August 2001

Environmental Technology Verification Report

PS ANALYTICAL LTD.
SIR GALAHAD II MERCURY CONTINUOUS EMISSION MONITOR

Prepared by

Battelle

. . . Putting Technology To Work

Battelle

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV

U.S. Environmental Protection Agency

Battelle
. . . Putting Technology To Work

Massachusetts Department of Environmental Protection

ETV Joint Verification Statement

TECHNOLOGY TYPE: **Continuous Emission Monitor**

APPLICATION: **MEASURING ELEMENTAL AND OXIDIZED MERCURY EMISSIONS**

TECHNOLOGY NAME: **Sir Galahad II (SG-II)**

COMPANY: **PS Analytical Ltd.**

ADDRESS:
Arthur House, Crayfields
Ind'l. Est., Main Road,
Orpington
Kent BR5 3HP, UK

PHONE: +44 (0) 1689 891211
FAX: +44 (0) 1689 896009

WEB SITE: **http://www.psanalytical.com**

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially 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 standards and testing organizations; with stakeholder groups that consist 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 protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of six technology centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of continuous emission monitors used to measure mercury in flue gases. This verification statement provides a summary of the test results for the PS Analytical Ltd. Sir Galahad II (SG-II) mercury continuous emission monitor (CEM).

VERIFICATION TEST DESCRIPTION

The verification test was conducted over a three-week period in January 2001 at the Rotary Kiln Incinerator Simulator (RKIS) facility at EPA's Environmental Research Center, in Research Triangle Park, North Carolina. This mercury CEM verification test was conducted jointly by Battelle's AMS Center, EPA's Office of Research and Development, and the Massachusetts Department of Environmental Protection. A week of setup and trial runs was followed by two weeks of verification testing under different flue gas conditions. The daily test activities provided data for verification of the following performance parameters of the SG-II: relative accuracy in comparison to reference method results, correlation with the reference method, precision in sampling at stable flue gas conditions, calibration/zero drift from day to day, sampling system bias in transfer of mercury to the CEM's analyzer, interference effects of flue gas constituents on CEM response, response time to rising and falling mercury levels, response to low levels of mercury, data completeness over the course of the test, and setup and maintenance needs of the CEM. The Ontario Hydro (OH) draft American Society for Testing and Materials mercury speciation method was used as the reference method in this verification test. Paired OH trains were sampled at two locations in the RKIS duct to establish the precision of the OH method.

Quality assurance (QA) oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a data quality audit of 10% of the test data, a series of performance evaluation audits on several measurements at the RKIS, and both an internal and an external technical systems audit of the procedures used in this verification. EPA QA staff also conducted an independent technical systems audit at the RKIS.

TECHNOLOGY DESCRIPTION

The SG-II is an automated continuous emission monitor for elemental mercury and total vapor-phase mercury in combustion flue gases and other gas streams. The SG-II consists of a Model S235C400 mercury speciation module and an enclosed cabinet housing the SG-II amalgamation atomic fluorescence mercury detector (PSA 10.525), a stream selector module (PSA S235S100), personal computer, monitor, and keyboard, and a mercury calibration source (PSA 10.533). The speciation module converts oxidized mercury in the sample gas to elemental mercury by means of a proprietary aqueous reagent, allowing separate detection of elemental mercury and total mercury. The speciation module is approximately 75 cm wide x 45 cm deep x 90 cm high (30 in. wide x 18 in. deep x 36 in. 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 in. wide x 30 in. deep x 72 in. high) and is mounted on wheels. A heated Teflon diaphragm pump draws a filtered sample flow of approximately 5 L/min 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 elemental mercury. In the other gas stream, oxidized mercury is reduced to elemental mercury, producing an elemental mercury concentration equivalent to the original sum of oxidized and elemental mercury. 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.

VERIFICATION OF PERFORMANCE

Relative accuracy: During the first week of verification testing, the SG-II provided an accuracy relative to the OH method of 20.6% for total mercury, at total mercury levels of about 7 to 8 $\mu g/m^3$. Testing showed relative accuracy of 22.8% for elemental mercury, and 27.2% for oxidized mercury at elemental mercury levels of approximately 6 to 7 $\mu g/m^3$ and oxidized mercury levels of approximately 1 to 1.5 $\mu g/m^3$. In the second week of verification testing, the SG-II provided a relative accuracy of 32.8% for total mercury, at total mercury levels of about 70 to 120 $\mu g/m^3$. Relative accuracy of 29.6% for elemental mercury, and 33.3% for oxidized mercury was found at elemental mercury levels ranging from about 5 to 25 $\mu g/m^3$ and oxidized mercury levels ranging from about 45 to 110 $\mu g/m^3$.

Correlation with the reference method: The coefficient of determination (r^2) of the SG-II and OH elemental mercury results was 0.853 based on data from both weeks combined. The corresponding r^2 value for oxidized mercury was 0.951, and for total mercury was 0.957.

Precision at stable flue gas conditions: Precision of the SG-II response was assessed in periods of stable mercury levels in the flue gas during the 15 OH sampling periods. The precision of the SG-II response for elemental mercury was within 10% relative standard deviation (RSD) in 13 of the 15 periods. For total mercury, precision was within 10% RSD in 11 of the 15 periods and within 15% in 14 of the periods.

Calibration/zero drift: Analysis of zero gas and elemental mercury standard gases in the first week of testing gave average zero gas responses of 0.001 (± 0.001) $\mu g/m^3$ and standard gas responses of 15.1 (± 0.39) $\mu g/m^3$. The standard gas results equate to a 2.6% RSD. Zero gas readings in the second week were 0.001 (± 0.006) $\mu g/m^3$, and standard gas responses were 53.5 (± 1.34) $\mu g/m^3$. These standard gas results equate to a 2.5% RSD.

Sampling system bias:. The bias in transport of elemental mercury through the inlet system of the SG-II ranged from -0.3 to -4.9%.

Interference effects of flue gas constituents: Elevated levels of sulfur dioxide, nitrogen oxides, carbon monoxide, and hydrogen chloride had no significant effect on SG-II response to elemental or total mercury in flue gas. The presence of chlorine reduced elemental mercury readings to nearly zero, but caused no significant change in the total mercury readings. When these gases were all present at once in the flue gas, the SG-II readings for both elemental and total mercury were close to those seen with only mercury in the flue gas.

Response time to changing mercury levels: The SG-II operated with a 5- to 6-minute sampling/analysis cycle and achieved 95% or greater response to changes in mercury concentration within a single cycle.

Response to low levels of mercury: The SG-II produced a nearly quantitative response to as little as 0.57 $\mu g/m^3$ of mercury in flue gas (the lowest concentration tested), and response at nominal levels of 0.57 to 4.5 $\mu g/m^3$ of mercury was within about 10% of the nominal levels.

Data completeness: Data completeness for the SG-II was 100%.

Setup and maintenance needs: No significant repair or maintenance was needed. The SG-II uses 1 to 1.5 L/day of aqueous reagents to measure elemental and total mercury and consumes about 200 cubic feet of high-purity argon in a week of continuous operation

Gabor J. Kovacs Date
Vice President
Environmental Sector
Battelle

Gary J. Foley Date
Director
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

Gina McCarthy Date
Assistant Secretary for Pollution Prevention,
Environmental Business and Technology
Massachusetts Executive Office of Environmental Affairs

August 2001

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

PS Analytical Ltd.
Sir Galahad II
Mercury Continuous Emission Monitor

by

Thomas Kelly
Charles Lawrie
Karen Riggs
Battelle
Columbus, Ohio 43201

Jeffrey Ryan
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

with support from

Massachusetts Department of Environmental Protection

Notice

Foreword

The U.S. 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 six 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/07/07_main.htm.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we would like to thank Bea Weaver, Adam Abbgy, and Paul Webb of Battelle. We thank those staff of EPA's Environmental Research Center who provided assistance in the field tests. We also acknowledge the support of Chris Winterrowd and other staff of ARCADIS Geraghty & Miller for their work in operating the test facility, conducting Ontario Hydro sampling, and reporting data for this report. The participation of Dr. Warren Corns of PS Analytical Ltd. in the verification test is gratefully acknowledged.

Contents

Figures

Tables

List of Abbreviations

AMS	Advanced Monitoring Systems
ANOVA	analysis of variance
APCS	air pollution control system
CEM	continuous emission monitor
Cl_2	chlorine
CO	carbon monoxide
CO_2	carbon dioxide
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GFCIR	gas filter correlation infrared
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
HCl	hydrogen chloride
Hg	mercury
Hg^o	elemental mercury
KCl	potassium chloride
$KMnO_4$	potassium permanganate
L/min	liters per minute
m^3	cubic meters
MDEP	Massachusetts Department of Environmental Protection
mg/m^3	milligrams per cubic meter
mL	milliliter
NDIR	non-dispersive infrared
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_x	nitrogen oxides
O_2	oxygen
OD	outside diameter
OH	Ontario Hydro
ORD	Office of Research and Development
PE	performance evaluation
ppb	parts per billion
ppm	parts per million
psig	pounds per square inch gauge
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RA	relative accuracy

RKIS	Rotary Kiln Incinerator Simulator
RSD	relative standard deviation
SO_2	sulfur dioxide
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) has created 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 substantially 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, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups that consist 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 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 emissions in combustion flue gas. This verification report presents the procedures and results of the verification test for 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. The following description of the SG-II is based on information provided by the vendor.

The SG-II is an automated continuous emission monitor for elemental mercury and total vapor-phase mercury 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 elemental mercury by means of a proprietary aqueous reagent, allowing separate detection of elemental mercury and total mercury. The speciation module is approximately 75 cm wide x 45 cm deep x 90 cm high (30 in. wide x 18 in. deep x 36 in. 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 in. wide x 30 in. deep x 72 in. high) and is mounted on wheels. The detector cabinet of the SG-II is shown in Figure 2-1.

Figure 2-1. SG-II Mercury Continuous Emission Monitor

A heated Teflon diaphragm pump draws a filtered sample flow of approximately 5 L/min 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 elemental mercury. In the other gas stream, oxidized mercury is reduced to elemental mercury, producing an elemental mercury concentration equivalent to the original sum of oxidized and elemental mercury. 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 pg of mercury. In this verification test, a sample flow of 0.5 L/min was passed through the preconcentration trap for 1 to 2 minutes. The resulting detection limit for vapor phase mercury is approximately 0.001 µg/m^3, with a linear dynamic range of up to 2,500 µg/m^3. The PSA 10.533 mercury source provides a stable 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

A key feature of the SG-II is the Windows®-based operating software, which provides ease and flexibility in calibrating and operating the instrument and in recording and displaying data. The duration, flow rate, and sequencing of the elemental and total mercury measurements is controlled by the software, as is the operation of the SG-II detector, the graphical display of data, and the scheduling of internal calibration checks. The software continually checks for alarm outputs from the various modules and alerts the operator 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 Pilot-Scale Verification of Continuous Emission Monitors for Mercury*.(1) The SG-II was verified for its measurement of elemental, oxidized, and total mercury by comparison to reference method measurements, by challenges with interferant species, and by repeated sampling of elemental mercury standard gases. The test activities provided data for verification of the following performance parameters of the SG-II:

- Relative accuracy in comparison to reference method results
- Correlation with the reference method
- Precision in sampling at stable flue gas conditions
- Calibration/zero drift from day to day
- Sampling system bias in transfer of mercury to the CEM's analyzer
- Interference effects of flue gas constituents on CEM response
- Response time to rising and falling mercury levels
- Response to low levels of mercury
- Data completeness over the course of the test
- Setup and maintenance needs of the CEM.

All but the last parameter listed were evaluated quantitatively, using data produced by the planned sequence of tests. The data used to verify these parameters are specified later in this section, and the statistical calculations used to quantify these parameters are presented in Section 5 of this report. The last parameter listed, setup and maintenance needs, was evaluated qualitatively by observing the operation and maintenance of the CEM by vendor staff during the test.

The verification test was conducted over a three-week period in January 2001 at the Rotary Kiln Incinerator Simulator (RKIS) facility at EPA's Environmental Research Center, in Research Triangle Park, North Carolina. The RKIS is a gas-fired, two-stage, pilot-scale incinerator that allows flue gas composition to be manipulated by injecting pollutant gases, particulate matter, and mercury at various points within and downstream of the combustion zone. The RKIS flue gases pass through an extended length of duct before entering an air pollution control system (APCS). When mercury is introduced into the facility flue gas, the facility must operate as a permitted hazardous waste facility, with limitations on hours of operation and personnel training.

In particular, mercury injection into the RKIS flue gas could be performed only between the hours of 6:00 AM and 6:00 PM.

This mercury CEM verification test was conducted jointly by Battelle's AMS Center, EPA's Office of Research and Development (ORD), and the Massachusetts Department of Environmental Protection (MDEP). Specifically, ORD research programs on mercury chemistry and emissions made major contributions to this verification test in the form of planning and organization, facility operations, data acquisition, and leadership in conducting the tests at the RKIS. The MDEP provided financial support and provided comments on the test plan for this verification. In addition to these collaborations, important contributions to the study were made by the staff of ARCADIS Geraghty & Miller, Inc. Under subcontract with EPA/ORD, ARCADIS staff operated the test facility and associated monitoring equipment and conducted ancillary tasks, such as sampling, to confirm the concentrations of commercially prepared elemental mercury gas standards. Under subcontract with Battelle, ARCADIS staff performed reference flue gas mercury sampling, coordinated the analysis of those samples, and provided the resulting data for this report.

The schedule for the mercury CEM verification followed that stated in the test/QA plan,(1) in that a week of setup and trial runs was followed by two weeks of verification testing under different flue gas conditions. The overall schedule of the test is shown in Table 3-1.

