2); and impingers 5-7 ($KMnO_4$). Mercury was not detected in any of the blank train samples. The detection limits for analysis of these fractions (in terms of mass of mercury detectable) were 0.019 µg, 0.005 µg, 0.021 µg, and 0.031 µg, respectively, which correspond to stack gas concentrations of less than 0.001 µg/dscm under all sampling conditions in this verification. Thus, the blank OH train results confirm the cleanliness of the OH train preparation and analysis procedures. The recovery of mercury spiked into blank train samples as part of the PE audit also met the prescribed criteria, as described in Section 4.3.2.

Mercury spike recovery was also evaluated using sample fractions from selected trains used for the 18 OH method runs in the TSCA stack. Those spike recoveries ranged from 85 to 101%, and the results for duplicate spikes never differed by more than 4%, well within the 10% duplicate tolerance required by the OH method.

4.3 Audits

4.3.1 Technical Systems Audit

Battelle's Quality Manager performed a pre-test evaluation and an internal TSA of the verification test at the TSCAI. The TSA ensures that the verification test is conducted according to the test/QA plan(1) and that all activities in the test are in compliance with the AMS Center QMP.(8)

The pre-test evaluation consisted of a visit on May 14, 2002, by a representative of the Battelle Quality Manager to observe trial OH method sampling and to audit the laboratory conducting the OH method analyses. Trial sampling was observed at the facilities of SEI, and analytical procedures were observed at STL, both in Knoxville, Tennessee. The Battelle representative was a staff member highly familiar with the sampling and analysis requirements of the OH method. He used detailed checklists to document the performance of OH method train preparation, sampling, sample recovery, chain of custody, and sample analysis. All observations were documented in an evaluation report, which indicated no adverse findings that could affect data quality. An amendment to the test/QA plan(1) was prepared as a result of this evaluation, documenting several minor procedural changes implemented in the OH sample recovery by STL. These procedural changes were based on the experience of STL personnel in conducting OH mercury analyses and other metals analyses, as well as on the numbers and types of analyses needed for this verification. The most significant such changes were

- The analysis of one matrix spike duplicate for each type of sample received (i.e., filter catch and probe rinse, KCl impingers, H_2O_2 impingers, etc.), rather than the duplicate and triplicate analyses stated in section 13.4.2.3 of the OH method.

- The analysis of one spiked sample for each type of sample received, rather than a spike after every 10 samples as stated in section 13.4.2.4 of the OH method.

- The use of a 25% tolerance on spike recovery values based on the requirements of EPA Method 7460 for metals analysis, rather than the 10% tolerance stated in section 13.4.2.4 of the OH method.

The Battelle Quality Manager conducted the TSA in a visit to the TSCAI test location on August 8, 2002, which was the first day of OH sampling in the first intensive period. In that visit he toured the incinerator and CEM locations; observed the OH method sampling; observed OH sample recovery and documentation in the on-site laboratory at the ETTP; reviewed Battelle notebooks, gas standard certifications, and the CEM data acquisition procedures; and conferred with the CEM vendors and facility personnel. The TSA report from this audit found no issues that could adversely affect data quality. All records from both the pre-test evaluation and the TSA are permanently in the custody of the Battelle Quality Manager.

4.3.2 Performance Evaluation Audits

A series of PE audits was conducted on several measurement devices at the TSCAI facility to assess the quality of the measurements made in the verification test. These audits were performed by Battelle staff and were carried out with the cooperation of SEI staff. These audits addressed only measurements that factored directly into the data used for verification, i.e., the CEMs undergoing testing were not the subject of the PE audit. Each PE audit was performed by analyzing a standard or comparing to a reference that was independent of standards used during the testing. Each PE audit procedure was performed once during the verification test, with the exception that blank OH sampling trains were spiked with a mercury standard during both the first and last intensive OH sampling periods, approximately six weeks apart. Table 4-4 summarizes the PE audit results on several measurement devices at the TSCAI facility.

Table 4-4. Summary of PE Audits

Measurement Audited	Date	Audit Method	Observed Difference	Acceptable Difference
Flue gas O_2	8/9/02	Comparison to independent O_2 measurement	0.16% O_2(a) 0.24% O_2	1% O_2
Flue gas CO_2	8/9/02	Comparison to independent CO_2 measurement	0.0% of reading(b) 3.3% of reading	10% of reading
OH gas flow rate	8/7/02	Comparison to independent flow measurement	1.3%(c) 3.2%	5%
Flue gas temperature	8/7/02	Comparison to independent temperature measurement	0.33%(c) 0.07%	2% absolute temperature
Barometric pressure	8/7/02	Comparison to independent barometric pressure measurement	0.5" H_2O	0.5" H_2O
Impinger weights (electronic balance)	8/7/02	Weighing certified weights	0.37% (1.7 g at 454 g)	greater of 1% or 0.5 g

(a) The two results shown are for the two Siemens Oxymate 5E units (Serial Nos. D1-447 and D3-491, respectively) used at the TSCAI facility.

(b) The two results shown are for the two Siemens Ultramat 22P units (Serial Nos. U01-483 and A03-277, respectively) used at the TSCAI facility.

(c) The two results shown are for the two NuTech meter boxes designated Unit A (Serial No. 80563) and Unit B (Serial No. 008068), respectively.

Table 4-4 shows the type of measurement audited, the date the PE audit was conducted, the basis for the audit comparison, the difference between the measurement and the PE audit value, and the acceptable difference stated in the test/QA plan. As Table 4-4 shows, all the PE audits met the required tolerances stated in the test/QA plan.(1) The PE audits for O_2 and CO_2 were conducted by sampling the same cooled and dried flue gas analyzed by the facility's CEMs for these gases. The O_2 and CO_2 content of the flue gas were about 9.5% O_2 and 6% CO_2. The independent audit monitor and the facility CEMs sampled this gas simultaneously for the PE audit. As noted in the footnotes to Table 4-4, both of the dual O_2 monitors and dual CO_2 monitors installed at the TSCAI facility were audited. The gas flow rate measurements of the two OH trains were audited using a certified mass flow meter. The temperature measurements were audited at ambient temperature (approximately 27°C), rather than in the flue gas, because of the limited access to the TSCAI stack. The PE audit of the electronic balance used certified weights of approximately 200 and 500 grams; the observed agreement shown in Table 4-4 is for the 500-gram weight, which showed the greater percentage deviation. A planned audit of the flue gas static pressure(1) was not conducted, because the minimal differential relative to atmospheric pressure (approximately -0.25 inches of H_2O) makes this measurement both difficult to audit and relatively unimportant in calculating the reference mercury results. An amendment to the test/QA plan was prepared and approved to document this change.

