Environmental Technology Verification Report

LUMEX LTD.
MERCURY CONTINUOUS EMISSION MONITOR

Prepared by

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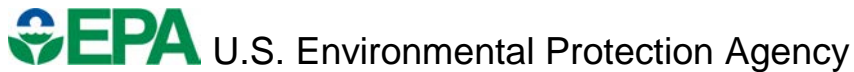
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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV✓

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Massachusetts Department of ENVIRONMENTAL PROTECTION

ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Emission Monitor

APPLICATION: MEASURING ELEMENTAL AND TOTAL MERCURY EMISSIONS

TECHNOLOGY NAME: Lumex Mercury CEM

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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 Lumex Ltd. 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 Lumex CEM: 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, and a 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 Lumex CEM is a real-time continuous monitor for elemental and total mercury. The Lumex CEM is based on the analytical approach of cold vapor atomic absorption spectroscopy for detection of elemental mercury, with Zeeman high-frequency polarization background correction. The multipath optical cell and the Zeeman reduction of background interferences are designed to provide high sensitivity with minimal interferences from the combustion gas matrix. The sensitivity of this approach allows continuous real-time operation with no preconcentration and desorption steps. The CEM uses catalytic pyrolysis to decompose oxidized mercury to elemental mercury for detection, and thus uses no wet chemical reagents and no external gas supplies. The Lumex CEM is a two-channel instrument, in which one mercury detector operates with the catalytic pyrolyzer and one without, thereby providing simultaneous and continuous readings of total and elemental mercury, respectively. The Lumex CEM is microprocessor controlled by an RS-232 communications link. Software includes Windows-based data acquisition and processing. Readings can be reported at intervals from 1 second to 3 minutes; in this verification, data from both channels of the CEM were recorded at 1-second intervals. The Lumex CEM is a new device; during this verification test, modifications were made by Lumex staff that may have affected verification results. In addition, the Lumex CEM suffered accidental damage during the verification test that required substituting two external mercury detectors for the internal detectors in the CEM. Those external detectors were Lumex RA 915+ portable mercury detectors, designed for sensitive, fast-response measurements of elemental mercury. RA 915+ Serial No. 167 was used for detection of elemental mercury and RA 915+ Serial No. 164 was used for detection of total mercury by connection downstream of the catalytic pyrolyzer in the Lumex CEM. The RA 915+ units use the same detection approach as the CEM's internal detectors, and thus were a reasonable substitute that allowed verification to continue. The period when the RA 915+ detectors were used instead of the CEM's detectors is clearly indicated in this report.

VERIFICATION OF PERFORMANCE

Relative accuracy: During the first week of verification testing, the Lumex CEM provided accuracy relative to the OH method of 58.2% for total mercury, at levels of about 7 to 8 µg/m³. Testing showed relative accuracy of 50.2% for elemental mercury, and 99% for oxidized mercury, at elemental mercury levels of about 6 to 7 µg/m³ and oxidized mercury levels of about 1 to 1.5 µg/m³. In the second week of verification, the Lumex instruments provided relative accuracy of 71% for total mercury, at total mercury levels of approximately 70 to 120 µg/m³. Relative accuracy of 107% for elemental mercury, and 69.4% for oxidized mercury, was found at elemental mercury levels ranging from about 5 to 25 µg/m³ and oxidized mercury levels ranging from about 45 to

110 µg/m^3. These RA results were caused primarily by a consistent underestimation of all mercury concentrations by the Lumex CEM, that may have been due to both losses of mercury in the inlet systems, and low pyrolyzer temperatures for much of the test.

Correlation with the reference method: The coefficient of determination (r^2) of the Lumex and OH elemental mercury results was 0.052, based on the data from both weeks of verification. The corresponding r^2 values for oxidized mercury and total mercury were 0.631 and 0.621, respectively.

Precision at stable flue gas conditions: Precision of the Lumex 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 Lumex response for elemental mercury was within 10% in five of the 15 periods, and within 15% in eight of the periods. For total mercury, precision was within 10% RSD in eight of the 15 periods and within 15% in 11 of the periods. These precision results include both variability in the test facility and in the Lumex instruments.