Table 3-1. General Schedule of the ETV Mercury CEM Verification Test

Date	Verification Test Activities
January 8-12, 2001	Installation of vendor CEMs; shakedown of facility operations and mercury injection procedures; trial sampling of flue gas
January 15-19, 2001	Verification testing with flue gas composition approximating that of a coal-fired power plant
January 22-25, 2001	Verification testing with flue gas composition approximating that of a municipal waste incinerator
January 26, 2001	Packing of vendor CEMs; end of test

The first and second weeks of verification testing (January 15 to 19 and 22 to 25, respectively) were similar, in that largely the same daily sequence of tests was conducted in each of these weeks. However, as noted in Table 3-1, the flue gas composition differed between the two weeks.

It should be pointed out that, although facility shakedowns and trial sampling of flue gas were conducted during the week of January 8 to 12, relatively little time was available for the mercury CEMs to sample the full flue gas matrix. The variety of startup activities made it impossible to conduct full days of trial flue gas sampling. This situation contrasts with the normal installation procedures for such CEMs, in which one or two days are often allotted for extensive sampling of the facility flue gas to tailor the CEM operation for the facility. The verification results reported here must be considered in light of this mode of operation.

The daily schedule of the verification test is illustrated in Table 3-2, which shows the testing activities conducted on each day and the CEM performance parameters addressed by each activity. The exact times when specific test procedures were done are noted when appropriate elsewhere in this report. On each day of the week, the SG-II was challenged with a zero gas and a commercial compressed gas standard of elemental mercury. These gases were supplied to the analyzer one at a time as a test of day-to-day stability and speed of response. This test was done twice a day, except that on the last day of each week it was done only once. Monday through Wednesday of each week, the flue gas was sampled simultaneously by the SG-II and the Ontario Hydro(2) reference method. On Thursday and Friday of the first week, interference and low-level mercury response tests were done, respectively.

Throughout the verification test, the SG-II was operated by a single representative of PS Analytical Ltd. The intent of the testing was for the SG-II to operate in a manner simulating operation at a combustion facility. Therefore, once the verification test began, no recalibration was performed. The SG-II's internal standard system was used as a means of monitoring the behavior of the CEM in routine operation. PS Analytical Ltd. staff prepared reagents, maintained the monitor's inlet system, and handled recovery of data from the SG-II.

3.2 Test Conditions

The SG-II was one of four mercury CEMs tested in this verification effort. All verification testing took place simultaneously, so that all CEMs were subjected to exactly the same test conditions.

3.2.1 RKIS Conditions

The natural gas combustor of the RKIS was operated continuously throughout the test period, to maintain elevated duct temperatures and thereby minimize the chance of retention and subsequent release of mercury by the refractory or other components of the system. The flue gas from the natural gas combustor was spiked with gases, mercury, and particulate matter to achieve different representative flue gas compositions. In all cases, once the required injection rates of mercury, gases, and particulate matter were established, at least 30 minutes of stabilization time was allowed before the start of any reference method sampling or verification data collection.

Mercury was injected into the RKIS flue gas using a peristaltic pump and aqueous solutions of mercury(II) nitrate or chloride ($HgCl_2$). Different injection locations and injection solutions were tried in trial runs to achieve stable total mercury levels and a reasonable split between elemental and oxidized mercury in the duct. The final selection was to use mercury(II) chloride solutions, with different injection locations (i.e., different injection temperatures) to achieve different elemental/oxidized splits in the two weeks of testing.

Table 3-2. Schedule of Daily Activities in the Mercury CEM Verification Test

Test Day	AM/PM	Activity (Performance Parameters)
Monday 1/15/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Tuesday 1/16/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Wednesday 1/17/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Thursday 1/18/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Spiking of flue gas with interferant gases (Interferences)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Friday 1/19/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time, Sampling System Bias)
	AM/PM	Preparation of low Hg levels in flue gas (Low-Level Response)
Monday 1/22/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Tuesday 1/23/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Wednesday 1/24/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time)
Thursday 1/25/01	AM/PM	Repeat of some interference tests (Interferences)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, Response Time, Sampling System Bias)

Potential interferant gases (sulfur dioxide, nitrogen oxides, carbon monoxide, hydrogen chloride, chlorine) were injected into the RKIS duct downstream of the combustion zone, using cylinders of the pure compressed gases as the source. Nitrogen oxides in the flue gas were prepared by injection of nitric oxide (NO). The target gas levels were established by monitoring the concentration in the duct using the RKIS facility CEMs (see Table 3-3), rather than by estimation based on dilution in the duct flow. The only exception was for chlorine, for which no CEM was available. The chlorine concentration was established by first injecting chlorine into the flame zone of the RKIS, where complete conversion of chlorine to hydrogen chloride is thermodynamically assured, and measuring the resulting hydrogen chloride using the hydrogen chloride CEM. The chlorine injection rate was then maintained, but moved to a lower temperature injection point and the concentration of HCl was measured again. The chlorine concentration was established from the difference in the two HCl readings.

Particulate matter was injected into the duct at the downstream end of the RKIS combustion zone, using a K-Tron Soder Model KCLKT20 screw feeder, which incorporated a strain gauge measurement of the mass of material injected. The fly ash used was a lignite coal fly ash, specially chosen for its low reactivity with mercury. The low target particulate loading (30 mg/m^3) required operating the feeder at the extreme low end of its operating range and resulted in substantial variation in the particulate loading in the duct (see below).

Figure 3-1 shows two views of the RKIS test facility and indicates the locations of the injection points for particulate matter, mercury, and interferant gases. Also shown are the port locations RM1 (Port 2) and RM2 (Port 8) where the reference Ontario Hydro (OH) method samples were collected. That sampling is presented in detail in Section 3.2.3. Between these two locations, at Ports 6 and 7, were the sampling locations of the mercury CEMs undergoing testing; the SG-II was located at Port 7. The SG-II test setup is described in more detail in Section 3.2.2. Figure 3-1 also shows the sampling location for the facility CEMs, downstream of all the sampling locations. The CEMs in place at the RKIS for this test are shown in Table 3-3.

The test conditions maintained throughout OH sampling in the two weeks of verification testing were intended to represent a coal-fired power plant flue gas and an incinerator flue gas, respectively. Table 3-4 summarizes the target and actual average levels of mercury and of the other constituents in the flue gas in the two weeks of testing. In general, the actual constituent levels in the flue gas were close to the target levels. The mercury present during the first week of testing was predominantly in elemental form. During the second week of testing, to challenge the speciation capabilities of the CEMs, the injected mercury was predominantly in oxidized form. The flue gas water and oxygen contents were very consistent throughout both weeks of testing, at about 7% water and 14.6% oxygen, and the flue gas temperature at the CEM sampling ports was 400 to 430°F .

3.2.2 SG-II Operation

The SG-II was installed next to the duct, at the port identified as Port 7 in Figure 3-1. The SG-II's inlet system consisted of a ½" OD quartz tube extending to near the center of the duct, through a 2" OD stainless steel sheath tube connected to the port fittings of the duct. The outer end of the

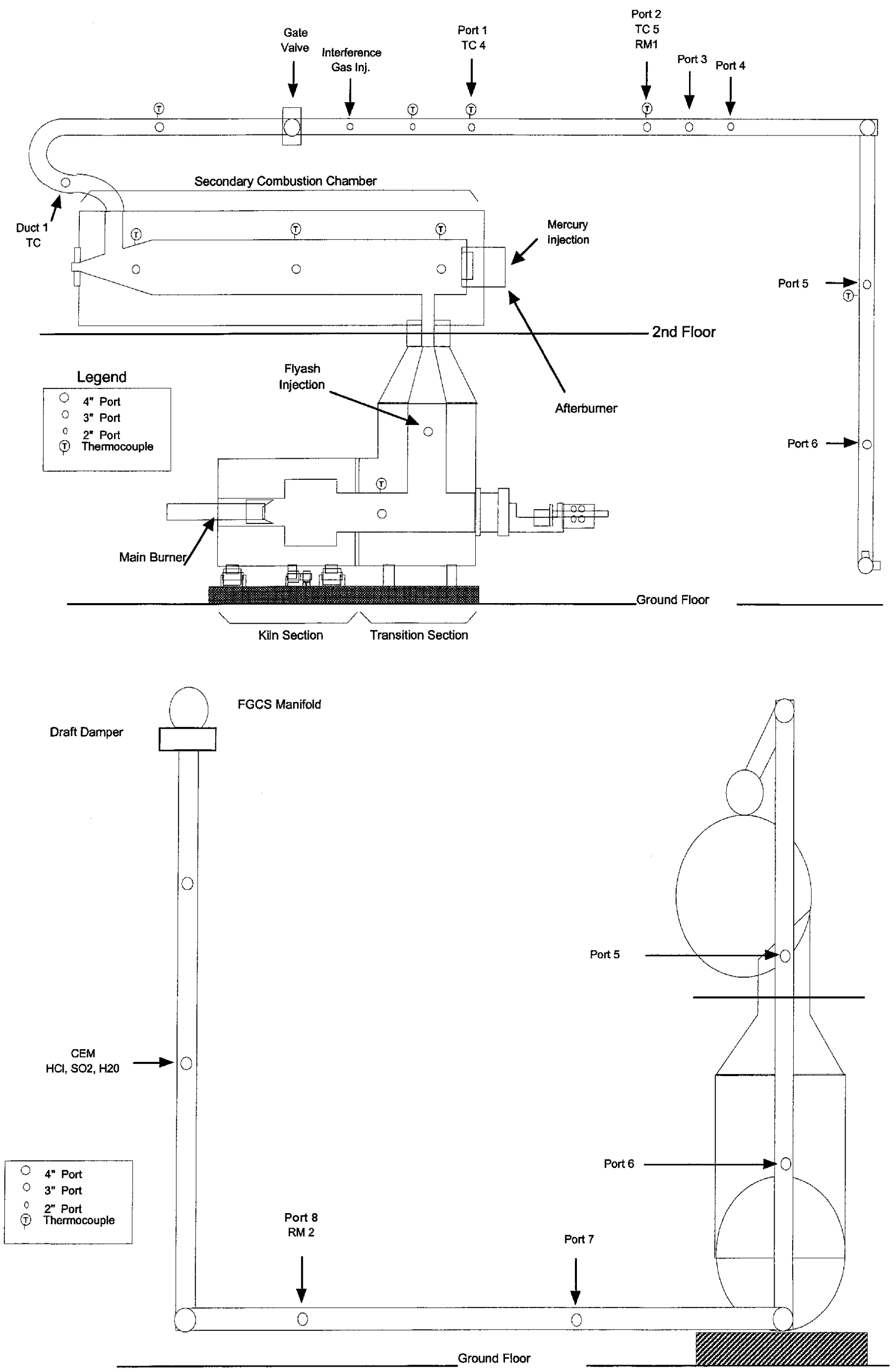

Figure 3-1. Side View (top) and End View (bottom) of the RKIS Test Facility

Table 3-3. Summary of RKIS CEMs

Analyte	CEM	Principle	Measurement Range(s)
O_2	Rosemount Analytical Model 755R	Paramagnetic	0 - 25%
CO_2	Fuji Electric ZRH-1 Gas Analyzer	NDIR	0 - 20%
CO	Horiba Model PIR 2000	NDIR	0 - 500 ppm
NO/NO_x	Thermo Environmental Model 10	Chemiluminescent	0 - 500 ppm
SO_2	Bodenzeewerk Model MCS 100	GFCIR	0 - 250, 0 - 2,500 ppm
HCl	Bodenzeewerk Model MCS 100	GFCIR	0 - 100, 0 - 1,000 ppm

Table 3-4. Target Flue Gas Constituent Concentrations (and Actual Ranges) Used in Verification Test

Test Week	Total Hg (µg/m^3)	SO_2 (ppm)	NO_x (ppm)	HCl (ppm)	Particles (mg/m^3)
One	8[a] (7.3 - 7.8)	1,000 (952 - 978)	250 (226 - 245)	25 (21.5 - 24.3)	30 (0.2 - 71)
Two	80[b] (72 - 119)	50 (51 - 63)	150 (137 - 159)	100 (77 - 92)	30 (2 - 54)

[a] Predominantly elemental mercury; actual range based on average OH results in each OH run.

[b] Predominantly oxidized mercury; actual range based on average OH results in each OH run.

quartz tube was connected by a ball joint to a glass container holding a glass fiber thimble filter. That glass container was supported by a steel mesh cage; and the container, filter, and cage were heated by means of a fitted heating mantle. A sample flow of about 5 L/min was drawn through heated 1/4" OD Teflon tubing from the filter holder to the S235C400 speciation module of the SG-II. Sampling was not isokinetic.

The nature of the inlet system is an important factor in verifying the performance of a mercury CEM, because the materials and temperature of the inlet may affect the chemical speciation and even the quantity of mercury that reaches the CEM. Since the CEMs were verified in this test partly by comparison to the OH method, each vendor was informed of the characteristics of the inlet system used with the OH trains. Vendors then made their own decisions about how best to sample the flue gas to assure consistent comparisons with the OH method. In the inlet system used with the SG-II, the filter was maintained at about 350°F, and the heated line from the filter holder to the SG-II was maintained at about 340°F. At the vendor's discretion, due to the low particulate matter loading, the SG-II inlet filter was changed only after the first week of testing. The SG-II determines vapor-phase elemental and total mercury only (vapor-phase oxidized mercury is determined by difference), so the particulate matter collected on the filter was not analyzed.

The SG-II is a batch-wise, rather than truly continuous, mercury monitor. That is, the SG-II cycled through a sampling and analysis sequence, and alternated between measurements of elemental and total mercury, at intervals programmed by the operator. The main characteristic of the SG-II's operation in this verification was that the actual sampling time of the CEM occupied only a small portion of the instrument's measurement cycle. Throughout the first week of verification testing, the SG-II alternated equally between elemental and total measurement modes, providing a reading every 5 to 6 minutes. In each measurement cycle, the SG-II sampled 0.5 L/min of the gas treated in the S235C400 speciation module for one minute, for a total sample volume of 0.5 L, and was operated on an attenuation range of 10. In the second week of verification testing, with much higher total and oxidized mercury levels, the SG-II performed two measurements of total mercury for each measurement of elemental mercury. In each 5 to 6-minute measurement cycle, the SG-II sampled 0.5 L/min of the treated sample gas for two minutes, for a total sample volume of 1 L. In that time period, the SG-II was operated on an attenuation range of 1, the least sensitive setting. The output of the SG-II was recorded on the built-in personal computer.