The PE audit of the OH train mercury recovery and analysis was performed by spiking blank OH trains with NIST-traceable mercury solutions. In each case, impingers 1 (KCl), 4 (H_2O_2/HNO_3), and 5 ($KMnO_4/H_2SO_4$) of a blank OH train were spiked. In the first week of OH sampling, each impinger was spiked with 1 mL of a 10-µg/mL mercury solution; and in the final week of OH sampling, each impinger was spiked with 1 mL of a 30-µg/mL mercury solution. Table 4-5 identifies the OH trains that were spiked, the date of the spike, the amount of the spike, and the analytical results for each spiked impinger in the train (i.e., impingers 1, 4, and 5 of each OH train).

Table 4-5. Results of PE Audit of OH Train Recovery and Analysis

Train	Date	Impinger Number	Hg Spiked (µg)	Hg Found (µg)	Observed Agreement	Target Agreement
17A	8/8/02	1	10	9.7	3%	25%
		4	10	7.8	22%	25%
		5	10	8.3	17%	25%
28A	9/16/02	1	30	32.5	8.3%	25%
		4	30	26.7	11.0%	25%
		5	30	30.6	2.0%	25%

Table 4-5 shows that all of the six spike recoveries were well within the target of 25% agreement with the spiked values that was stated in the amended test/QA plan (see Section 4.3.1). Furthermore, four of the six results were near or within the 10% tolerance stated in the OH method.(2) These results support the validity of the OH reference method results used in this verification.

4.3.3 Data Quality Audit

An audit was conducted to trace the test data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on data leading to verification results were checked. The Battelle Quality Manager reviewed the procedures and results of this audit, and conducted his own independent review of a small portion of the data.

Chapter 5
Statistical Methods

This chapter presents the statistical procedures that were used in calculations for verifying the performance factors listed in Section 3.1.

5.1 Relative Accuracy

RA was verified by comparing the SG-II results against the reference results for each parameter that the SG-II measured. The average of the paired OH train results was used as the reference value for each OH run. The SG-II readings in each OH run were averaged for comparison to the reference data.

The RA of the SG-II with respect to the reference method was calculated using

$$RA = \frac{\left|\bar{d}\right| + \frac{t_{0.975}}{\sqrt{n}} SD}{\bar{X}_{RM}} \tag{1}$$

Where

$\left|\bar{d}\right|$ = the absolute value of the arithmetic mean of the differences, d, of the paired SG-II and reference method results

$\bar{X}_{RM}$ = arithmetic mean of the reference method results

n = number of data points

$t_{0.975}$ = the *t*-value at the 97.5% confidence with n-1 degrees of freedom

SD = standard deviation of the differences between the paired SG-II and reference method results.

RA was calculated separately for the first and last weeks of OH sampling (n = 10 and n = 8, respectively) and for all reference data combined (n = 18).

5.2 Correlation with Reference Method

Correlation of the SG-II with the OH method was calculated using the same data used to assess RA. Correlation was calculated for each parameter measured by the SG-II. The coefficient of determination (r^2) was calculated to determine the degree of correlation of the SG-II results with the reference method results. This calculation was conducted using data from the first week, the last week, and both weeks of OH reference method samplings.

5.3 Precision

As described in Section 3.3.4.3, precision was assessed based on the individual readings provided by the SG-II over the duration of OH method sampling Runs 9 and 12. Precision of the SG-II was determined by calculating the percent relative standard deviation (RSD) of a series of SG-II Hg_T measurements made during stable operation of the TSCAI in these OH runs. The %RSD is the ratio of the standard deviation of those readings to the mean of the readings, expressed as a percentage:

$$\%RSD = \frac{SD}{\overline{X}} \times 100 \qquad (2)$$

where

SD = standard deviation of the SG-II readings
$\overline{X}$ = mean of the SG-II readings.

The calculated precision values from Equation 2 include the variability of the TSCAI stack gas mercury concentration, as well as the variability of the SG-II itself. To estimate the precision of the SG-II, it was assumed that the two sources of variability combine in root-mean-square fashion, with the variability of the TSCAI mercury concentration represented by the variability of the aqueous waste feed rate. Consequently, the CEM precision was estimated in terms of a %RSD by means of Equation 3:

$$\%RSD_R = [(\%RSD_{WF})^2 + (\%RSD_{CEM})^2]^{1/2} \qquad (3)$$

where $\%RSD_R$ is the relative standard deviation of the CEM readings, $\%RSD_{WF}$ is the relative standard deviation of the aqueous waste feed readings, and $\%RSD_{CEM}$ is the resulting relative standard deviation attributable to the CEM variability. It must be noted that the total variability of the TSCAI may not be fully represented by the variability of the waste feed rate. Consequently, the CEM variability ($\%RSD_{CEM}$) calculated from Equation 3 must be considered as the maximum variability that could be attributable to the CEM.

5.4 Sampling System Bias

Sampling system bias (B) reflects the difference in SG-II response when sampling Hg^o standard gas through the SG-II's entire sample interface, compared with that when sampling the same gas directly at the SG-II's mercury analyzer, i.e.:

$$B = \frac{R_a - R_i}{R_a} \times 100 \qquad (4)$$

where

R_i = SG-II reading when the standard gas is supplied at the sampling inlet
R_a = SG-II reading when the standard is supplied directly to the analyzer.