Calibration/zero drift: Calibration and zero drift were determined by repeated analysis of zero gas and elemental mercury standard gases. The failure of the Lumex CEM and subsequent substitution of the RA 915+ detectors interrupted the continuity of this portion of the test. Both the Lumex CEM and the RA 915+ detectors gave consistent readings on zero gas in both weeks of testing. Six analyses of a mercury standard gas with the Lumex CEM in the first week of verification gave average responses of 15.7 ($\pm$ 7.9) and 14.7 ($\pm$ 6.9) µg/m^3 for elemental and total mercury, respectively. These values equate to percent RSD's of 50.3 and 46.7%, respectively. Three analyses of the same standard with the RA 915+ detectors in the first week gave 13.2 ($\pm$ 0.35) and 11.7 ($\pm$ 3.0) µg/m^3, respectively, for percent RSD values of 2.7% and 25.4%. Seven analyses of a different standard by the RA 915+ detectors in the second week of verification gave readings of 55.3 ($\pm$ 2.98) and 58.3 ($\pm$ 3.55) µg/m^3 for elemental and total mercury, respectively. These standard gas results equate to percent RSD values of 5.4% and 6.1%, respectively.

Sampling system bias: Sampling system bias of the inlet systems used with the Lumex CEM and RA 915+ detectors was determined using elemental mercury gas standards. The bias in transport of elemental mercury through the entire inlet systems ranged from -20.5 to -44.5%.

Interference effects of flue gas constituents: Elevated levels of sulfur dioxide, nitrogen oxides, and carbon monoxide had little effect on Lumex CEM response to elemental or oxidized mercury in flue gas. However, the presence of hydrogen chloride or chlorine reduced elemental mercury readings from about 5 µg/m^3 to less than 1 µg/m^3, and the total mercury readings were also reduced by half or more in the presence of these species. When these gases were all present at once in the flue gas, the Lumex elemental mercury readings remained below 1 µg/m^3, and the total mercury readings were only about 60% of those with the same mercury level but no interferants present.

Response time to changing mercury levels: The Lumex CEM exhibited rise and fall times that varied substantially, usually ranging between about 30 seconds and 100 seconds.

Response to low levels of mercury: The Lumex CEM (with RA 915+ detectors in place) responded to as little as 0.57 µg/m^3 of mercury in flue gas, but the response to concentrations of 0.57 to 4.5 µg/m^3 averaged only about 55% of the nominal mercury concentration. Loss of mercury in the CEM's inlet system is one possible cause for the low response at low mercury levels.

Data completeness: Data completeness cannot be estimated well because of the changes in detectors used and the modifications made to Lumex inlet systems and the pyrolysis unit during the test.

Setup and maintenance needs: The setup and operation of the Lumex instruments was relatively simple, and the pyrolysis approach requires no chemical reagents or solutions and no external gas supplies. Routine maintenance

was limited to that required for the ice bath condensers in the sampling inlets. However, failure of the Lumex CEM early in the verification test required substitution of the RA 915+ detectors to continue the verification.

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US EPA ARCHIVE DOCUMENT

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Lumex Ltd.
Mercury Continuous Emission Monitor

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The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency and recommended for public release. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

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.

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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
HCl	hydrogen chloride
H_2O	water
Hg	mercury
Hg^o	elemental mercury
$HgCl_2$	mercuric chloride
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
N	nitrogen
NIST	National Institute of Standards
NO	nitric oxide
NO_x	nitrogen oxides
OD	outside diameter
O_2	oxygen
OH	Ontario Hydro
ORD	Office of Research and Development
PE	performance evaluation
ppb	parts per billion
psig	pounds per square inch gauge
ppm	parts per million
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 Lumex Ltd. 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 Lumex Ltd. mercury CEM. The following description of the Lumex CEM is based on information provided by the vendor.

The Lumex CEM is a real-time continuous monitor for elemental and total mercury. The Lumex CEM is based on the analytical approach of cold vapor atomic absorption spectroscopy for detection of elemental mercury, with Zeeman high-frequency polarization background correction. The use of a multipath optical cell and the Zeeman reduction of background interferences are designed to provide high sensitivity with minimal interferences from the combustion gas matrix. The sensitivity of this approach allows continuous real-time operation with no preconcentration and desorption steps. The CEM uses catalytic pyrolysis to decompose oxidized mercury to elemental mercury for detection, and thus uses no wet chemical reagents and no external gas supplies.
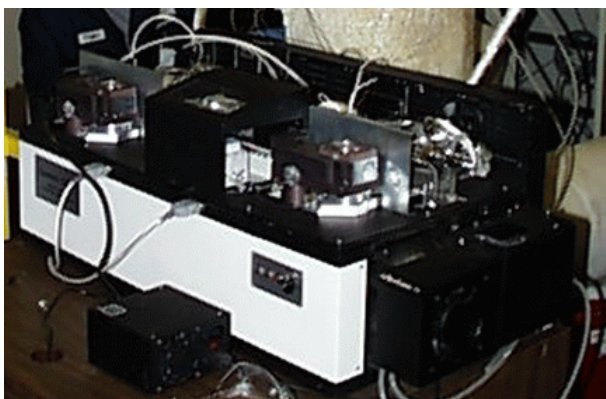
Figure 2-1. Figure 2-1. Lumex Ltd. Mercury Continuous Emission Monitor