3.2.3 Ontario Hydro Reference Method

The OH mercury speciation method(2) was used as the reference method in this verification test, because of the need for a recognized approach to verify the elemental and oxidized mercury measurements made by the CEMs. Since the OH method is not officially designated as a reference method by EPA or the American Society for Testing and Materials, it was judged necessary to document the precision of the OH method itself during the verification test. As a result, in each OH sampling run, two OH trains were operated simultaneously at *each* of the two reference sampling points at the RKIS (Port 2, or RM1, and Port 8, or RM2, in Figure 3-1). At each location, two trains were placed at ports on opposite sides of the duct (designated 2A, 2C, 8A, and 8C, respectively), with their inlet probes positioned close together near the center of the duct. Thus, four OH trains were used for sampling at the same time in each OH run. Each OH train used a separate inlet probe and heated filter and sampled isokinetically near the duct centerline. An EPA Method 2 traverse was conducted at each OH sampling location, both before and after each OH run, to set the isokinetic sampling rate. The average of pre-and post-run traverses was used for final calculations.

The particulate filters in the OH trains were maintained at 250°F. No heating was applied to the sample probe, instead the sample temperature dropped naturally from the duct temperature to the filter temperature in passage from the probe to the filter. A sampling flow of about 1 m^3/hr (about 16.7 L/min) was used in all OH runs.

None of the CEMs undergoing verification determined particulate mercury. As a result, the particulate filters from the OH trains were used for two purposes: to determine particulate mercury and to determine the particulate mass loading in the duct. For each OH run, one of the particulate filters from each sampling location (RM1 and RM2, Figure 3-1) was used for gravimetric determination of particle mass loading. The other was analyzed for particulate phase mercury. This approach provided a check on the particulate mercury level, while avoiding the expense of additional Method 5 runs to determine the particle loading. As detailed in Section 4.2.1, the particulate mercury determined by the OH sampling was negligible.

The meter boxes of the paired OH trains at each location were located side by side to allow monitoring by a single operator during sampling. During the runs, OH train data were recorded by hand on data sheets prepared for this test and also were entered immediately into an Excel spreadsheet running on a laptop computer at the sampling location. That spreadsheet automatically calculated run parameters, such as percent of isokinetic sampling rate, providing rapid and accurate control of the sampling process.

The OH trains were prepared by ARCADIS staff in a dedicated laboratory close to the RKIS high bay. Trains were brought to the RKIS for sampling and returned to the same laboratory for sample recovery immediately after sampling. Blank trains (one per day of OH sampling) were also brought to one of the sampling locations at the RKIS and returned along with the sampled trains for sample recovery. The glassware set used for the blank train was chosen at random each day from the several sets on hand. In addition, blank samples were taken of all reagents and rinse solutions used in the OH method. Samples were recovered into uniquely identified pre-labeled glass containers according to OH method procedures. Samples were delivered by ARCADIS staff within about 24 hours after sampling to Oxford Laboratories, in Wilmington, North Carolina, for analysis. Staff of Oxford Laboratories verified sample identities from chain-of-custody sheets before beginning sample analysis.

OH sampling was conducted under conditions of stable flue gas composition, on Monday, Tuesday, and Wednesday of each test week (i.e., on January 15 to 17 and 22 to 24, 2001). Two OH runs per day, of two hours each, were made during the first week. Three OH runs per day, of one hour each, were made during the second week. Typical sampled gas volumes were about 2 cubic meters and 1 cubic meter in the first and second weeks of testing, respectively. Table 3-5 shows the actual schedule of OH sampling in the verification test. The OH sampling proceeded smoothly, with the single exception of Run 9, which was interrupted by failure of the mercury solution injection pump. That run was resumed after repair of the pump, and no data were lost.

3.3 Verification Procedures

This section describes the specific procedures used to verify the CEM performance parameters that were listed in Section 3.1. The statistical procedures used to calculate the verification results are described in Section 5 of this report.

3.3.1 Relative Accuracy

Relative accuracy was assessed by the quantitative comparison of the mercury results from the OH method to those from the tested CEM. For the SG-II, this comparison was made for elemental, oxidized, and total mercury. The SG-II results during the period of each OH run were averaged for comparison to the OH result. In making this comparison, it must be noted that the cycle time of the SG-II was 5 to 6 minutes, during which time gas was sampled for only one or

Table 3-5. Schedule of OH Sampling Runs During Mercury CEM Verification

Week	Run Number	Date	Start Time	End Time
One	1	1/15/01	12:07	14:08
	2	1/15/01	15:36	17:37
	3	1/16/01	12:12	14:13
	4	1/16/01	15:45	17:45
	5	1/17/01	10:58	12:59
	6	1/17/01	14:21	16:22
Two	7	1/22/01	11:32	12:33
	8	1/22/01	13:25	14:25
	9	1/22/01	16:15	16:51[a]
			17:40	18:07[a]
	10	1/23/01	10:47	11:47
	11	1/23/01	12:50	13:51
	12	1/23/01	16:00	17:01
	13	1/24/01	11:15	12:15
	14	1/24/01	14:30	15:31
	15	1/24/01	16:15	17:16

[a] Run 9 was interrupted by a failure of the peristaltic pump used to inject mercury solution into the RKIS; the run was resumed after fixing the pump and allowing concentrations to stabilize.

two minutes. This difference in sampling coverage was not important when flue gas mercury levels were constant, as in most OH runs. However, in a few cases, spikes in the indicated mercury level were observed simultaneously on more than one of the participating CEMs as a result of inadvertent brief changes in flue gas composition. The impact of such a spike on the SG-II result could be different from the impact on the corresponding OH result. Consequently, the data were reviewed for the impact of such spikes on the accuracy calculation.

The accuracy was calculated separately for the two different test conditions, i.e., the 24 OH results from the first week of testing and the 36 OH results from the second week were the basis for separate calculations of accuracy.

3.3.2 Correlation with Reference Method

The correlation of the SG-II with the OH results was assessed using the same data used to assess accuracy. The average SG-II elemental and total mercury results over each OH sampling run were calculated and compared to the corresponding OH results.

3.3.3 Precision

Precision of the SG-II was determined based on the individual SG-II results for elemental and total mercury in each OH sampling run. The relative standard deviation of the successive SG-II readings was calculated as the measure of precision. This calculation was intended to assess CEM variability under conditions of stable mercury levels. Consequently, this calculation was limited to those time periods in which CEM data, facility data, and the observations of testing staff indicated that mercury addition and mercury flue gas levels were stable. Occasional spikes in mercury concentration were excluded from the calculation of precision, provided that the spikes were attributable to occurrences at the test facility, either by corroboration of multiple CEMs, or by observations of testing staff.

3.3.4 Calibration/Zero Drift

Day-to-day drift in SG-II response to calibration and zero gases was assessed by sampling zero gas (nitrogen) and a commercial standard of elemental mercury in nitrogen with the monitor each day. The standard gases used for this procedure are described in Section 3.4.1. Those gases were not used as absolute mercury standards, but only as sources of stable mercury levels over the test period. The calibration/zero check was done twice on each day of testing, before and after all other test activities. However, on the last day of each week, this test was done once and was combined with a check of the sampling system bias (see Section 3.3.5). A low concentration mercury standard (~ 15 $\mu g/m^3$) was used in the first week, and a higher concentration standard (~ 50 $\mu g/m^3$) was used in the second week, to parallel the flue gas mercury levels used (see Table 3-4).

Drift was assessed in terms of the range and relative standard deviation of the repeated zero and calibration checks. Separate assessments of drift were made for the two weeks of testing.

3.3.5 Sampling System Bias

In nearly all cases, the drift checks described in Section 3.3.4 were conducted by supplying the zero and standard gases directly at the analyzer inlet of the CEM. However, on the last day of each week of testing, a drift check conducted in that manner was followed immediately by a similar check in which each gas was supplied at the inlet of the CEM's flue gas sampling system. The ratio of the CEM response at the analyzer to that through the entire sampling system determined the bias caused by the sampling system.

The sampling system bias test was performed by supplying the mercury standard or zero gas to a side arm on the sampling probe upstream of the particle filter. The gas was supplied in excess, and gas flow beyond that drawn by the SG-II was vented through the probe into the duct. The gas supplied in this way passed through the probe, filter, and heated sampling lines before entering the speciation module of the SG-II.

3.3.6 Interferences

On Thursday, January 18, the same low mercury level used on previous days (see Table 3-4) was established in the RKIS flue gas. The addition of mercury alone continued for approximately two hours, during which time the SG-II sampled the flue gas to establish a baseline level of response. Then, with the mercury injection continuing as before, a series of potential interferant gases was injected into the flue gas, first one at a time, and then in combination. Finally, the gases were turned off, and the mercury injection alone was continued for about another half hour. The effect of the interferant gases was assessed by the changes in SG-II response occurring during the introduction of the gases.

Table 3-6 summarizes the schedule of the interference test on January 18. Shown are the substances injected into the RKIS flue gas in successive time intervals during this test. The concentrations shown in Table 3-6 are the target concentrations; actual concentrations were maintained within ± 10% of the target values.

Table 3-6. Schedule of January 18, 2001, Interference Test

		Substances Injected in Flue Gas (Target Concentration, ppm)				
Time	Hg[a] (µg/m^3)	NO	CO	SO_2	HCl	Cl_2
11:05 - 13:06	8					
13:06 - 13:39	8	500				
13:39 - 14:16	8		500			
14:16 - 15:05	8			2,000		
15:05 - 15:50	8				250	
15:50 - 16:30	8					10
16:30 - 17:06	8	500				10
17:06 - 17:36	8	500	500	2,000	250	10
17:36 - 18:02[b]	8					

[a] Approximate total mercury level.

[b] Brief inadvertent injection of Cl_2 to the duct occurred near the start of this time period.

3.3.7 Response Time

Response time of the SG-II was determined in both weeks of the test, as part of the calibration/ zero drift test. The rise time and fall time were determined by recording successive SG-II readings when the delivery of elemental mercury standard gas was started or stopped, respectively. The time to reach 95% of the final value was estimated from successive readings. The 5- to 6-minute cycle time of the SG-II limited the resolution of the time response determination. As a result, the response time is stated in terms of the percentage of response achieved in a single measurement cycle.

3.3.8 Low-Level Response

The mercury levels shown in Table 3-4 were not intended to challenge the detection limit of the SG-II. Instead the ability of the SG-II to detect low mercury levels was tested by a procedure conducted on January 19. On that day, the SG-II initially sampled RKIS flue gas with no mercury present, but with sulfur dioxide, nitrogen oxide, and hydrogen chloride present at the concentrations used in the first week of testing (i.e., 1,000 ppm, 250 ppm, and 25 ppm, respectively; Table 3-4). Injection of mercury then began, starting with a low mercury concentration, and stepping upwards in concentration at time intervals of about one-half hour. After the highest mercury concentration, the mercury injection was shut off, and flue gas without added mercury was again sampled. The mercury solutions used for this test had aqueous concentrations of 0.304 to 2.45 µg/mL, sufficient to produce total flue gas mercury concentrations of nominally 0.57 to 4.54 µg/m^3. The actual flue gas mercury concentrations were not determined; as a result, the nominal total mercury concentrations are used for comparison to the CEM results. The low-level response of the SG-II was determined based on the lowest mercury concentration detected above the flue gas background. Table 3-7 summarizes the schedule for this test.

Table 3-7. Schedule of January 19, 2001, Low-Level Response Test

Time Period	**Nominal Flue Gas Total Hg Concentration (µg/m^3)**
10:44 - 11:39	0
11:39 - 12:21	0.57
12:21 - 12:56	1.13
12:56 - 13:33	2.27
13:33 - 14:15	4.54
14:15 - 14:55	0

3.3.9 Data Completeness

Data completeness was determined by comparing the data recovered from the SG-II to the amount of data expected upon completion of all portions of the verification test. Data completeness was evaluated in terms of the percentage of total data recovered.

3.3.10 Setup and Maintenance Needs

Setup and maintenance needs were documented qualitatively, through observation and communication with the vendor during the verification test. Factors noted included the frequency of scheduled maintenance activities, the extent of any downtime, the number of staff operating or maintaining the CEM, and the quantity of consumables used and/or waste materials produced.

3.4 Equipment and Materials

3.4.1 Commercial Elemental Mercury Standards

Four commercial compressed gas standards of elemental mercury in nitrogen were used as stable sources of elemental mercury for verification of day-to-day instrument calibration drift and sampling system bias. These gases were purchased from Spectra Gases, Inc., Branchburg, New Jersey. Spectra Gases reported the nominal prepared mercury concentration of each standard and performed an initial analysis of each cylinder in November 2000, using a commercial CEM of a different design than those participating in the verification test. In addition, each of these standards was sampled before and after the verification test, using a miniature impinger train modeled after the OH method. Collected samples were then submitted for laboratory mercury analysis, along with the collected samples from OH flue gas sampling, to determine the cylinder gas mercury content. The protocol for conducting this miniature impinger sampling was subjected to review by ARCADIS and EPA staff and was approved by EPA prior to use in this study.(3) Unfortunately, the pre-test analysis results showed evidence of excessive loss of mercury in sampling the gas with the mini-impinger train. This possibility was subsequently confirmed by conducting the sampling with a different pressure regulator on the mercury gas standard. The regulator originally used was shown to remove some mercury from the gas and to require extremely long equilibration times to achieve stable delivery of mercury. Consequently, the pre-test results are not valid. Post-test results from the mini-impinger train, and from an EPA-owned mercury CEM like the one used by the gas vendor, are shown in Table 3-8.