Since the effect of the inlet is expected to be a negative bias on measured Hg levels, R_i is expected to be less than R_a. Equation 4 thus gives a positive percent bias value for what is understood to be an inherently negative bias. In rare instances R_i was found to exceed R_a slightly due to normal instrument variation. In such instances, B was reported as 0.0%.

The purpose of this part of the verification was to assess the bias introduced by the sampling probe, filter, and long (>100-foot) sampling lines in sampling Hg^o. It must be pointed out that delivery of the standard gas to the sample inlet also required a Teflon line over 100 feet in length. Thus, the observed bias may include a contribution from the standard gas delivery system, as well as from the sampling system.

5.5 Relative Calibration and Zero Drift

Calibration and zero drift were reported in terms of the mean, relative standard deviation, and range (maximum and minimum) of the readings obtained from the SG-II in the repeated sampling of the same Hg^o standard gas and of zero gas. The relative standard deviation of standard gas or zero gas readings was calculated according to Equation 2 above. This calculation, along with the range of the data, indicates the variation in zero and standard readings.

The SG-II was challenged with three Hg^o gas standards in this test, cylinders CC133537, CC133612, and CC133619, which had nominal average Hg^o concentrations of 14.9, 35.6, and 39.3 $\mu g/m^3$, respectively. These nominal averages are based on all analyses of the gas standards from August 8, 2002, through November 21, 2002, (Table 3-7), i.e., excluding the vendor's initial pre-test analysis of the standards in March 2002.

5.6 Response Time

The response time refers to the time interval between the start of a step change in mercury input and the time when the SG-II reading reached 95% of the final value. Both rise time and fall time were determined. SG-II response times were obtained in conjunction with a calibration/zero drift check or sampling system bias check by starting or stopping delivery of the mercury standard gas to the SG-II or sampling interface, recording all readings until stable readings were obtained, and estimating the 95% response time.

5.7 Data Completeness

Data completeness was assessed by comparing the data recovered from the SG-II with the amount of data that would be recovered upon completion of all portions of these test procedures.

5.8 Operational Factors

Maintenance and operational needs were documented qualitatively, both through observation and through communication with the vendor during the test. Factors noted included the frequency of scheduled maintenance activities, the down time of the SG-II, and staff time needed for maintaining it during the verification test.

Chapter 6
Test Results

The results of the verification test of the SG-II are presented below for each of the performance parameters.

6.1 Relative Accuracy

Table 6-1 lists the OH reference method results and the corresponding SG-II results for Hg° and Hg_T in all 18 OH sampling runs. The OH results are the averages of the results from the paired A and B trains in each run; the SG-II results are the averages of the SG-II readings over the period of each OH run.

The SG-II operates by switching at five-minute intervals between Hg° and Hg_T measurements, which are conducted alternately rather than simultaneously. The SG-II also determines Hg_{OX} by difference between successive Hg° and Hg_T measurements. This difference approach is subject to greater uncertainty when Hg° comprises the great majority of Hg_T, as in this test. In fact, the SG-II Hg_{OX} results were found to be unrealistic relative to the OH reference method results. For example, Table 6-1 shows instances in which the SG-II Hg° value exceeded the Hg_T value, most notably in OH Run 16. In that run the waste feed was packets of solid waste of relatively high mercury content, with no accompanying liquid waste. This waste is likely to have produced a variable mercury content in the flue gas, which may have been difficult to determine accurately with the SG-II's batch analysis process. After inspection of the data, it was concluded that the conditions of this test were not appropriate for determining Hg_{OX} with the SG-II, and no relative accuracy comparison for Hg_{OX} was conducted.

Table 6-1 shows that the SG-II readings were usually lower than the corresponding OH results for Hg° and Hg_T, sometimes by a factor of two or more, throughout both weeks of OH sampling. Table 6-2 shows the resulting RA values for the SG-II, for Hg° and Hg_T, based on the first week, the last week, and both weeks of OH sampling. The RA for Hg_T was substantially improved in the last week of OH sampling, relative to the first week, but the RA for Hg° did not show the same improvement. The overall RA results for Hg° and Hg_T are 54.7% and 59.8%, respectively. The RA results for Hg_T improve to 42.8% if OH Run 16 is excluded, but no other substantial change in RA for Hg° or Hg_T would result from exclusion of any single OH run.

Table 6-1. Summary of Results from OH Reference Method and SG-II (µg/dscm)

Date	OH Run Number	Hg° (µg/dscm)		Hg_T (µg/dscm)	
		OH	SG-II	OH	SG-II
8/8/2002	7	1.49	1.64	1.65	1.61
	8	0.18	0.09	0.36	0.25
8/9/2002	9	18.1	8.04	18.4	11.6
	10	36.8	11.8	37.2	26.8
8/10/2002	11	42.3	29.8	42.6	30.2
	12	47.6	29.5	48.1	33.2
	13	37.4	28.0	37.8	30.6
8/11/2002	14	40.7	23.4	41.1	22.5
	15	67.5	40.2	68.9	40.4
	16	184.4	134.6	198.8	91.9
9/16/2002	18	70.9	41.7	71.6	56.4
	19	77.0	48.9	77.5	64.7
9/17/2002	20	83.5	42.2	84.1	60.5
	21	52.2	27.0	52.5	29.9
9/18/2002	22	22.8	14.8	23.1	15.8
	23	32.8	22.1	33.1	22.9
9/19/2002	24	23.2	7.92	23.4	13.3
	25	59.2	20.1	60.0	29.2

Table 6-2. Relative Accuracy Results for the SG-II

Test Period	Relative Accuracy (%)	
	Hg°	Hg_T
First Week (n = 10)	57.7	87.2
Last Week (n = 8)	66.4	44.1
Overall (n = 18)	54.7	59.8

6.2 Correlation with the Reference Method

The correlations of the SG-II readings with the OH results for Hg° and Hg_T were calculated using the data shown in Table 6-1. To illustrate the correlations, Figures 6-1a and 6-1b show linear regression plots of the SG-II results against the corresponding OH results for Hg° and Hg_T, respectively. The linear regression equations and coefficients of determination (r^2) are shown on the graphs. Table 6-3 shows the r^2 values for the first and last weeks of OH sampling, and for the two periods combined, for Hg° and Hg_T.