The Lumex CEM is a two-channel instrument, in which one mercury detector operates with the catalytic pyrolyzer and one without, thereby providing simultaneous and continuous readings of total and elemental mercury, respectively. Figure 2-1 shows the instrument as installed for this verification test. The pyrolyzer is an electrically heated coil of Nichrome wire located within a quartz tube that forms part of the sample gas flow path. In principle, particulate mercury, as well as oxidized vapor-phase mercury, can be reduced by the pyrolyzer, allowing detection of total mercury (i.e., elemental plus oxidized plus particle-bound) in real time. The sample flow rate of the Lumex CEM is 2 L/min. The nominal measurement range of the CEM is from 0.5 to 5,000 $\mu g/m^3$ of mercury. The Lumex CEM is microprocessor controlled by an RS-232 communications link. Software includes Windows-based data acquisition and processing. Readings can be reported at intervals from 1 second to 3 minutes; in this verification data from both channels of the CEM were recorded at 1-second intervals.

The Lumex CEM is a new device; and, during this verification test, modifications were made by Lumex staff that may have affected verification results. The temperature and means of control of the pyrolyzer and the arrangement of the inlet system to the unit are two key examples. The potential impact of those modifications is noted where pertinent throughout this report. In addition, the Lumex CEM suffered damage during the verification test that required substituting two external mercury detectors for the internal detectors in the CEM. Those external detectors were Lumex RA 915+ portable mercury detectors, designed for sensitive, fast-response measurements of elemental mercury. RA 915+ No. 167 was used for detection of elemental mercury and RA 915+ No. 164 was used for detection of total mercury by connection downstream of the catalytic pyrolyzer in the Lumex CEM. The RA 915+ units use the same detection approach as the CEM's internal detectors, and thus were a reasonable substitute that allowed verification to continue. The period when the RA 915+ detectors were used instead of the CEM's internal detectors is clearly indicated in this report.

The Lumex CEM was approximately 30 inches wide by 15 inches high by 20 inches deep (76 centimeters wide by 38 centimeters high by 51 centimeters deep).

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 Lumex Ltd. CEM 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 Lumex CEM:

- 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 Lumex 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 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.

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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 Lumex CEM 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 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 Lumex CEM 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 Lumex CEM was operated by representatives of Lumex Ltd. The intent of the testing was for the Lumex CEM to operate in a manner simulating operation at a combustion facility. Therefore, once the verification test began, no recalibration was performed. Lumex Ltd. maintained the monitor's inlet system and handled recovery of data from the Lumex CEM.

3.2 Test Conditions

The Lumex CEM 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) 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)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Tuesday 1/16/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Wednesday 1/17/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Thursday 1/18/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift)
	AM/PM	Spiking of flue gas with interferant gases (Interferences)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
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)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Tuesday 1/23/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Wednesday 1/24/01	AM	Zero/Hg° standard gas (Calibration/Zero Drift)
	AM/PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift)
Thursday 1/25/01	AM/PM	Repeat of some interference tests (Interferences)
	PM	Zero/Hg° standard gas (Calibration/Zero Drift, 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 thermo-dynamically 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 Lumex CEM was located at Port 6. The Lumex CEM 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 Lumex CEM Operation