Table 3-8 lists the mercury standards used, along with the vendor's nominal prepared concentration and initial analysis result, provided by Spectra Gases. Also listed in Table 3-8 are the cylinder concentrations determined post-verification in March 2001 by means of the mini-impinger sampling method and an EPA-owned mercury CEM.

Table 3-8. Mercury Standard Gas Identification and Analysis Results

		Pre-Test	Post-Test	
Cylinder Number	Prepared Hg°Conc. (µg/m³)[a]	Gas Vendor Analysis (µg/m³)	OH Mini-Train Analysis (µg/m³)	EPA CEM Analysis (µg/m³)
CC19870	12.5	14	11.7	9.3
CC19931	14.1	16	13.6	13.0
CC20219	44.0	49	50.2	47.0
CC20291	49.8	55	46.8	50.6

[a] Concentrations in µg/m³ converted from ppbv concentrations stated by Spectra Gases, using a conversion factor of 1 ppbv elemental mercury = 8.3 µg/m³ at 20°C and 1 atmosphere pressure.

Table 3-8 shows generally good consistency among the gas vendor's prepared mercury concentrations, the gas vendor's own pre-test analysis, and the post-test analyses. In particular, the agreement between the mini-impinger OH samples obtained post test and the vendor's prepared concentration is within 6.4%, 3.5%, 14.1%, and 6.0%, respectively, for cylinders CC19870, CC19931, CC20219, and CC20291. This agreement is good, considering the novel nature of these standards and the four-month time interval between their preparation and the post-test analysis.

Cylinders CC19931 and CC19870 were prepared at full cylinder pressure of 2,000 psig. However, because of vapor pressure limitations of elemental mercury, cylinders CC20291 and CC20219 were prepared with an initial pressure of only 900 psig. To assure consistent testing of day-to-day drift, each CEM undergoing verification was challenged repeatedly with just one gas standard in each week of testing. In addition, to assure sufficient gas to complete the testing in each week, the gas standards were assigned to participating CEMs in such a way as to balance the consumption of all standard gases. Thus, the SG-II was challenged in the first week of testing only with mercury standard cylinder number CC19870 and, in the second week, only with cylinder number CC20219. In both weeks of testing, the use of those cylinders was shared among the SG-II and two other CEMs. The final gas pressures in the elemental mercury standards at the conclusion of testing were approximately 900 psig and 1,000 psig in cylinders CC19870 and CC19931, respectively, and approximately 300 psig and 550 psig in cylinders CC20219 and CC20291, respectively.

The mercury standard cylinders were used with miniature low-volume stainless steel regulators (Spectra Gases 04-1D3EATNN-018), which were flushed for about 30 minutes before use with a 0.5 L/min flow of the standard gas. The delivery plumbing from the regulators was originally made almost entirely of SilcoSteel® fittings, i.e., stainless steel internally coated with a layer of glass. However, long equilibration times were observed in first supplying the 12.5 and 14.1 µg/m³ standards to the CEMs in the first week of testing. Consequently, the delivery system was modified to consist of all Teflon, except for the regulator itself. This change notably improved the delivery of the mercury gas standards to the CEMs.

3.4.2 Performance Evaluation Equipment

Performance evaluation (PE) audits were conducted on several key measurements at the RKIS. Each of those audits was conducted using a reference standard or measurement system provided by Battelle that was independent of that used in the verification test. Table 3-9 lists the PE audit equipment used and, when appropriate, the date of the calibration of the audit equipment prior to the verification test. The PE audit of the OH mercury analysis was done by spiking blank trains with a dilution of a National Institute of Standards and Technology (NIST)-traceable mercury standard. The results of the PE audits are reported in Section 4.3.2.

Table 3-9. Performance Evaluation Audit Equipment Used for the Verification Test

Measurement Audited	PE Equipment	Date Calibrated	Source of Calibration
Flue gas O_2 and CO_2	LandTec GA-90 Gas Analyzer, Model GA1.1 (S. No. 693)	12/19/00	Vendor
Flue gas temperature	Fluke Model 52, (S. No. 73970010) with Type K Thermocouple	11/29/00	Battelle Instrument Lab
Barometric pressure	Taylor Model 2250M Aneroid Barometer (Inventory No. LN163610)	12/20/00	Battelle Instrument Lab
Flue gas pressure	Magnehelic Model 2005 (S. No. R51006LG64)	10/25/00	Battelle Instrument Lab
Impinger weighing	Cenco Class T Weight Set (200 g and 500 g weights)	1/3/01	Battelle Instrument Lab
Ontario Hydro mercury analysis	EM Science Atomic Absorption Standard MX0399-2, traceable to NIST SRM #1333.	NA	Vendor

Chapter 4
Data Quality

The quality of the verification data was assured by quality assurance and quality control (QA/QC) procedures, performed in accordance with the quality management plan (QMP) for the AMS Center(4) and the test/QA plan(1) for this verification test. Minor deviations from the test/QA plan were documented in the verification records at the RKIS during testing. Deviations required the approval of Battelle's AMS Center Manager. A planned deviation form was used for documentation and approval of each of the following changes:

1. The elemental mercury gas standards were not analyzed by the University of North Dakota Energy and Environmental Research Center because the procedure to be used would have consumed a substantial fraction of each standard.

2. The performance evaluation for oxygen and carbon dioxide measurements at the RKIS used an electrochemical monitor for these gases rather than paramagnetic and infrared monitors, as stated in the plan.

3. The solution used for the injection of mercury into the RKIS duct was made with mercuric chloride instead of mercuric nitrate.

4. As a result of the use of mercuric chloride rather than mercuric nitrate for the injection solution, the stock solution was made up with hydrochloric acid instead of nitric acid, and no additional acid was added in making up dilutions of the stock solution.

5. Recovered OH samples were stored at room temperature before delivery to the analytical laboratory, consistent with OH method requirements, instead of under refrigeration.

6. To better test the capabilities of the mercury CEMs, the low-level response test was conducted with flue gas mercury levels of about 0.5, 1, 2, and 4 $\mu g/m^3$ instead of 1, 2, 4, and 8 $\mu g/m^3$.

7. The RKIS carbon dioxide CEM was changed before the verification test began. A Fuji Electric Model ZRH-1 was in place at the RKIS, instead of the Horiba VIA 510 stated in the test/QA plan.

8. Calculation of interference effects in terms of “relative sensitivity” was not done, since this calculation was inappropriate in situations where chemical transformations of mercury species took place.

None of these deviations had any significant effect on the quality of the verification data.

4.1 Facility Calibrations

Continuous monitors for oxygen, carbon monoxide, carbon dioxide, nitrogen oxides, sulfur dioxide, and hydrogen chloride are installed at the RKIS and its associated APCS to monitor system performance and document flue gas composition. For this verification test, those monitors were calibrated according to standard facility practice on each test day. Calibration procedures consisted of a multipoint calibration check at the start of the day and a drift check at the end of the day. On days when OH sampling was conducted, the drift check was also conducted after each OH run. All calibration results were within the allowable tolerances for drift and linearity. All calibration results were documented for inclusion in the verification data files.

Flue gas water content was determined from impinger weights in the OH trains by means of an electronic balance located in the OH train preparation/recovery laboratory. Copies of the calibration records for that balance were included in the data file.

Key measurements that factored directly into the verification test results were also the subject of PE audits, as described in Section 4.3.2. Those measurements included the facility CEMs for oxygen and carbon dioxide and the balance used for determination of water.

4.2 Ontario Hydro Sampling and Analysis

The preparation, sampling, and recovery of samples from the OH trains followed all aspects of the QA/QC requirements in the OH method. A daily blank train was prepared, kept at either the upstream or downstream sampling location during sample runs, and recovered along with the sampled trains. The impinger glassware used for preparing the blank train was selected at random each day from among the several sets used, so that blank results reflect the actual state of the sampling equipment. All required reagent blanks were collected, and additional reagent blanks (beyond those required in the method) of the acetone rinse reagent and of the 5% w/v potassium permanganate called for in Section 13.2.8.3 of the OH method were collected. A sample numbering system was implemented that provided unique identification of each train and of each recovered sample from that train. This numbering system was implemented by means of preprinted labels applied to sample containers arranged in order of sample recovery for each train. The recovered samples were delivered to the analytical laboratory within about 24 hours after collection. Oxford Laboratories, which conducted the OH analyses, similarly adhered to all requirements of the OH analytical process. Replicate analysis of samples was performed as required by the OH method, and all results met the 10% acceptance criterion. The analytical results for each set of analyses were accompanied by data quality documentation that reported the laboratory calibration procedures and results applicable to those analyses.

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 Precision

The results of the OH flue gas sampling and analysis are shown in Tables 4-1a-c and 4-2a-c, for the first and second weeks of verification testing, respectively. Tables 4-1a and 4-2a show the elemental mercury results, Tables 4-1b and 4-2b the oxidized mercury results, and Tables 4-1c and 4-2c the total vapor-phase mercury results from the OH runs. Particulate mercury, determined on one OH particulate filter at each location in each OH run, was not detectable during the first week of verification testing. During the second week of testing, of the 18 filters analyzed for particulate mercury, 11 showed mercury of less than 0.5 $\mu g/m^3$, five showed levels 0.5 to 1 $\mu g/m^3$, and two showed levels of 1.0 to 1.5 $\mu g/m^3$. Thus, particulate mercury was a negligible fraction of the total mercury present in RKIS flue gas.

Inspection of the data in these tables shows that, in nearly all cases, the agreement between duplicate OH results (i.e., the precision of the OH method) was good at both the upstream and downstream sampling locations. Furthermore, the mercury levels determined at the upstream location generally agreed closely with those at the downstream location. This observation indicates that little loss of mercury or change in mercury speciation occurred during the transit of flue gas from one location to the other. The variability in OH results was larger in the second week of sampling (Tables 4-2a-c) than in the first week (Tables 4-1a-c). This undoubtedly results in part from the greater proportion of oxidized mercury present in the second week. The oxidized mercury is more difficult to transport and sample, and the proportion of oxidized mercury may have varied due to small variations in RKIS conditions (e.g., temperature). Day-to-day variations in mercury results in the second week are also due in part to changes in delivery conditions. Most notably, the pump used to inject the mercury solution into the RKIS failed during OH Run 9 on January 22 and was replaced with a different pump. The higher total mercury levels measured on January 23 and 24, relative to those on January 22, are probably due to a slightly higher delivery rate on those days.

To quantify the characteristics of the OH reference data before using them for verification of the SG-II, the OH data were subjected to a statistical analysis, addressing three issues:

- The precision of the duplicate OH results at both the upstream and downstream sampling locations

- The agreement between the mercury levels determined by the OH method at the upstream and downstream sampling locations

- The identification of any outliers in the data.

These issues were addressed separately for the elemental, oxidized, and total mercury data.

Table 4-1a. Elemental Mercury Results from OH Sampling in the First Week of Verification Testing

		Elemental Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/15/01	Run 1	6.78	6.49	6.28	6.29
1/15/01	Run 2	6.20	6.23	6.18	5.98
1/16/01	Run 3	6.51	6.52	6.09	6.12
1/16/01	Run 4	6.43	7.00	7.55	6.50
1/17/01	Run 5	6.31	6.53	6.03	5.95
1/17/01	Run 6	6.10	6.56	5.29	5.99

Table 4-1b. Oxidized Mercury Results from OH Sampling in the First Week of Verification Testing

		Oxidized Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/15/01	Run 1	1.11	1.11	1.23	1.07
1/15/01	Run 2	0.93	1.11	1.20	1.36
1/16/01	Run 3	1.05	1.05	1.25	1.12
1/16/01	Run 4	1.09	0.99	1.40	1.26
1/17/01	Run 5	1.32	1.29	1.42	1.30
1/17/01	Run 6	1.70	1.42	1.64	1.68

Table 4-1c. Total Mercury Results from OH Sampling in the First Week of Verification Testing

		Total Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/15/01	Run 1	7.89	7.60	7.51	7.36
1/15/01	Run 2	7.13	7.34	7.38	7.34
1/16/01	Run 3	7.56	7.57	7.34	7.24
1/16/01	Run 4	7.52	7.99	8.95[a]	7.76
1/17/01	Run 5	7.63	7.82	7.45	7.25
1/17/01	Run 6	7.80	7.98	6.93	7.67

[a] Shaded cells indicate data excluded as outliers.

Table 4-2a. Elemental Mercury Results from OH Sampling in the Second Week of Verification Testing

		Elemental Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/22/01	Run 7	11.1	12.4	11.4	11.6
1/22/01	Run 8	14.3	15.1	13.6	11.5
1/22/01	Run 9	25.1	20.9	27.4	27.4
1/23/01	Run 10	3.5[a]	7.0	6.0	6.9
1/23/01	Run 11	8.2	9.3	7.2	7.5
1/23/01	Run 12	8.0	8.1	6.7	3.7[a]
1/24/01	Run 13	6.8	7.2	6.4	6.2
1/24/01	Run 14	4.9	5.4	6.3	5.7
1/24/01	Run 15	6.7	6.9	7.6	5.2

[a] Shaded cells indicate data excluded as outliers.

Table 4-2b. Oxidized Mercury Results from OH Sampling in the Second Week of Verification Testing

		Oxidized Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/22/01	Run 7	61.4	67.3	63.3	69.1
1/22/01	Run 8	71.2	75.2	67.2	67.4
1/22/01	Run 9	46.5	33.2[a]	44.0	46.0
1/23/01	Run 10	60.5[a]	97.0	96.3	97.7
1/23/01	Run 11	111.2	110.2	100.5	98.5
1/23/01	Run 12	113.8	114.3	105.5	70.5[a]
1/24/01	Run 13	88.0	88.0	85.6	84.5
1/24/01	Run 14	77.7	87.7	81.6	67.5
1/24/01	Run 15	86.9	91.4	84.8	81.8

[a] Shaded cells indicate data excluded as outliers.