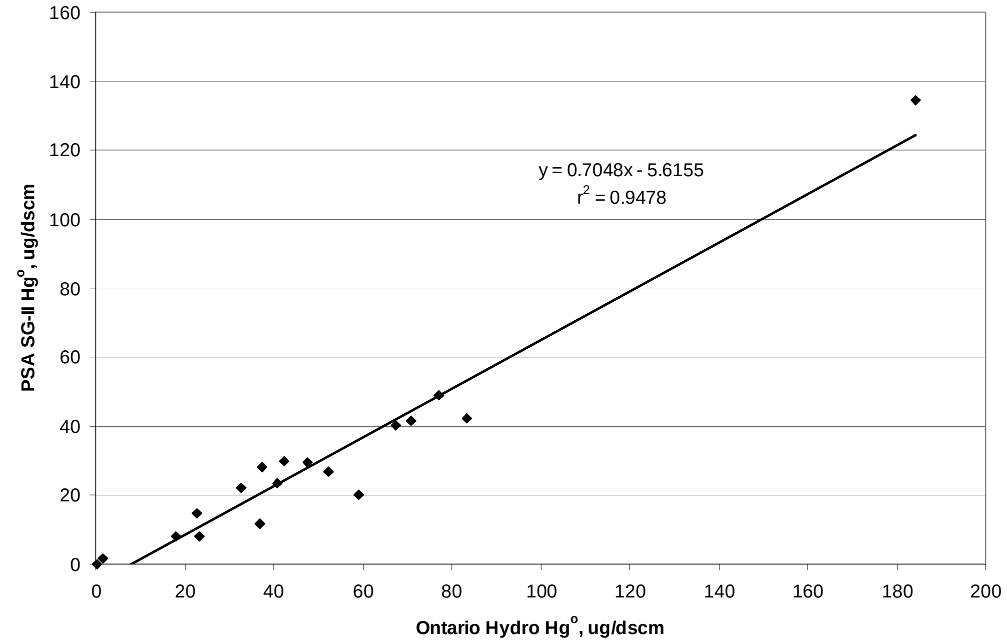

Figure 6-1a. Linear Regression Plot of SG-II Hg° Results Against OH Results

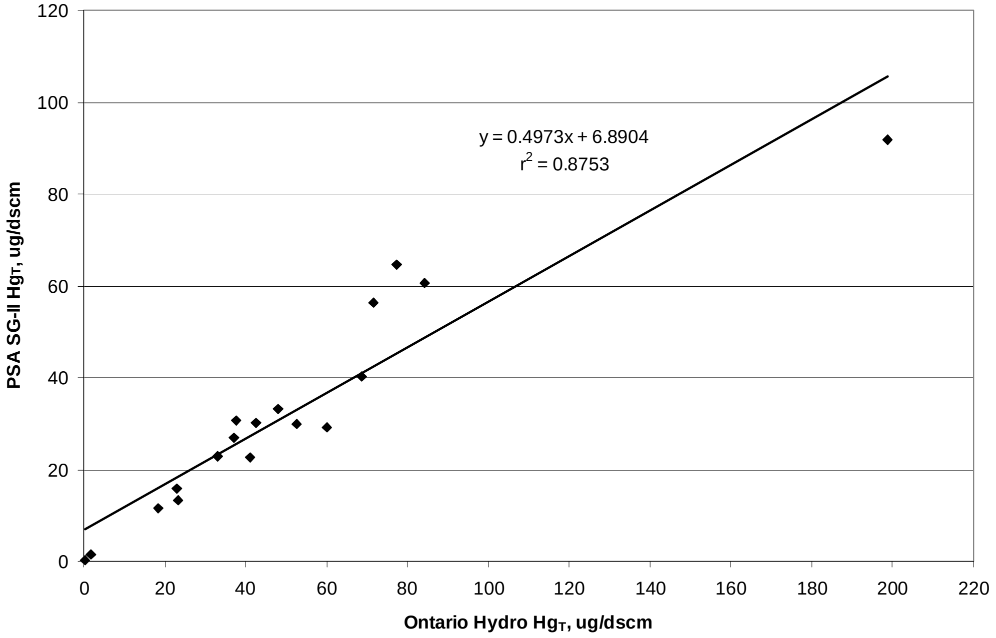

Figure 6-1b. Linear Regression Plot of SG-II Hg_T Results Against OH Results

Table 6-3. Coefficients of Determination (r^2) for Correlation of SG-II Results with OH Results

	r^2	
Test Period	**Hg°**	**Hg_T**
First Week (n = 10)	0.982	0.963
Last Week (n = 8)	0.827	0.894
Overall (n = 18)	0.948	0.875

Table 6-3 shows that the SG-II results were strongly correlated with the OH results for both Hg° and Hg_T, with all r^2 values exceeding 0.82. The overall r^2 value for Hg_T was 0.875.

6.3 Precision

Table 6-4 summarizes the observed precision of the SG-II, in terms of the stability of its Hg_T readings during two periods of relatively stable introduction of mercury in aqueous waste into the TSCAI. For OH Runs 9 and 12, Table 6-4 shows the %RSD of the aqueous waste feed rate into the TSCAI, the corresponding %RSD of the SG-II Hg_T readings, and the resulting estimate of the variability attributable to the SG-II, calculated according to Equation 3 in Section 5.3. (The integrated OH and average SG-II results in these two runs are shown in Table 6-1 above.)

Table 6-4. Precision of the SG-II During OH Runs 9 and 12

OH Run Number	Aqueous Feed Rate Variability ($\%RSD_{WF}$)	SG-II Hg_T Readings ($\%RSD_R$)	Maximum CEM Variability ($\%RSD_{CEM}$)
9	2.4	9.2	8.9
12	13.9	21.1	15.9

The results in Table 6-4 show that the SG-II readings of Hg_T exhibited variability of about 9 to 21%RSD under conditions of relatively stable mercury feed into the TSCAI. The maximum variability attributable to the SG-II was 8.9%RSD in OH Run 9 and 15.9%RSD in OH Run 12.