The Lumex CEM was installed on a table next to the RKIS duct, at the point where the duct turns from vertical to horizontal to run near the floor of the building (see Figure 3-1). Port 6 is located about 6 feet above the floor at this location and consists of three separate ports (A, B, and C) located at 90-degree intervals around the circumference of the duct. The Lumex CEM drew
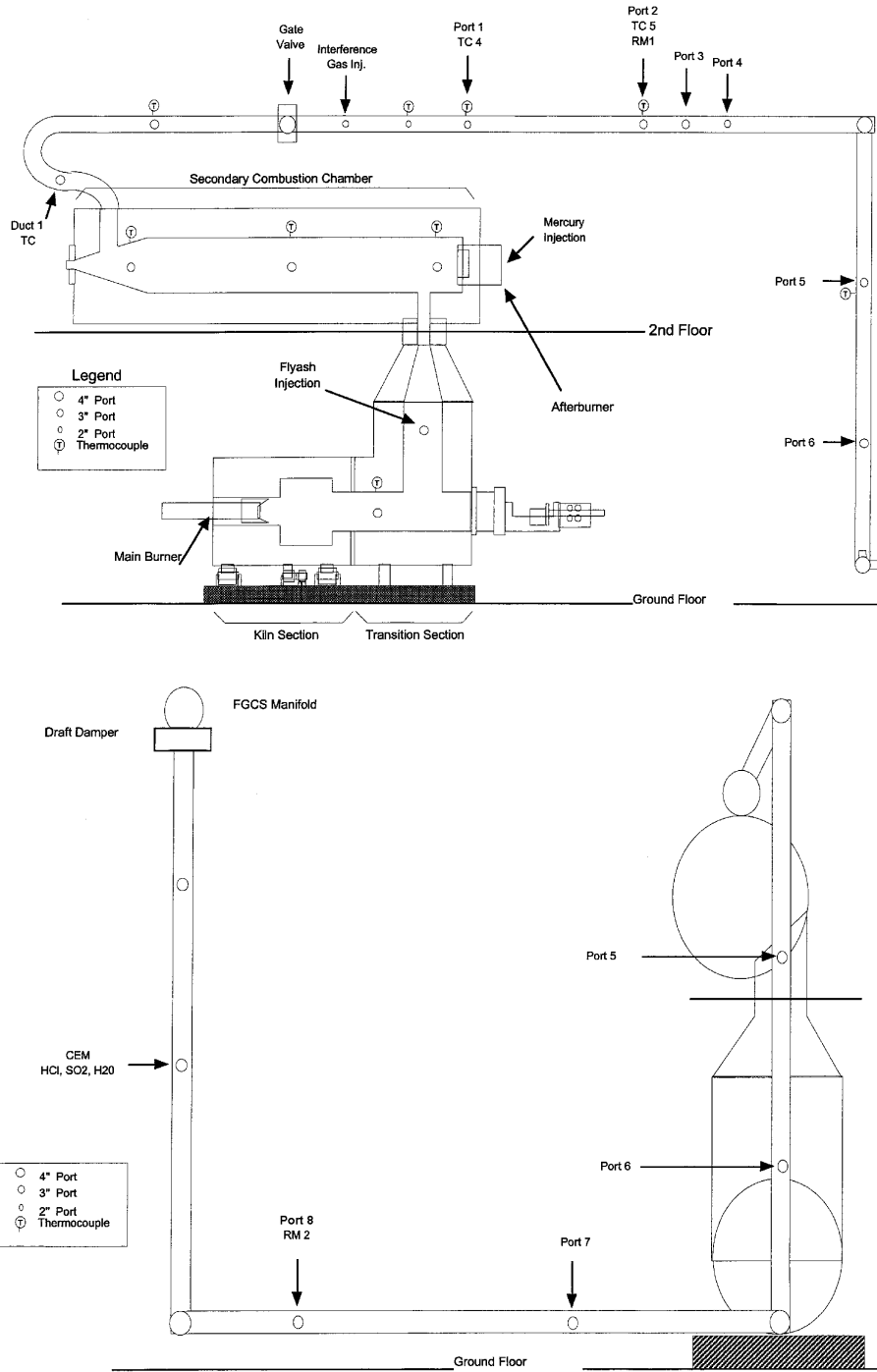
Figure 3-1. Side View (top) and End View (bottom) of the RKIS Test Facility

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 ($\mu g/m^3$)	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.
[b]Predominantly oxidized mercury

sample from Port 6C. The CEM operated normally through the first three days of verification testing (January 15 through 17), but was accidently damaged on January 18. From January 18 until the end of the verification test, elemental mercury data were provided by the Lumex RA 915+ detector Serial No. 167, which sampled from Port 6A, diametrically opposite the CEM's intake port. The intake probes for the CEM and the RA 915+ detector Serial No. 167 were positioned close to one another near the center of the duct. Also from January 18 on, the RA 915+ detector Serial No. 164 was connected to the Lumex CEM's internal plumbing downstream of the pyrolyzer to provide total mercury data. In this report, statements applying generally to the Lumex mercury measurements use the term "Lumex CEM," whether referring to data from the CEM itself or the CEM with substitute RA 915+ detectors. When more appropriate, the specific detector is specified. It is to be understood that all data from January 18 on are from the Lumex CEM, with the substitute detectors in place.