Table 4-2c. Total Mercury Results from OH Sampling in the Second Week of Verification Testing

		Total Hg (µg/m^3)			
		Upstream		Downstream	
Date	Port Location	2A	2C	8A	8C
1/22/01	Run 7	72.5	79.7	74.7	80.7
1/22/01	Run 8	85.4	90.2	80.7	78.9
1/22/01	Run 9	71.5	54.1[a]	71.4	73.4
1/23/01	Run 10	64.0[a]	104.0	102.3	104.6
1/23/01	Run 11	119.4	119.5	107.7	106.1
1/23/01	Run 12	121.8	122.5	112.2	74.1[a]
1/24/01	Run 13	94.9	95.2	92.0	90.7
1/24/01	Run 14	82.6	93.1	87.9	73.2
1/24/01	Run 15	93.6	98.3	92.4	87.0

[a] Shaded cells indicate data excluded as outliers.

The precision of duplicate OH trains at both sampling locations was assessed by Student's t-tests. Nonparametric Wilcoxon Rank Sum tests were also used to compare the results from the t-tests. The outcome of this analysis was that, in the first week of verification testing, the average agreement of paired OH trains was within 2.7% for elemental mercury, within 4.4% for oxidized mercury, and within 1.7% for total mercury. In the second week of testing, agreement of paired trains was within 14.8% for elemental mercury, within 7.2% for oxidized mercury, and within 8.1% for total mercury. These results are very good considering the low concentrations of mercury species and the difficulty of preparing and sampling oxidized mercury in the flue gas. The statistical analysis found no significant differences between the paired OH results (i.e., port A vs port C) for elemental, oxidized, or total mercury at either the upstream or the downstream sampling location.

Evaluation of upstream/downstream differences in the OH results used an analysis of variance (ANOVA) approach. Student's t-tests and Nonparametric Wilcoxon Rank Sum tests were also used to compare the results of the ANOVA. The statistical analysis found no significant differences between the upstream and downstream levels of elemental or total mercury in either week of testing. The upstream and downstream elemental mercury levels agreed on average within 4.9% and within 7.0% in the first and second week of testing, respectively. Those of total mercury agreed within 2.0% and within 4.3%, respectively. Similarly, in the second week of testing, the upstream and downstream levels of oxidized mercury agreed within 4.2%. On the other hand, a significant upstream/downstream difference of 11.2% in oxidized mercury was found in the first week of testing. However, it must be noted that this resulted from an average absolute difference of only 0.15 µg/m^3 at oxidized mercury levels of 1.2 to 1.3 µg/m^3. This absolute difference is comparable to the detection limit of the OH method. Although a significant upstream/downstream difference may be indicated by the statistical tests, the agreement between upstream and downstream oxidized mercury levels is still very good considering the low mercury levels present.

The analysis for outliers in the OH data relied on a studentized residual approach as the primary criterion, with COVRATIO and DFFITS statistics(5) as secondary criteria. A mercury measurement was considered an outlier if the primary criterion and at least one of the secondary criteria were met. The aim of this analysis was to identify OH results that were not accurate indications of the flue gas mercury content, rather than to eliminate data that resulted from facility or other variations. For example, the statistical analysis identified all the elemental mercury results from OH Run 9 (20.9 to 27.4 µg/m^3, Table 4-2a) as outliers relative to other data from the second week of testing. However, those values are thought to arise from the failure of the mercury solution delivery pump in that run and the interruption and resumption of mercury delivery to the RKIS. That is, the OH elemental mercury results from Run 9 are thought to reflect actual test facility variability. As a result, most of the OH results from Run 9 have been retained in the data set. On the other hand, the analysis did disclose a few outliers in the OH data, which are shown in Tables 4-1a-c and 4-2a-c in shaded cells. Those values were excluded from the calculations used to verify mercury CEM performance on the basis of the duplicate precision and upstream/downstream differences for individual results. In this analysis, the precision of paired results was compared to the average precision results stated above. Individual values showing differences greater than three times the average precision were excluded. As Tables 4-1 and 4-2 show, this procedure excluded a few individual values differing sharply from the other simultaneous OH results.

As a result of these analyses of the OH data, it was concluded that each OH result, excluding outliers, could be taken as a separate and independent measurement of flue gas composition. The result of excluding the outlying values is that, for the first week of testing, 24 values for elemental and oxidized mercury were used in the verification and 23 values for total mercury. For the second week of testing, 34 values for elemental mercury and 33 values for oxidized and total mercury were used.

4.2.2 Ontario Hydro Blank Trains

Table 4-3 shows the analytical results from the six blank OH trains collected during the verification test. This table lists the flue gas concentrations (in µg/m^3) that would be inferred from the blank train results, assuming gas sample volumes of 2 m^3 in the first week of testing and 1 m^3 in the second week. Results are shown for oxidized mercury (from the potassium chloride impingers of the OH trains) and for elemental mercury (from both the peroxide and potassium permanganate impingers of the OH trains). The detection limit for mercury in these samples was 0.1 µg. As Table 4-3 indicates, the great majority of blank train results were below the detection limit, and the few detectable mercury levels were negligible when compared to the levels actually found in the flue gas samples (Section 4.2.1). These results indicate that OH samples were not exposed to contamination sources during sample recovery, handling, and analysis.

Table 4-3. Equivalent Flue Gas Mercury Concentrations (µg/m^3) Found in Blank OH Trains

Date	Train ID	Oxidized Hg	Hg^o (H_2O_2)	Hg^o ($KMnO_4$)
1/15/01	I-GR-OHI-1[a]	< 0.05	< 0.05	0.29
1/16/01	I-GR-OHA-2[a]	<0.05	<0.05	<0.05
1/17/01	I-GR-OHB-3[a]	<0.05	<0.05	<0.05
1/22/01	II-GR-OHI-4[b]	<0.1	<0.1	0.31
1/23/01	II-GR-OHI-5[b]	<0.1	<0.1	<0.1
1/24/01	II-GR-OHI-6[b]	0.12	<0.1	<0.1

[a] Equivalent flue gas concentrations calculated from blank train results using assumed sample volume of 2 m^3.
[b] Equivalent flue gas concentrations calculated from blank train results using assumed sample volume of 1 m^3.

4.2.3 Ontario Hydro Reagent Blanks

A total of 39 samples of the various OH reagents were collected for analysis between January 15 and January 24, covering all impinger reagents and train rinse solutions. Mercury was found at detectable levels in only two of those 39 samples. The levels found in those two samples were negligible in terms of their equivalent flue gas mercury concentration when compared to the concentrations found in the actual flue gas samples (Section 4.2.1).

4.3 Mercury Mass Balance

Because of the potential for loss of mercury from the flue gas, a valuable QA exercise is to calculate the mass balance of mercury in the RKIS facility. This was done by comparing the total mercury result from each OH train (Section 4.2.1) to the expected total mercury level in the RKIS flue gas, based on the duct flow rates and the concentrations and flow rates of the injection solutions. The ratio of the OH total mercury to the expected total mercury, expressed as a percentage, is defined as the percent recovery of the injected mercury. Table 4-4 summarizes this comparison, showing percent recovery values for both the upstream and downstream OH results for both weeks of the verification test. In each case, the mean and standard deviation, maximum, minimum, and median of the percent recovery values are shown. The outliers identified in Section 4.2.1 were excluded from this calculation.

Table 4-4. Percent Recovery of Total Mercury Injected into the RKIS

Period	Parameter	Upstream Recovery (%)	Downstream Recovery (%)
Week One			
	Mean (Std. Dev.)	112.2 (13.1)	111.3 (8.7)
	Maximum	137.7	122.2
	Minimum	100.8	99.5
	Median	105.0	113.0
Week Two			
	Mean (Std. Dev.)	110.7 (14.2)	112.1 (14.4)
	Maximum	134.4	136.2
	Minimum	91.2	87.3
	Median	108.4	110.8

Table 4-4 shows that the mass balance for mercury injected into the RKIS was good. Over the entire verification test, the minimum mass balance value was 87.3% and the maximum was 137.7%. For both sampling locations in both weeks of testing, the average mass balance was about 111 to 112%. These results confirm that mercury injected into the RKIS was not lost, and in particular confirm that there was no significant difference in mercury levels between the upstream and downstream sampling locations. Table 4-4 does indicate that the OH results were usually higher than the expected mercury level by about 10 to 12%, on average.

4.4 Audits

4.4.1 Technical Systems Audit

Battelle's Quality Manager performed an internal technical systems audit (TSA) of the verification test on January 16 and 17, 2001, during the first week of testing. The TSA ensures that the verification test is conducted according to the test/QA plan(1) and that all activities associated with the test are in compliance with the AMS Center QMP.(4) On January 16 the Battelle Quality Manager visited the RKIS test site, where he toured the test area, observed the performance of OH method sampling, reviewed Battelle notebooks and calibration gas certificates, reviewed facility CEM calibration records, and met with the ARCADIS Quality Manager. On January 17, the Battelle Quality Manager visited Oxford Laboratories and reviewed the OH analysis procedures in use there. All the observations of the Battelle Quality Manager were documented in a TSA report. There were no findings of any issues that could adversely affect verification data quality. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

In addition to the internal TSA performed by Battelle's Quality Manager, an external TSA was conducted by EPA on January 23, 2001. The EPA external TSA included all the components of the internal TSA, except that EPA QA staff did not visit Oxford Laboratories. The findings of this TSA were documented in a report submitted to the Battelle Quality Manager. No adverse findings were noted in this external TSA.

4.4.2 Performance Evaluation Audits

A series of PE audits was conducted on several different measurements at the RKIS 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 EPA and ARCADIS staff. These audits addressed only those measurements that factored into the data used for verification. Each PE audit was performed by analyzing a standard or comparing to a reference independent of standards used during the testing (see Section 3.4.2). Each PE audit procedure was performed once during the verification test, with the exception that OH trains were spiked once in each week of testing. Table 4-5 summarizes the PE audits on several measurement devices of the RKIS; Table 4-6 summarizes the PE audit results from spiking OH trains.

Table 4-5 shows that all the PE audit results on measurement devices were well within the required tolerances stated in the test/QA plan.(1) The PE audit for oxygen and carbon dioxide was conducted by sampling the same gas entering the facility oxygen and carbon dioxide CEMs, using a portable monitor for those gases. This was done using a "T" fitting at the inlet of each facility CEM, so that the readings from the portable audit monitor and the CEMs were obtained

Table 4-5. Summary of PE Audits on Mercury CEM Verifications

Measurement Audited	Date	Audit Method	Observed Agreement	Required Agreement
Flue gas O_2	1/19/01	Comparison to independent O_2 measurement	0.1% O_2	1% O_2
Flue gas CO_2	1/19/01	Comparison to independent CO_2 measurement	5% of CO_2 reading	10% of CO_2 reading
Flue gas temperature	1/18/01	Comparison to independent temperature measurement	1.0% absolute T	2% absolute T
Local barometric pressure	1/15/01	Comparison to independent barometric pressure measurement	0.43 " H_2O	0.5 " H_2O
Flue gas pressure	1/19/01	Comparison to independent pressure measurement	0.02 " H_2O	0.5 " H_2O
Impinger weights (electronic balance)	1/18/01	Weighing certified weights	0.03% (0.14 g at 500 g)	Larger of 1% or 0.5 g

in simultaneous sampling of the flue gas. Duct temperature measurement was audited by inserting a calibrated thermocouple into the same location in the duct as the temperature probe used for Method 2 velocity measurements. The small temperature difference observed probably resulted from the inability to place the two probes at exactly the same location in the small duct.

Barometric pressure was audited using a calibrated aneroid barometer. Flue gas pressures were audited using a Magnehelic gauge installed in parallel with a set of similar gauges used for the Method 2 velocity determinations. Gauges with ranges of 0 to 0.25, 0 to 0.5, and 0 to 2 inches of water were audited. The PE audit of the electronic balance used certified weights of 200 and 500 grams; the observed agreement shown in Table 4-5 is for the 500-gram weight, which showed the greater percentage deviation.

The PE audit of the OH train mercury analysis was conducted once in each week of the test, and the results are summarized in Table 4-6. In the first week, impingers 1 (KCl), 4 (H_2O_2/HNO_3), and 5 ($KMnO_4/H_2SO_4$) of a blank OH train (I-LB-ST-1) were each spiked with 1 mL of a NIST-traceable solution containing 10 µg/mL of mercury. In the second week, the same impingers of a blank train (II-LB-ST-2) were each spiked with 3 mL of the same solution. As Table 4-6 shows, recovery of the spiked mercury was well within the 10% tolerance stated in the test/QA plan (1) for all spiked samples except the potassium permanganate impinger from the first spiked train. These results indicate that the OH analysis was accurate at spiked mercury levels comparable to those collected in the actual OH sampling. The high readings obtained in analysis of the 5 impinger from the first spiked train may have been caused by the need to spike that train twice. That is, train I-LB-ST-1 was originally spiked on January 18 and stored overnight for recovery.

Table 4-6. Results of PE Audit of OH Train Analysis

Date	Train	Impinger[a] Number	Spike[b] (µg)	Analyses 1st (µg)	 2nd (µg)	 Average (µg)	Observed Agreement[c] (%)	Required Agreement (%)
1/19/01	I-LB-ST-1	1	10	9.75	9.53	9.64	-3.6	10
		4	10	9.85	9.61	9.73	-2.7	10
		5	10	11.6	12.0	11.8	18	10
1/24/01	II-LB-ST-2	1	30	29.6	29.9	29.75	-0.8	10
		4	30	29.9	30.0	29.95	-0.2	10
		5	30	28.7	28.5	28.6	-4.7	10

[a] Impinger 1 = KCl, 4 = H_2O_2, 5 = $KMnO_4$.

[b] Amount of mercury injected based on dilution of NIST-traceable standard.

[c] Observed Agreement = (Average analysis - Spike)/Spike × 100.

However, inadvertent pressurization caused a spillover between impingers 4 and 5 overnight. As a result, the train was emptied, rinsed, refilled, and spiked on January 19, as indicated in Table 4-5. The higher-than-expected mercury level in impinger 5 may have resulted from contamination during this process.

4.4.3 Data Quality Audit

Battelle's Quality Manager audited at least 10% of the verification data acquired in the verification test. The Quality Manager traced the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing audit were checked.