6.4 Sampling System Bias

On four days during the verification test, an elemental mercury gas standard was supplied directly to the analyzer of the SG-II, and then to the inlet of the CEM's sampling system on the TSCAI stack. Table 6-5 shows the date, the mercury standard, and the SG-II readings obtained for each of these sampling system bias checks. The SG-II responses are the average of two or more successive stable readings on the standard gas. When the standard gas was supplied at the inlet, it was analyzed through both the Hg° and Hg_T channels of the SG-II. Since these are separate flow paths within the SG-II, separate calculations of the sampling system bias were made using Equation 4 in Section 5.4, and the results are shown in Table 6-5. In the sampling system bias checks conducted on August 8 and 9 and on September 17, all analyses were completed within about one hour. However, in the test on September 19, the analyses of gas supplied to the inlet occurred about seven hours after those at the analyzer.

Table 6-5. Sampling System Bias Results

Date	Hg° Standard[a]	Response at Inlet (R_i) ($\mu g/m^3$)		Response at Analyzer (R_a) ($\mu g/m^3$)	Bias[b] (%)	
		Hg°	Hg_T		Hg°	Hg_T
8/8/02	CC133537	16.86	17.35	18.10	6.9	4.1
8/9/02	CC133537	13.45	13.28	13.98	3.8	5.0
9/17/02	CC133537	14.74	15.29	15.17	2.8	0.0
9/17/02	CC133619	36.42	37.02	38.86	6.3	4.7
9/19/02[c]	CC133537	14.13	14.70	15.11	6.5	2.7
9/19/02[c]	CC133619	37.56	36.11	39.77	3.1	6.9

[a] See Section 3.4.2 for information on mercury standard gases.

[b] Calculated according to Equation 4, Section 5.4.

[c] Measurements at analyzer and at inlet separated by about seven hours.

Table 6-5 shows that all sampling system bias results were less than 7% for both measurement channels of the SG-II, and most results were less than 5%. In one of the bias checks, the average SG-II Hg_T response to standard gas at the inlet actually slightly exceeded the average response at the analyzer, indicating no sampling system bias.

6.5 Relative Calibration and Zero Drift

Mercury gas standards and zero gas (high purity nitrogen) were analyzed by the SG-II periodically throughout the verification test to assess the drift in calibration and zero response of the CEM. The results of these analyses are shown in Table 6-6, which lists the date of each analysis and the SG-II Hg° readings on zero gas and on the mercury standards. Four instances of multiple analyses conducted on a single day are included in the table. Also shown in Table 6-6 are the mean, standard deviation, %RSD, and range of the SG-II readings on zero gas and on the mercury standard gases.

Table 6-6 shows that the zero gas readings of the SG-II averaged -0.05 $\mu g/m^3$ over the duration of the verification test, with a standard deviation of 0.10 $\mu g/m^3$. These results indicate minimal drift of the zero readings of the SG-II. Eighteen analyses of the lowest concentration standard (CC133537) took place over a period of about six weeks and exhibited an RSD value of 11.9%. The 12 analyses of the middle concentration standard (CC133612) over a five-week period showed an RSD of 10.2%. It should be noted that the results for these two standards are greatly dependent on the first set of analyses conducted on August 22, which produced by far the lowest

Table 6-6. Calibration and Zero Drift Results

	SG-II Hg° Readings (µg/m³)			
Date	**Zero Gas[(a)]**	**Mercury Standard CC133537**	**Mercury Standard CC133612**	**Mercury Standard CC133619**
8/8/02	0.00	18.10		
8/9/02	0.05	13.98		
8/10/02	-0.06	14.94	36.96	
8/11/02	-0.28	14.52	37.55	
8/12/02	-0.11	14.50		
8/12/02		15.17	39.03	
8/22/02		9.56	25.54	
8/22/02		13.91	36.29	
8/29/02		16.50	36.28	
8/29/02		12.74	31.20	
9/4/02		13.65	34.00	
9/5/02		15.38	36.75	
9/11/02		15.29	34.86	
9/12/02		14.62	35.61	
9/16/02	0.02	13.52	34.10	32.47
9/17/02	-0.00	15.17		38.86
9/18/02	-0.06	15.79		39.20
9/19/02	0.02	15.11		38.77
Mean	-0.05	14.58	34.85	37.32
Std. Dev.	0.10	1.74	3.55	3.24
%RSD	--	11.9%	10.2%	8.7%
Range	-0.28 – 0.05	9.56 – 18.10	25.54 – 39.03	32.47-39.20

(a) High purity nitrogen used for zero checks.

readings for both of those standards. Exclusion of those values would result in RSD values of 8.3% and 5.9% for standards CC133537 and CC133612, respectively. Finally, the four analyses of the highest concentration standard (CC133619) over a four-day period resulted in an RSD of 8.7%.

6.6 Response Time

On several occasions during the verification test, successive readings were recorded at times when the SG-II switched from zero gas to a mercury standard gas, or vice versa, or from one standard gas to another. These records were used to evaluate the response time (i.e., the rise and fall times) of the SG-II. The SG-II is a batch analyzer, which, for the analysis of response time, provided readings at intervals of a few minutes. Consequently, the evaluation of response time, is reported in terms of the extent of response to a step change in mercury concentration that was achieved in each measurement cycle. Table 6-7 summarizes the response time data, showing the date and time of each reading, the indicated mercury concentration, and the resulting percent rise or percent fall in successive readings. Table 6-7 includes primarily data from tests in which the zero and standard gases were supplied to the mercury analyzer of the SG-II, as well as a few data from tests in which the gases were supplied directly to the inlet of the SG-II's sampling system.

Table 6-7 shows that the percentage response of the SG-II to rising mercury levels within one measurement cycle ranged from 84.7 to 99.6%, and averaged 94.8%. Thus the 95% rise time of the SG-II was essentially one measurement cycle. Table 6-7 also shows that the percentage response of the SG-II to falling mercury levels within one measurement cycle was nearly 100%, i.e., response dropped by 99.3% or more in all four cases in which fall time could be determined. Thus the 95% fall time of the SG-II is also within one measurement cycle.