Chapter 5
Statistical Methods

The following statistical methods were used to reduce and generate results for the performance factors.

5.1 Relative Accuracy

The relative accuracy (RA) of the SG-II with respect to the elemental and total mercury results of the reference (OH) method was assessed by the following equation, which is incorporated in EPA performance specifications for continuous emission monitoring systems:

$$RA = \frac{|\bar{d}| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\% \tag{1}$$

where *d* refers to the arithmetic difference between corresponding OH and SG-II results, and *x* corresponds to the OH result. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the 100(1 - α)th percentile of the distribution with n-1 degrees of freedom. To calculate RA, the OH and corresponding SG-II results were paired, and the differences between the paired results were calculated. Then, the absolute mean $\left|\bar{d}\right|$ and standard deviation (S_d) of those differences were calculated. The mean of the OH results $\left(\bar{x}\right)$ was calculated, and the value of t^{α}_{n-1} was taken from appropriate tables for the relevant values of *n* and *α*. The RA was determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). RA was calculated separately for the first and second week of testing. The OH results used for the RA calculation were as stated in Section 4.2.1.

5.2 Correlation with Reference Method

The degree of correlation of the SG-II with the reference method results was assessed in terms of the coefficient of determination (r^2), which is the square of the correlation coefficient (r). This calculation was made separately for the first and second week of testing, and also for the full data set from both weeks of testing.

5.3 Precision

Precision was calculated in terms of the percent relative standard deviation (RSD) of a series of CEM measurements made during stable operation of the RKIS, with mercury injected at a constant level into the combustion zone. During each OH sampling run, all elemental and total mercury readings from the SG-II were recorded, and the mean and standard deviations of those readings were calculated. Precision (*P*) was determined as

$$P = \frac{S}{\bar{X}} \times 100 \qquad (2)$$

where *S* is the standard deviation of the readings and $\bar{X}$ is the mean of the readings.

5.4 Calibration/Zero Drift

Calibration and zero drift were determined in a relative sense, rather than as deviations from an absolute standard, using the elemental mercury gas standards and high-purity nitrogen as zero gas. In the first week, nine elemental mercury standard readings, and nine zero readings, were used for this calculation. In the second week, seven readings of each type were available for this calculation. Drift was calculated in terms of the RSD, as

$$RSD = \frac{S}{\bar{x}} \; x \; 100 \qquad (3)$$

where $\bar{x}$ is the mean, and *S* the standard deviation, of the daily readings on standard or zero gas. This calculation, along with the range of the data, indicated the day-to-day variation in zero and standard readings.

5.5 Sampling System Bias

Sampling system bias was calculated as the difference in SG-II response when sampling elemental mercury standard gas through the SG-II's entire sample interface, compared to that when sampling the same gas directly at the SG-II analyzer, expressed as a percentage of the response at the analyzer. That is,

$$B = \frac{R_{si} - R_a}{R_a} \; x \; 100 \qquad (4)$$

where B is the percent bias, R_{si} is the reading when the standard gas is supplied at the sampling inlet, and R_a is the reading when the standard is supplied to the analyzer.

5.6 Interferences

Interferences were determined during sampling of combustion flue gas, in terms of the difference in response to a constant mercury level when potential interferant gases were added or removed. Interferences were assessed in terms of the effect of the interferant species (NO_x, CO, SO_2, HCl, Cl_2) introduced alone or together into the flue gas. The interferant levels were established by means of the facility CEM responses for each interferant, as described in Section 3.2.1.

5.7 Response Time

The response time was determined as the time after a step change in mercury concentration when the SG-II reading reached a level equal to 95% of that step change. Both rise time and fall time were determined. The SG-II response times were determined in conjunction with a calibration/zero drift check, by starting or stopping delivery of the elemental mercury standard gas to the SG-II's sampling interface, recording readings until stable readings were obtained and then estimating the 95% response time.

5.8 Low-Level Response

The ability of the SG-II to determine low mercury concentrations was assessed by comparing responses at nominal total mercury levels of 0, 0.57, 1.13, 2.27, and 4.54 $\mu g/m^3$ in the RKIS flue gas. This test was conducted in a flue gas matrix containing elevated levels of sulfur dioxide, nitrogen oxides, and hydrogen chloride, as described in Section 3.3.8. The lowest mercury level producing a response above that with no mercury added is of interest in this test.

Chapter 6
Test Results

6.1 Relative Accuracy

Table 6-1 shows the elemental, oxidized, and total vapor phase mercury results from the SG-II during the period of each OH sampling run. These results may be compared to the OH results in Tables 4-1 and 4-2. Note that the averages shown in Table 6-1 are based on 12 to 13 SG II measurements of elemental mercury, and an equal number of total mercury, in each 2-hour OH run in the first week of testing (i.e., OH Runs 1-6). The averages for the second week of testing (i.e., OH Runs 7-15) are based on 3 to 5 measurements of elemental mercury, and 6 to 9 measurements of total mercury, in each 1-hour OH run. The oxidized mercury averages in Table 6-1 are the calculated differences between corresponding total and elemental mercury averages.

In general, the SG-II results were similar to those of the OH method in the first week of testing, but less so during the second week. Comparison of Tables 4-1 and 4-2 with Table 6-1 shows that in the first week the SG-II indicated elemental, oxidized, and total mercury levels that were usually lower than, but in similar proportions to, the OH results for these species. The levels indicated by the SG-II were uniform from day to day, consistent with the OH results. In the second week, the SG-II elemental mercury results were close to the OH results in all runs except Run 9, for which a difference of nearly a factor of three was seen. In that week, the oxidized mercury results from the SG-II were found to be lower than those from the OH method. The total mercury results followed the same pattern because of the predominance of oxidized mercury in the duct in that week. These results suggest that the SG-II could not accommodate the high proportion and large concentration of oxidized mercury in the second week of testing. Given the difficulty of sampling oxidized mercury, it is possible that this disagreement may be due to loss of oxidized mercury in the inlet system of the SG-II. One possible factor could be differences in flow rates over the particle filters, i.e., the OH method used a flow of 16.6 L/min, and a new filter was used for each run; whereas the SG-II used a flow rate of 5 L/min, and the filter was changed after the first week of testing.

The results of the calculation of RA for the SG-II are shown in Table 6-2, which provides separate RA results for the two weeks of testing for measuring elemental, oxidized, and total vapor-phase mercury by the SG-II. The RA results reflect the observations noted above. The RA values of about 23 and 21%, respectively, for elemental and total mercury in the first week indicate that the SG-II agreed with the OH results for these species within about 1.5 to 2 µg/m^3, at their flue gas levels of roughly 6 to 8 µg/m^3 (Tables 4-1a and 4-1c). The 27% RA for oxidized

Table 6-1. Summary of Mercury Results from SG-II During OH Sampling Runs

Date	OH Run Number	SG-II Results (µg/m^3)		
		EM[a]	OM[a]	TM[a]
January 15	1	4.88	1.18	6.06
	2	4.88	1.07	5.95
January 16	3	5.13	1.08	6.21
	4	5.17	0.94	6.11
January 17	5	5.36	0.83	6.19
	6	5.01	1.06	6.07
January 22	7	9.1	47.7	56.8
	8	9.5	50.6	60.2
	9	9.6	45.9	55.4
January 23	10	5.3	68.2	73.6
	11	5.5	61.3	66.8
	12	5.2	67.4	72.5
January 24	13	6.2	65.0	71.2
	14	5.0	62.9	68.0
	15	5.0	71.1	76.0

[a] EM = elemental mercury, OM = oxidized vapor-phase mercury, TM = total vapor-phase mercury.

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

Test Period	Relative Accuracy (%)		
	Elemental Hg	Oxidized Hg	Total Vapor Hg
Week One	22.8	27.2	20.6
Week Two	29.6[a]	33.3	32.8

[a] Value based on excluding OH Run 9; if that run is included, RA is 50.4 %.

mercury in that week indicates that the SG-II generally agreed with the OH results within about 0.35 µg/m^3, based on the average OH oxidized mercury level of 1.25 µg/m^3 that results from the data in Table 4-1b.

The results in Table 6-2 for the second week reflect the fact that the SG-II read close to the OH results for elemental mercury, but consistently lower for oxidized mercury. The RA value for elemental mercury in week two was greatly affected by the poor agreement seen in OH Run 9. In that run, the mercury spikes caused by failure of the delivery pump may not have been completely observed by the SG-II in its elemental mercury mode, because that mode was run less often in this period of testing (see Section 3.2.2). As a result, OH Run 9 has been excluded from the elemental mercury accuracy calculation summarized in Table 6-2. The RA values for oxidized and total mercury in the second week reflect the consistently low readings obtained from the SG-II for oxidized mercury relative to the OH results. Note that these values are little affected by the inclusion or exclusion of OH Run 9, so that run is included in the RA calculation for oxidized and total mercury.

As described in Section 4.3, the OH total mercury results generally exceeded the expected mercury level in the duct by 10 to 12%. Thus, the agreement of the SG-II with the expected flue gas mercury levels was better than that shown in Table 6-2 relative to the OH results. This observation is noteworthy because the SG-II agreed closely with the expected flue gas mercury level in the low-level response test described in Section 6.8.

6.2 Correlation

The correlation of the SG-II monitor with the OH reference method was calculated using the elemental, oxidized, and total mercury results shown in Table 6-1. Correlation plots of the SG-II and OH data from the first week, second week, and both weeks combined are shown in Figures 6-1a to c, respectively. These figures also show the linear regression results and correlation coefficients (r) for elemental, oxidized, and total vapor-phase mercury. The resulting coefficients of determination (r^2) for each of these types of data for each week of testing and for both weeks combined, are shown in Table 6-3.

Table 6-3. Correlation of SG-II Data with OH Results

	Coefficient of Determination (r^2)		
Test Period	**Elemental Hg**	**Oxidized Hg**	**Total Vapor Hg**
Week One	0.012	0.042[a]	0.025
Week Two	0.837[b]	0.583	0.397
Both Weeks	0.853[c]	0.951	0.957

[a] This r^2 value is based on a negative value of r.

[b] Excludes OH Run 9; if included r^2 = 0.637.

[c] Excludes OH Run 9; if included r^2 = 0.688.

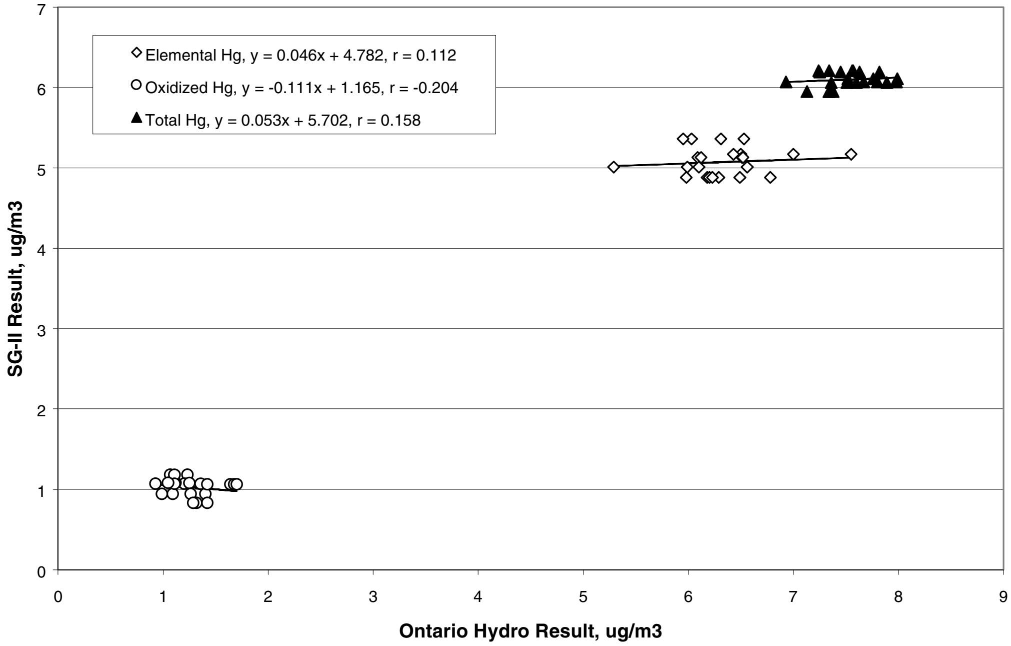

Figure 6-1a. Correlation of SG-II and OH Results from Week One of Verification

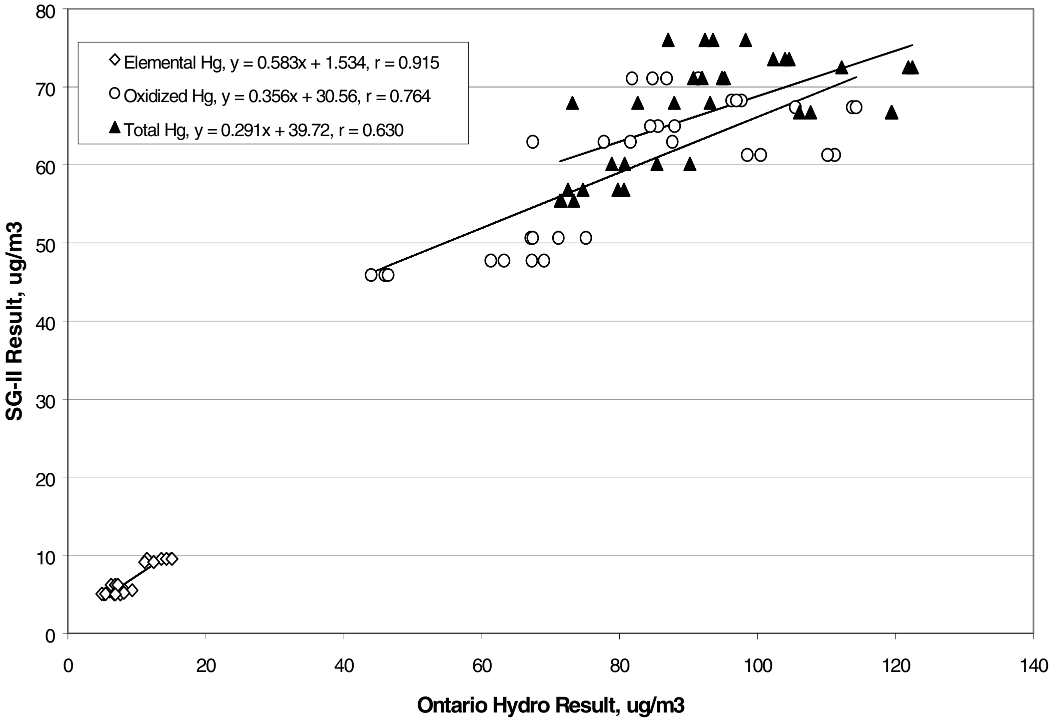

Figure 6-1b. Correlation of SG-II and OH Results from Week Two of Verification

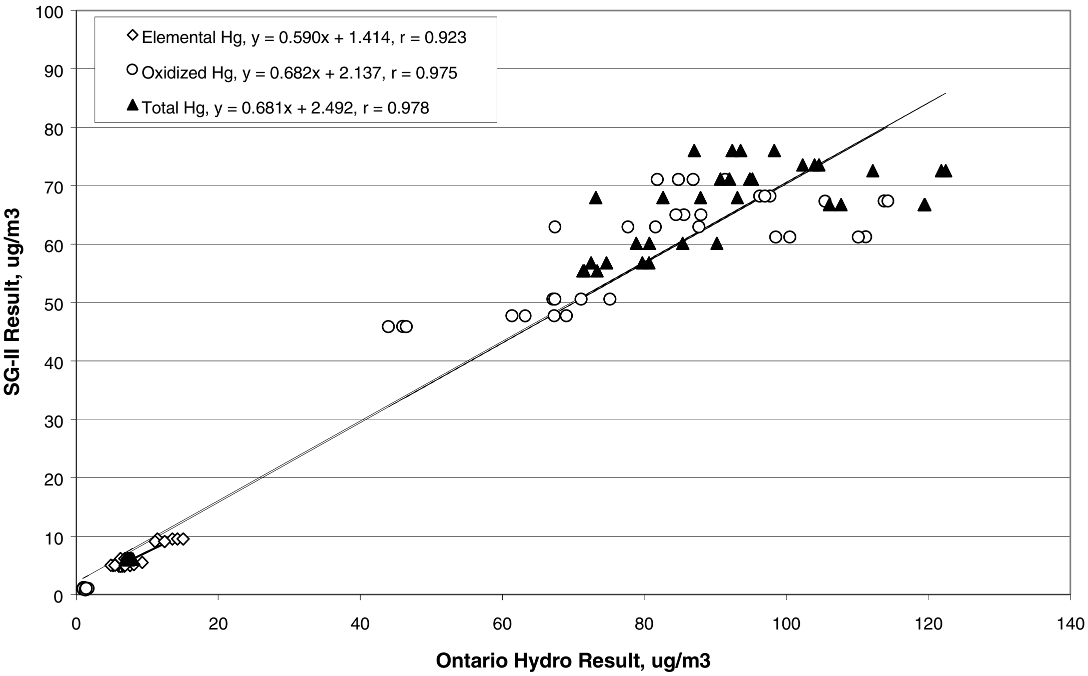

Figure 6-1c. Correlation of SG-II and OH Results from Both Weeks of Verification

The results in Table 6-3 show that r^2 values for all three mercury fractions were near zero in the first week of testing. The r^2 value for oxidized mercury in the first week results from a negative value of r (i.e., anticorrelation between the OH and SG-II results). These values are undoubtedly due in part to the limited range of mercury concentrations present in that first week. In the second week, the r^2 value for elemental mercury was highest and that for total mercury the lowest. The combined data set from both weeks is the largest and has the widest range of data values, and consequently is the most appropriate for calculating correlation. When data from both weeks were combined, strong correlation was found for oxidized and total mercury (r^2 values exceeding 0.95), and moderately strong correlation was found for the elemental mercury data ($r^2 = 0.85$). Note that, as was the case for the RA calculation above, the elemental mercury comparison for OH Run 9 was excluded from this calculation of correlation.

6.3 Precision

The precision of SG-II response for elemental and total mercury was calculated from the repeated analyses of flue gas under nominally constant conditions in the fifteen OH sampling periods. Table 6-4 shows the calculated precision results, in terms of the percent relative standard deviation (% RSD) of the elemental and total readings in each period. The mean and standard deviations of the readings are also shown.

The aim of this test was to assess the precision of the SG-II under constant flue gas conditions. Unfortunately, occasional spikes in mercury concentration did occur during testing. When these spikes were corroborated by the response of multiple mercury CEMs as having been caused by the facility, or were clearly associated with occurrences at the facility, the spikes were removed from the data before precision was calculated. For example, the precision results for OH Run 9 in Table 6-4 exclude large spikes that were caused by the failure of the mercury solution delivery pump. On the other hand, excursions of a single CEM that were not coincident with similar excursions of other CEMs, or not attributable to any occurrence at the RKIS, were not removed from the data. The footnote to Table 6-4 indicates those results for which spikes in the data were removed before calculation of the percent RSD. Note that because of the operating mode of the SG-II in the second week of verification, as few as three elemental mercury measurements were obtained from the SG-II during each OH run in that week.

The results in Table 6-4 indicate that the precision of the SG-II monitor for elemental mercury was within 10% RSD in 13 of the 15 OH sampling periods. In OH runs 14 and 15, larger percent RSD values were found. For total mercury, the SG-II exhibited precision within 10% RSD in 11 of the 15 OH sampling periods, and within 15% in 14 of the periods. In OH Run 10, substantial variability was observed in the total mercury response of the SG-II, but this variability could not be correlated with facility events or the response of other CEMs, so no corrections were made to the data. The results in Table 6-4 indicate not only that the SG-II exhibited precision usually within 10% RSD, but that in most cases the RKIS facility maintained highly stable mercury levels.

6.4 Calibration/Zero Drift

The daily SG-II readings on zero gas and elemental mercury standard gas are listed in Table 6-5. The data from the two weeks of testing are listed separately because of the different standard gases used. Note that when gas is introduced at the SG-II, as in these drift checks, no distinction is possible between elemental and total mercury. As a result, Table 6-5 shows only a single SG-II response for each drift check.

Table 6-6 summarizes the calibration/zero drift results in terms of the mean, standard deviation, pecent RSD, maximum, and minimum of the zero and standard gas responses in each week. The first analysis of the mercury standard gas in the first week was excluded from the drift calculation because, as described in Section 3.4.1, the materials and procedure for delivering that standard did not allow proper equilibration in that first run.

Tables 6-5 and 6-6 show that the SG-II gave stable response to both zero and standard gases. In particular, response to the low-level elemental mercury standard gas showed a 2.6% RSD in the first week of testing, and response to the higher level standard gas showed a 2.5% RSD value in the second week. These observations show the stability of the SG-II, and also support the utility of the elemental mercury standards for confirming CEM stability. The mercury concentrations in the gas standards are not known absolutely, but the average mercury concentrations reported by the SG-II for the two standard gases (15.1 and 53.5 $\mu g/m^3$, respectively) are both within 10% of the concentrations of 14 and 49 $\mu g/m^3$, based on analysis by the gas vendor (Table 3-8, Section 3.4.1).

Table 6-4. Precision Results for the SG-II

		Elemental Mercury		Total Vapor Mercury	
Date	OH Run Number	Mean (Std. Dev.)	% RSD	Mean (Std. Dev.)	% RSD
1/15	1	4.88 (0.15)	3.1	5.78 (0.20)	3.5[a]
	2	4.88 (0.13)	2.7	5.95 (0.33)	5.5
1/16	3	5.13 (0.13)	2.5	5.95 (0.11)	1.8[a]
	4	5.07 (0.12)	2.3[a]	5.96 (0.17)	2.9[a]
1/17	5	5.36 (0.33)	6.1	6.19 (0.26)	4.2
	6	5.01 (0.22)	4.5	6.07 (0.28)	4.7
1/22	7	9.10 (0.54)	5.9	56.8 (5.80)	10.2
	8	9.53 (0.25)	2.7	55.5 (2.69)	4.8[a]
	9	9.56 (0.85)	8.9	50.7 (1.91)	3.8[a]
1/23	10	5.33 (0.23)	4.3	73.6 (18.2)	24.7
	11	5.50 (0.24)	4.3	66.8 (3.7)	5.6
	12	5.16 (0.18)	3.4	72.5 (8.86)	12.2
1/24	13	6.17 (0.33)	5.3	71.2 (4.46)	6.3
	14	5.03 (0.98)	19.5	68.0 (1.44)	2.1
	15	4.97 (1.21)	24.3	76.0 (8.5)	11.2

[a] Brief spikes in data removed prior to calculation of precision.

Table 6-5. Zero and Standard Gas Responses of the SG-II

	Date	Zero Gas (μg/m^3)	Standard Gas (μg/m^3)
Week One	1/15/01	0.001	13.1[a]
		0.002	14.8
	1/16/01	0.000	14.8
		0.001	15.0
	1/17/01	0.002	15.3
		0.003	15.3
	1/18/01	0.000	15.8
		0.003	15.2
	1/19/01	-0.001	14.6
Week Two	1/22/01	-0.005	51.5
		-0.005	53.4
	1/23/01	0.001	55.4
		-0.003	52.4
	1/24/01	0.013	55.0
		0.002	53.7
	1/25/01	0.002	53.4

[a] This value excluded from calculation of drift; delivery procedure for elemental mercury standard gas not properly equilibrated.

6.5 Sampling System Bias

Table 6-7 shows the results of providing the elemental mercury gas standards directly to the SG-II, and at the inlet of the PSA sampling probe, on January 19 and 25, 2001. Shown are the final stable readings on the zero gas and the mercury standard. Note that when gas is supplied at the probe inlet, both elemental and total mercury readings are obtained, so both are shown in Table 6-7. The resulting bias in transport of the elemental mercury standard through the entire inlet and speciation system is also shown in each case. When elemental mercury passes through the inlet system of the SG-II, the elemental and total mercury readings of the SG-II should be the same.

Table 6-6. Summary of Calibration /Zero Drift Results for the SG-II

	Result	Zero Gas (µg/m^3)	Standard Gas (µg/m^3)
Week One	Mean	0.001	15.1
	Std. Devn.	0.001	0.39
	% RSD	NA	2.6
	Maximum	0.003	15.8
	Minimum	-0.001	14.6
Week Two	Mean	0.001	53.5
	Std. Devn.	0.006	1.34
	% RSD	NA	2.5
	Maximum	0.013	55.4
	Minimum	-0.005	51.5

Table 6-7. Results of Sampling System Bias Test of the SG-II

		Elemental Mercury Response		Total Vapor-Phase Mercury Response	
Date	Gas Supplied To:	Zero Gas (µg/m^3)	Standard Gas (µg/m^3)	Zero Gas (µg/m^3)	Standard Gas (µg/m^3)
1/19/01	Analyzer	-0.001	14.573	-0.001	14.573
	Probe Inlet	0.011	14.548	0.030	14.392
Sampling System Bias for Hg^o		**-0.3%**[a]		**-1.5%**	
1/25/01	Analyzer	0.002	53.350	0.002	53.350
	Probe Inlet	-0.001	50.714	0.003	52.077
Sampling System Bias for Hg^o		**-4.9%**		**-2.4%**	

[a] Bias calculated as described in Section 5.5, using zero-corrected standard response through inlet, relative to zero-corrected standard response at analyzer.

Table 6-7 shows that the bias in transport of elemental mercury to the SG-II's speciation unit and on to the detector was -0.3 to -1.5% with the lower level standard, and -2.4 to -4.9% with the higher level standard. Thus the calculated negative bias of the inlet system in sampling elemental mercury was less than 5% in all cases. Results obtained for the total mercury measurement channel of the SG-II were similar to those for the elemental mercury channel.

6.6 Interference Effects

The effect of interferences was tested by injecting a constant level of mercury into the RKIS and altering the levels of several interferants, as described in Section 3.3.6. Figure 6-2 illustrates the elemental and total mercury response of the SG-II during this test on January 18. The dashed vertical lines indicate the time periods in which each of the indicated interferants or combinations of interferants was introduced.

Figure 6-2 shows that 500 ppm nitric oxide, 500 ppm carbon monoxide, and 2,000 ppm sulfur dioxide had little effect on the total mercury readings of the SG-II. Elemental mercury readings increased from about 5 to 6.5 $\mu g/m^3$ upon the addition of nitric oxide, but returned to the pre-addition levels once only carbon monoxide or sulfur dioxide was added. Addition of 250 ppm hydrogen chloride to the duct caused only a temporary increase in elemental mercury response, with little effect on the total mercury readings. In contrast, replacement of the hydrogen chloride with 10 ppm of chlorine had a dramatic effect on the elemental mercury readings, driving them nearly to zero. However, the total mercury readings of the SG-II were unaffected by the presence of the chlorine. Addition of nitric oxide along with the chlorine caused the elemental mercury readings to rise only slightly, while again the total mercury readings remained stable. When all the interferants were added at once, the SG-II total mercury readings remained the same, and the elemental readings increased and were again close to those with only mercury present. (Difficulties in stabilizing the additions of all species at once led to spikes in response at the start of this period.) Thus, Figure 6-2 shows that the SG-II total mercury responses were largely unaffected by the presence of a variety of potential interferences and that, even for elemental mercury, the SG-II is not subject to serious interference from simultaneous high levels of several key pollutants. Note that the low value for elemental mercury around 17:40 in Figure 6-2 results from an inadvertent large injection of chlorine into the duct for a brief period.