6.7 Data Completeness and Operational Factors

The operational factors associated with use of the SG-II were evaluated by SEI staff, who operated the SG-II during the five-week period of routine monitoring. These operators recorded observations on daily maintenance, repair, expendables use, waste generation and disposal, etc., in a separate logbook for each CEM. The SG-II vendor also recorded activities in the first and last weeks of the field period. Particular attention was paid to the cause and extent of any down time of the SG-II during the field period. Table 6-8 lists the dates of significant down time of the SG-II during the entire verification period, along with the duration of the down time, the duration of the service time, and a description of the cause and resolution of each problem.

The operation and maintenance activities listed in Table 6-8 include only those that were not required by the test/QA plan (e.g., time required to conduct zero and standard gas checks was not considered down time) and that were responsible for either CEM down time or for operator intervention. In the case of the SG-II, routine calibration checks using the CEM's internal mercury standard (the "Cavkit") also were not included in Table 6-8 because these checks required minimal operator intervention. The Cavkit checks are typically used as an automated QC feature of the SG-II. On the other hand, the time needed for recalibration of the SG-II with an absolute standard mercury vapor source is included in Table 6-8 because this is a manual procedure carried out externally to the CEM. As Table 6-8 shows, the most common maintenance needed on the SG-II included frequent calibration checks, preparation of the aqueous reagents, and changing of argon cylinders. The latter two activities were performed every few days. The most common repair problems had to do with the liquid flow system in the mercury speciation module. Problems occurred in maintaining the liquid reagent flows and levels in the impingers; in mass flow control of the sample gas flows through the impingers; in shutdowns due to moisture carryover from the impingers; and in the buildup of a yellow precipitate that clogged the liquid flow. These problems were the cause of four periods of down time ranging from 10 hours to more than 34 hours, on August 15, 20, and 31 and September 8. The total down time

Table 6-7. Summary of Data Used to Estimate Response Time

Date	Time	Zero/Span Gas	Analyzer/ Inlet[(a)]	SG-II Response (µg/m^3)	Result
8/10/02	16:55	CC133537[(b)]	A	14.94	
	17:00	CC133612	A	36.62	98.5% rise in one cycle
	17:05	CC133612	A	36.90	
	17:10	CC133612	A	36.96	
8/11/02	17:26	CC133537	A	14.52	
	17:31	CC133612	A	35.58	91.4% rise in one cycle
	17:35	CC133612	A	36.67	96.2% rise in two cycles
	17:40	CC133612	A	37.55	
	17:45	Z	A	-0.01	99.3% fall in one cycle
	17:50	Z	A	-0.26	
	17:54	Z	A	-0.28	
9/4/02	9:50	CC133537	A	13.65	
	9:56	CC133612	A	33.44	97.2% rise in one cycle
	10:01	CC133612	A	34.00	
9/11/02	13:19	CC133537	A	15.29	
	13:24	CC133612	A	33.08	84.7% rise in one cycle
	13:29	CC133612	A	36.21	99.6% rise in two cycles
	13:34	CC133612	A	36.29	
9/12/02	11:06	CC133537	A	14.62	
	11:11	CC133612	A	37.07	99.6% rise in one cycle
	11:16	CC133612	A	37.17	
9/16/02	19:07	Z	A	0.02	
	19:12	CC133619	A	31.83	98.5% rise in one cycle
	19:16	CC133619	A	32.33	
9/17/02	16:18	CC133537	A	15.17	
	16:23	CC133619	A	38.24	97.4% rise in one cycle
	16:28	CC133619	A	38.24	
	16:33	CC133619	A	38.86	
	16:37	Z	A	0.07	99.8% fall in one cycle
	16:42	Z	A	0.00	

Table 6-7. Summary of Data Used to Estimate Response Time (continued)

Date	Time	Zero/Span Gas	Analyzer/ Inlet[a]	SG-II Response (µg/m^3)	Result
9/19/02	10:16	CC133537	A	15.11	
	10:21	CC133619	A	37.89	90.8% rise in one cycle
	10:26	CC133619	A	38.82	94.5% rise in two cycles
	10:31	CC133619	A	40.21	
	10:36	CC133619	A	38.77	
	10:40	Z	A	0.16	99.6% fall in one cycle
	10:45	Z	A	0.06	
	10:50	Z	A	0.05	
	10:55	Z	A	0.02	
9/19/02	18:32	CC133537	I	14.70	
	18:37	Z	I	0.16	99.5% fall in one cycle
	18:41	Z	I	0.08	

[a] Indicates whether zero and standard gases were supplied to the CEM's mercury analyzer (A) or to the inlet (I) of the CEM's sampling system.

[b] See Section 3.4.2 for information on mercury standard gases.

experienced during the six-week test period was 7,100 minutes (approximately 118 hours, or about 5 days), and the required service time during the same period was 1,730 minutes (28.8 hours). The total down time amounted to about 11.7% of the total duration of the field period (August 8 through September 19), so that data completeness was 88.3%.

The cost of the SG-II also was considered as an operational factor. The approximate purchase cost of the SG-II as tested was $70,000.

Table 6-8. Extent of Down Time and Service Time

Date	Down Time (a)	Service Time (b)	Activity
8/9/02	1 hour (hr)	1 hr	Recalibrated SG-II using vapor-injection method.
8/9/02	20 min	20 min	Recalibrated SG-II using vapor-injection method.
8/10/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
8/10/02	5 min	5 min	Recalibrated SG-II using vapor-injection method.
8/11/02	15 min	15 min	Recalibrated SG-II using vapor-injection method.
8/11/02	25 min	25 min	Recalibrated SG-II using vapor-injection method.
8/12/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
8/12/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
8/12/02	25 min	25 min	Changed collection time from 2 to 1 minute and changed calibration factor (CF) from 1 to 2.
8/12/02	NA(c)	10 min	Emptied liquid waste containers into sump.
8/13/02	3 hr	10 min	Changed argon cylinder after finding system in standby mode due to empty argon cylinder.
8/13/02	30 min	30 min	Liquid level in the total mercury channel impinger appeared to be high, and liquid was bubbling excessively over to chiller. Heated Teflon valve for total mercury channel in speciation unit was slightly closed to reduce bubbling in the impinger. Mass flow controller (MFC) was inadvertently shut down. Logged out and logged in to restart operating system and reset mass flow controller to 25%. Afterward, liquid level still appeared to be high.
8/14/02	45 min	1 hr	Performed daily checks. Total mercury impinger liquid level still appeared to be too high and the Hg° impinger level was too low. Noticed that no waste was flowing into the Hg° waste container. The mass flow meter dialog box indicated “MD” rather than a setpoint of 25%. Notified the vendor of symptoms.