6.7 Response Time

The rise and fall times of the SG-II response were tested as part of the zero and standard gas checks done to assess calibration and zero drift (Section 6.4). Table 6-8 shows the data used for the response time determinations, listing successive SG-II readings when the standard gas delivery was started and/or stopped. Those data points showing the rise or fall of response, and the final reading with the gas standard, are shown. Intervening readings, which changed only slightly from one to the next, are omitted as indicated by the footnote to Table 6-8.

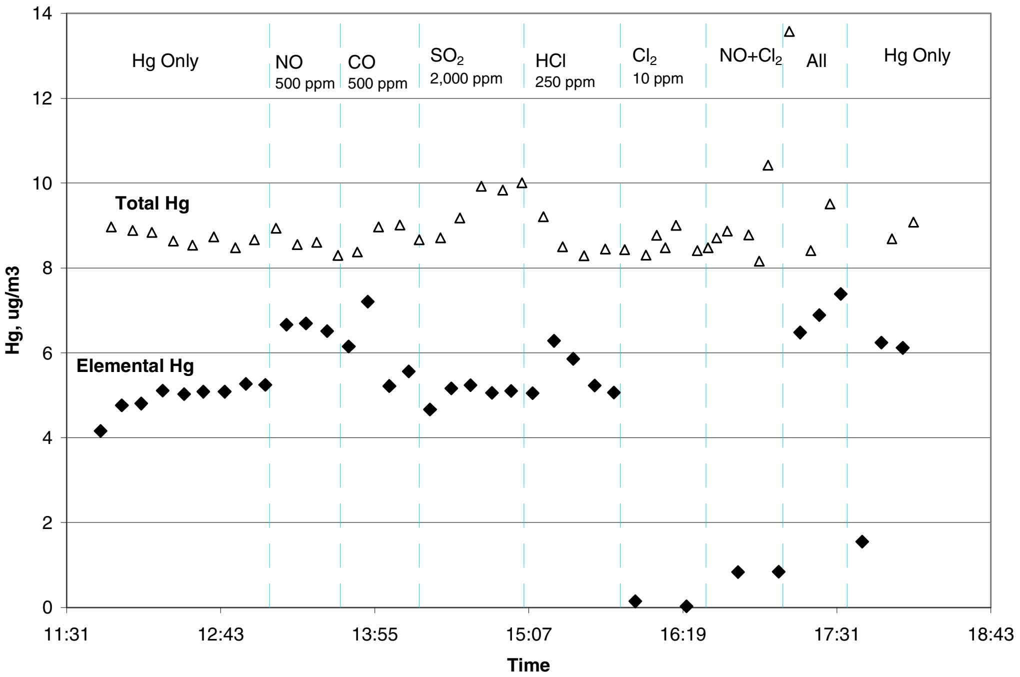

Figure 6-2. SG-II Response in Interference Test, January 18, 2001

The 5- to 6-minute cycle time of the SG-II, during which gas is sampled for only a minute or two, must be considered when defining the response time of the CEM. The response time of the CEM is most easily expressed in terms of the fraction of response achieved in one measurement cycle. Table 6-9 summarizes the observed response times expressed in this way, listing the percentage of full response achieved in one measurement cycle after the standard gas was started and/or stopped. Table 6-9 shows that the percentage response of the SG-II was almost always 95 to 100% within one measurement cycle. Thus the 95% response time of the SG-II as operated in this verification was essentially one measurement cycle.

6.8 Low-Level Response

Figure 6-3 illustrates the response of the SG-II to low levels of mercury injected into the duct, as described in Section 3.3.8. The dashed vertical lines indicate the time periods during which each nominal total mercury level was introduced. Both the elemental and total mercury responses of the SG-II are shown in Figure 6-3.

Table 6-8. Data Used to Determine Response Time of the SG-II (Readings in µg/m^3)

Week One			Week Two		
Date	**Time**	**Reading (µg/m^3)**	**Date**	**Time**	**Reading**
1/16/01 a.m.	08:28	0.000	1/22/01 a.m.	09:58	-0.005
	08:34	12.42		10:04	51.239
	08:48	14.803[a]		10:15	51.545[a]
1/16/01 p.m.	19:18	0.001	1/22/01 p.m.	18:28	-0.005
	19:23	14.053		18:34	52.502
	19:37	15.000[a]		18:46	53.44[a]
				18:51	0.064
1/17/01 a.m.	09:24	0.002	1/23/01 a.m.	09:22	0.001
	09:29	14.836		09:28	54.745
	09:43	15.312[a]		09:45	55.365[a]
1/17/01 p.m.	18:05	0.003	1/23/01 p.m.	17:41	-0.003
	18.:10	15.128		17:47	50.846
	18:19	15.305		18:04	52.387[a]
1/18/01 p.m.	18:40	0.003	1/24/01 a.m.	09:03	0.013
	18:45	14.629		09:09	54.191
	19:04	15.156[a]		09:26	54.956[a]
1/19/01 a.m.	10:04	14.573[a]	1/24/01 p.m.	18:41	0.002
	10:11	0.024		18:47	53.564
				19:04	53.705[a]
				19:10	0.229
			1/25/01 a.m.	09:04	0.002
				09:10	53.197
				09:28	53.350[a]
				09:33	-0.003

[a] Final reading, intervening readings omitted.

Table 6-9. Results of Response Time Tests on the SG-II

Rise/Fall Time	Date	Percent Response Achieved in One Cycle
Rise Time		
	1/16/01 a.m.	83.9
	1/16/01 p.m.	93.7
	1/17/01 a.m.	96.9
	1/17/01 p.m.	98.8
	1/18/01 p.m.	96.5
	1/22/01 a.m.	99.4
	1/22/01 p.m.	98.2
	1/23/01 a.m.	98.9
	1/23/01 p.m.	97.1
	1/24/01 a.m.	98.6
	1/24/01 p.m.	99.7
	1/25/01 a.m.	99.7
Fall time		
	1/19/01 a.m.	99.8
	1/22/01 p.m.	99.9
	1/24/01 p.m.	99.6
	1/25/01 a.m.	100

Figure 6-3 shows that the SG-II responded to all mercury concentrations injected, producing a sharp response above the flue gas background even with the injection of as little as 0.57 µg/m^3 of mercury. The added mercury was detected largely in the form of elemental mercury. The primary observation from these data is that the SG-II is clearly sensitive enough to detect mercury at levels well below 1 µg/m^3. Furthermore, the increases in response were in quantitative agreement with the nominal mercury levels injected. For example, with a nominal added mercury concentration of 4.54 µg/m^3 in the duct, the SG-II gave a total mercury response about 4 µg/m^3 above flue gas background. When the SG-II total mercury responses at each mercury level are averaged, a regression of average SG-II response vs. nominal mercury level gives the equation SG-II = 0.90 × (mercury, µg/m^3) + 0.057 µg/m^3, with $r^2 = 0.997$. These results show that the SG-II is capable of accurate detection of mercury at concentrations near and below 1 µg/m^3.

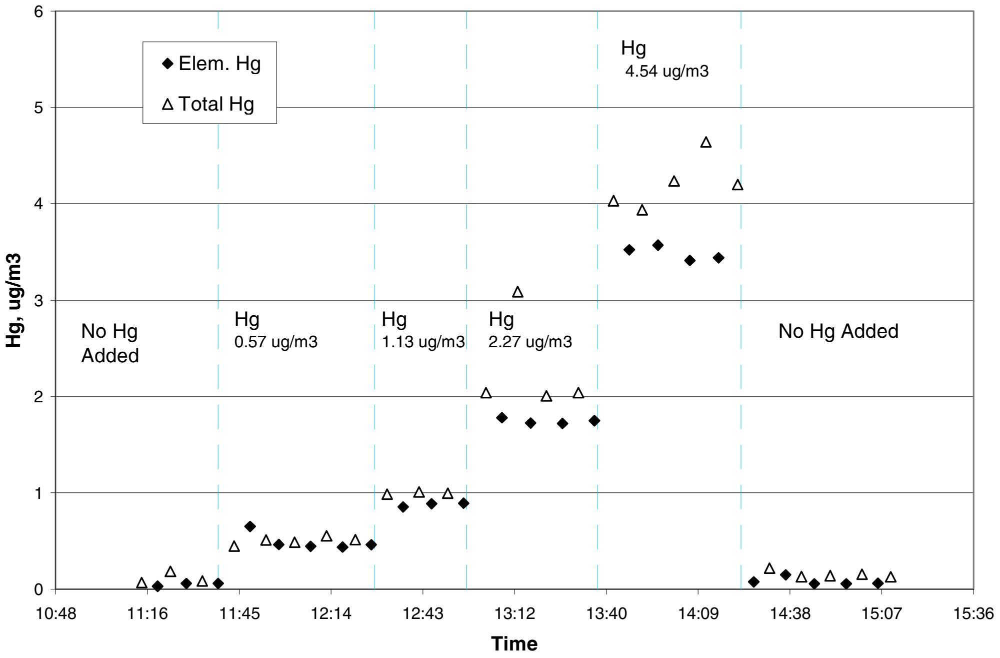

Figure 6-3. Low-Level Response Test for the SG-II, January 19, 2001

6.9 Data Completeness

The SG-II operated reliably throughout all of the verification test procedures, and no test data were lost as a result of any malfunction or down time. Consequently, the data completeness was 100%.

6.10 Setup and Maintenance

The SG-II was set up and operated by one representative of PS Analytical, who was on site for both weeks of the verification test. The SG-II was set up and ready to sample flue gas within about a half day after the needed utilities were in place. The SG-II setup proceeded smoothly, and operation of the instrument was trouble-free throughout the test. Preventive maintenance was not scheduled or performed during the test. The instrument requires an external supply of high purity argon gas. As operated in this verification, a standard cylinder of argon (containing approximately 200 cubic feet of gas) would last about one week in continuous operation. Other consumables consisted of the 1 to 1.5 L of reagent solutions used in the SG-II per day, which resulted in an equal quantity of waste solutions requiring disposal.

6.11 Cost

As tested, the approximate purchase price of the SG-II monitor is about $70,000.

Chapter 7
Performance Summary

During the first week of verification testing, the SG-II provided an accuracy relative to the OH method of 20.6% for total vapor-phase mercury, at levels of about 7 to 8 µg/m^3. Testing showed relative accuracy of 22.8% for elemental mercury, and 27.2% for oxidized mercury at elemental mercury levels of about 6 to 7 µg/m^3 and oxidized mercury levels of about 1 to 1.5 µg/m^3. In the second week of verification testing, the SG-II provided an RA of 32.8% for total vapor-phase mercury, at levels of about 70 to 120 µg/m^3. Relative accuracy of 29.6% for elemental mercury, and 33.3% for oxidized mercury, was found at elemental mercury levels ranging from about 5 to 25 µg/m^3 and oxidized mercury levels ranging from about 45 to 110 µg/m^3. The RA values in the second week resulted primarily from underestimating the oxidized mercury, which comprised the great majority of the mercury present.

The coefficient of determination (r^2) of the SG-II and OH elemental mercury results was 0.853 with data from both weeks combined. The corresponding r^2 value for oxidized mercury was 0.951, and for total mercury was 0.957.

Precision of the SG-II response was assessed in periods of stable mercury levels in the flue gas during the 15 OH sampling periods. The precision (as percent RSD) of the SG-II response for elemental mercury was within 10% in 13 of the 15 periods. For total mercury, precision was within 10% RSD in 11 of the 15 periods and within 15% in 14 of the periods. These precision results include both variability in the test facility and in the SG-II.

Calibration and zero drift were determined by repeated analysis of zero gas and elemental mercury standard gases. Nine such analyses in the first week of verification gave average zero gas responses of 0.001 (± 0.001) µg/m^3 and standard gas responses of 15.1 (± 0.39) µg/m^3. The standard gas results equate to a 2.6% RSD. Seven such analyses in the second week of verification gave zero gas readings of 0.001 (± 0.006) µg/m^3, and standard gas responses of 53.5 (± 1.34) µg/m^3. These standard gas results equate to a 2.5% RSD.

The SG-II operated with a 5- to 6-minute sampling/analysis cycle and achieved 95% or greater response to changes in mercury concentration within a single cycle.

Sampling system bias of the inlet system used with the SG-II was determined using elemental mercury gas standards. The bias in transport of elemental mercury through the inlet system ranged from -0.3 to -4.9%.

Elevated levels of sulfur dioxide, nitrogen oxides, carbon monoxide, and hydrogen chloride had no significant effect on SG-II response to elemental or total mercury in flue gas. The presence of chlorine reduced elemental mercury readings to nearly zero, but caused no significant change in the total mercury readings of the SG-II. When these gases were all present at once in the flue gas, the SG-II readings for both elemental and total mercury were close to those seen with only mercury in the flue gas.

The SG-II produced a nearly quantitative response to as little as 0.57 $\mu g/m^3$ of mercury in flue gas (the lowest concentration tested), and response at nominal levels of 0.57 to 4.5 $\mu g/m^3$ of mercury was within about 10% of the nominal levels.

Data completeness for the SG-II was 100%, and no significant repair or maintenance was needed. The unit uses 1 to 1.5 liters per day of aqueous reagents to measure elemental and total mercury, and would consume about 200 cubic feet of high-purity argon in a week of continuous operation.

Chapter 8
References

1. *Test/QA Plan for Pilot-Scale Verification of Continuous Emission Monitors for Mercury*, Battelle, Columbus, Ohio, November 30, 2000.

2. *Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)*, American Society for Testing and Materials, Draft Method, October 27, 1999.

3. *Test Procedure for the Determination of Elemental Mercury (Hg °) Concentration from Compressed Gas Standards Using Modified Ontario Hydro Mini-Impinger Trains,* prepared by ARCADIS Geraghty & Miller, Research Triangle Park, North Carolina, for Work Assignment No. 2-18 of EPA Contract No. 68-C-99-201, January 11, 2001.

4. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, Version 2.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, October 2000.

5. Belsley, D. A., Kuh, E., and Welsch, R. E., *Regression Diagnostics,* John Wiley and Sons, New York, 1980.