Table 6-8. Extent of Down Time and Service Time (continued)

Date	Down Time [(a)]	Service Time [(b)]	Activity
8/15/02	18 hr	2 hr	Found SG-II in standby mode due to Conditioner 1 alarm (moisture on Hg_T channel sensor). Dried the sensor and restarted the system, but the liquid level in the Hg_T channel impinger was too high. Stopped the instrument until receiving further instructions from vendor. Reinitialized the mass flow controller and reset to 25% per instructions from the vendor. Discovered that the peristaltic pump tubing for the Hg° reagent line was reversed so that the direction of flow was from the impinger to the clean reagent container. Adjusted the flow through the Hg_T channel impinger to match the flow through the Hg° channel impinger. Reversed the tubing and restarted the system at 12:08.
8/16/02	15 min	15 min	Changed argon cylinders and switched from UHP argon to industrial grade argon. (Obtained vendor approval via telephone on 8/15/02). Recalibrated SG-II using vapor-injection method.
8/19/02	5 min	5 min	Changed argon cylinders.
8/20/02	17 hr 35 min	5 min	Found system in standby mode due to Conditioner 1 alarm. Restarted system. Buildup of yellow precipitate in Hg_T impinger appeared to worsen.
8/21/02	10 min	25 min	Prepared seven liters of Hg° reagent and four liters of Hg_T reagent.
8/22/02	30 min	30 min	Replaced Hg_T impinger with a clean impinger. Replaced peristaltic pump tubing for Hg° and Hg_T reagent lines. Emptied condensate container for excess flue gas line. Instrument recalibrated using vapor injection method.
8/23/02	5 hr	1 hr	Found system in standby mode with two alarms: empty argon cylinder and Conditioner 1 alarm. Liquid in the Hg_T Peltier cooler impinger had reached the moisture sensor causing the conditioner alarm. Changed argon cylinders. Replaced peristaltic pump tubing for Hg_T and Hg° waste lines. Restarted system.

Table 6-8. Extent of Down Time and Service Time (continued)

Date	Down Time [a]	Service Time [b]	Activity
8/24/02	10 min	10 min	Discovered peristaltic tubing for Hg_T waste line disconnected from waste container drain line. Paused the SG-II, cleaned up spill on the floor, reconnected the lines, and restarted the system at 8:30.
8/24/02	20 min	1 hr	Recalibrated SG-II using vapor-injection method. Prepared four liters of Hg_T reagent and three liters of Hg° reagent. Recalibrated SG-II again using vapor-injection method.
8/26/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
8/26/02	10 min	10 min	Changed argon cylinders.
8/26/02	NA	1 hr	Prepared five liters of Hg° reagent and four liters of Hg_T reagent.
8/29/02	1 hr	1 hr	Replaced Hg_T impinger and peristaltic pump lines.
8/29/02	30 min	30 min	Recalibrated SG-II using vapor-injection method.
8/31/02	10 hr 10 min	25 min	Found system in standby mode due to Conditioner 1 alarm as a result of liquid in the Hg_T Peltier cooler impinger. The peristaltic pump tubing for the Hg_T waste line was pinched. Drained impinger and dried moisture sensor. Moved to a new position on the tubing and swapped tubing holders on the peristaltic pump. Restarted the system.
9/2/02	10 min	10 min	Found SG-II in alarm. Argon cylinder was empty. Changed argon cylinders.
9/3/02	10 min	10 min	Emptied condensate container for flue gas bypass line.
9/3/02	NA	1 hr 15 min	Prepared seven liters of Hg° reagent and four liters of Hg_T reagent. Observed yellow precipitate in the Hg_T waste line downstream of the Peltier cooler impinger and the peristaltic pump.
9/4/02	20 min	20 min	Replaced the peristaltic pump tubing for the reagent lines. Replaced the Hg_T impinger. Recalibrated SG-II using vapor-injection method.

Table 6-8. Extent of Down Time and Service Time (continued)

Date	Down Time [(a)]	Service Time [(b)]	Activity
9/5/02	35 min	35 min	Found the drain elbow from the Hg_T Peltier cooler impinger plugged with yellow precipitate. Removed, cleaned, and reinstalled the elbow and waste line.
9/6/02	NA	2 hr	Prepared 10 liters of Hg_T reagent and eight liters of Hg° reagent.
9/7/02	15 min	15 min	Replaced the Hg_T impinger due to low instrument response.
9/8/02	34 hr 20 min	1 hr 35 min	Found SG-II in standby mode due to Conditioner 1 alarm resulting from liquid in the Hg_T Peltier cooler impinger. Elbow beneath impinger was plugged with yellow precipitate. Removed elbow, cleaned, and reinstalled. Discharge line that mates to elbow had swollen and had difficulty making up connection. Replaced peristaltic pump tubing for Hg_T waste line. Changed argon cylinders.
9/9/02	NA	10 min	Heard pressurized air leak from polyflow tubing airline. Identified source of the leak and wrapped in duct tape temporarily.
9/10/02	NA	10 min	Permanently repaired polyflow tubing airline with Swagelok connector.
9/10/02	20 min	20 min	Replaced elbow at base of Hg_T Peltier cooler impinger with parts sent by vendor. Nipple on impinger broke off while replacing the elbow, thus replaced the impinger also. The original Teflon union that connects the impinger to the moisture sensor was loose, so replaced this union.
9/11/02	NA	40 min	Adjusted excess flow on Channel 1 from 600 to 350 ml/min. Replaced peristaltic pump tubing for both reagent lines and for Hg° waste line.
9/11/02	10 min	45 min	Noticed that liquid levels in the Hg_T and Hg° impingers were low. Further noticed bubbling in the reagent tanks. Moved reagent line tubing to two different bridges and the bubbling stopped. Bridges were either not seated properly or just needed to be swapped out.

Table 6-8. Extent of Down Time and Service Time (continued)

Date	Down Time [(a)]	Service Time [(b)]	Activity
9/11/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
9/12/02	5 min	5 min	Changed argon cylinders.
9/13/02	NA	1 hr 15 min	Prepared six liters of Hg° reagent and six liters of Hg_T reagent.
			Observed small amount of liquid on Teflon Swagelok fitting at base of Hg_T Peltier cooler impinger. Slightly tightened connection and moved bridge for Hg_T waste line to new position on peristaltic pump.
9/13/02	35 min	35 min	Replaced the Hg_T impinger.
9/13/02	10 min	10 min	Recalibrated SG-II using vapor-injection method.
9/15/02	20 min	20 min	Recalibrated SG-II using vapor-injection method.
			Liquid level in Hg° impinger appeared to be low. Moved the bridge to a different position on the Hg° reagent tubing. Emptied the liquid waste containers.
9/15/02	5 min	1 hr	Changed argon cylinders.
			Prepared one liter of Hg° reagent and one liter of Hg_T reagent.
9/16/02	NA	NA	Vendor representative came to site to check SG-II before starting OH reference method testing. Routine maintenance and operation of SG-II returned to vendor.
9/16/02	16 hr	NA	Found system in standby mode due to nearly closed valve on argon cylinder.
9/16/02	50 min	50 min	Restarted argon flow to instrument. Changed Hg_T reagent chemistry to overcome yellow precipitate problem. Recalibrated SG-II using vapor-injection method.
9/17/02	25 min	25 min	Recalibrated SG-II using vapor-injection method.
9/18/02	20 min	20 min	Recalibrated SG-II using vapor-injection method.

Table 6-8. Extent of Down Time and Service Time (continued)

Date	Down Time [(a)]	Service Time [(b)]	Activity
9/18/02	20 min	20 min	During the second half of Run 22, noticed that MFC had fallen to 20% of full-scale deflection (FSD). To overcome this issue, decreased MFC to 12.5% FSD and set CF to 4.
9/18/02	1 hr 5 min	1 hr 5 min	At the end of Run 23, noticed that MFC had fallen to 10% FSD. This could cause a slight negative bias to the results. The unit was inspected and the sample block valve was causing a restriction. The block valve was bypassed to resolve the problem.
			Changed argon cylinders.
			Recalibrated SG-II using vapor-injection method.
9/19/02	15 min	15 min	Observed that the system ran without problem during the night. The MFC was set to 25% FSD and the CF to 2.
			Recalibrated SG-II using vapor-injection method.
TOTAL	7,100 min	1,730 min	88.3% availability and 28.8 service man-hours [(d)]

(a) Down Time = time that the CEM was not operating, or was operating but not reporting reliable measurements. The period over which down time was evaluated begins at the start of OH method testing on 8/8/02 and ends at the conclusion of testing on 9/19/02. The amount of time was rounded to the nearest 5 minutes.

(b) Service Time = time spent to perform daily checks, conduct routine operation and maintenance activities, and troubleshoot problems. The period over which service time was evaluated begins at the start of OH method testing on 8/8/02 and ends at the conclusion of testing on 9/19/02. The amount of time was rounded to the nearest 5 minutes.

(c) NA = not applicable.

(d) Availability = the ratio of time that the CEM was not experiencing down time to the total time available for monitoring mercury emissions from the start of OH reference method testing on 8/8/02 to the end of testing on 9/19/02. The total time that was available for monitoring was 60,936 minutes or 1,015.6 hours.

Chapter 7
Performance Summary

The RA of the SG-II for measuring Hg_T and Hg^o was verified by comparison with the results of 18 sampling runs using dual trains of the OH reference method at Hg_T levels of <1 to 200 µg/dscm. The overall RA results were 54.7% and 59.8% for Hg^o and Hg_T, respectively. The RA for Hg_T is 42.8% if OH Run 16 is excluded from the calculation.

Correlation of the SG-II Hg° and Hg_T results with the OH results showed r^2 values of 0.948 and 0.875, respectively, when all 18 OH results were included.

Precision of the SG-II was estimated using two OH sampling periods having relatively stable introduction of mercury in aqueous waste into the TSCAI. The estimated maximum variability attributable to the SG-II was 8.9% and 15.9% for these two periods.

The bias introduced by the SG-II sampling system was evaluated by introducing Hg° standard gas both at the SG-II and at the inlet to the sampling system. Sampling system bias was 2.8% to 6.9% for Hg° and 0.0% to 6.9% for Hg_T in the two measurement channels of the SG-II.

Zero gas and mercury gas standards were used to assess the calibration drift of the SG-II throughout the verification test. Zero gas readings over the six-week field period averaged -0.05 (±0.10) $\mu g/m^3$, indicating minimal drift of the SG-II zero readings. Eighteen analyses of an approximately 14.9 $\mu g/m^3$ Hg° standard over six weeks resulted in an RSD of 11.9% (8.3% with one outlier excluded). Twelve analyses of an approximately 35.6 $\mu g/m^3$ standard over five weeks resulted in an RSD of 10.2% (5.9% with one outlier excluded). Four analyses of an approximately 39.3 $\mu g/m^3$ Hg° standard over four days resulted in an RSD of 8.7%.

Rise and fall times of the SG-II response were determined at times of switching between zero and mercury standard gases. The SG-II achieved 95% rise and fall times in approximately one measurement cycle.

The SG-II data completeness was 88.3%. The most common maintenance needed was replacement of chemical reagent solutions and argon cylinders, which was done every few days. The most common operational problems were in the liquid flow system of the mercury speciation module.

Chapter 8
References

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