The pyrolyzer in the Lumex CEM was modified as the verification progressed. Improvement of the heating and insulation of the valve and pyrolyzer in the CEM took place on several occasions, starting on January 17. On January 23, the temperature of the pyrolyzer was increased; and, by January 24, a temperature controller was in place on the pyrolyzer, and its temperature was much

higher than before (i.e., the Nichrome wire glowed cherry red after this modification). These changes undoubtedly affected the performance of the CEM and are noted where appropriate in presenting the test results.

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. The inlet systems used with the Lumex instruments varied and were modified as the verification progressed. No inlet particulate filter was used with either the Lumex CEM or the substitute RA 915+ detectors. The inlet system used with the Lumex CEM at the start of the study on January 15 consisted of several feet of heated 1/4-inch OD stainless steel tubing, which extended into the center of the duct at Port 6C and connected to a heat-wrapped three-way stainless steel valve on the back of the Lumex CEM. This inlet configuration was used until the failure of the CEM on January 18. At that point the RA 915+ detector No. 164 was put in place to determine total mercury. For that installation, an ice bath condenser was inserted in the sample flow path between the CEM's pyrolyzer and the RA 915+ No. 164 detector. This configuration was used for all further testing.

A separate inlet was used for the RA 915+ detector No. 167 for elemental mercury measure-ments. That inlet consisted of several feet of heated 1/4-inch OD stainless steel tubing, which extended into the center of the duct at Port 6A and connected directly to an ice bath condenser. Gas passing through the condenser was then drawn into the RA 915+ detector. Silicone rubber tubing was used to make connections between the RA 915+ detectors and ice bath condensers in both inlet systems.

Data from the Lumex CEM or the RA 915+ detectors were recorded at 1-second intervals throughout the verification test using laptop computers. Data from the Lumex CEM (and later the RA 915+ detector No. 164) were recorded in one set of files, and data from the RA 915+ detector No. 167 in a separate set of files. Data files were turned over to Battelle at the end of each test day, along with appropriate file documentation. Lumex staff provided additional summaries and graphical material after the verification test.

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 center-line. 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.

Although, in principle, the Lumex CEM could determine total mercury (including the particulate mercury component), experience at the RKIS indicated that little to no mercury would be found in the particulate matter. 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, and, consequently, the total mercury readings of the Lumex CEM were compared to the total vapor phase mercury results from the OH method.

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 auto-matically 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

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.

shows the actual schedule of OH sampling in the verification test. The OH sampling proceeded smoothly, with the single exception of a run 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 Lumex CEM, this comparison was made for elemental, oxidized, and total mercury. Oxidized mercury results for the Lumex CEM were calculated by Battelle by subtracting elemental mercury results from total mercury results. The Lumex CEM results during the period of each OH run were averaged for comparison to the OH result.

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 Lumex CEM with the OH results was assessed using the same data used to assess accuracy. The average Lumex CEM elemental mercury results over each OH sampling run were calculated and compared to the corresponding OH results.

3.3.3 Precision

Precision of the Lumex CEM was determined based on the Lumex CEM results in each OH sampling run. The relative standard deviation of the successive Lumex CEM 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 Lumex CEM 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 ($\sim 15\ \mu g/m^3$) was used in the first week, and a higher concentration standard ($\sim 50\ \mu g/m^3$) 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 withdrawing the Lumex sampling probe from the duct and connecting the tip of the probe to a Teflon line supplying the zero or calibration gas. A "T" fitting in the line allowed venting of a small excess flow of gas beyond that drawn by the Lumex CEM. The gas supplied in this way passed through the probe, water condenser, and sampling lines before entering the Lumex CEM or RA 915+ detector. Standard gas was also introduced at intermediate points in the inlet system to identify the origin of any sampling system bias.

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 Lumex CEM 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 Lumex CEM 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.

3.3.7 Response Time

Response time of the Lumex CEM 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 Lumex CEM readings when the delivery of elemental mercury standard gas was started or stopped, respectively. The time required to rise or fall 95% of the way to the final value was estimated from successive 1-second readings.

3.3.8 Low-Level Response

The mercury levels shown in Table 3-4 were not intended to challenge the detection limit of the Lumex CEM. Instead the ability of the Lumex CEM to detect low mercury levels was tested by a procedure conducted on January 19. On that day, the Lumex CEM initially sampled RKIS flue

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

		Substances Injected in Flue Gas (Target Concentration, ppm)				
Time	Hg[a] ($\mu g/m^3$)	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.

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 flue gas mercury concentrations of nominally 0.57 to 4.54 µg/m^3. The low-level response of the Lumex CEM 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 ($\mu g/m^3$)
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 Lumex CEM 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 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

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

Cylinder Number	Prepared Hg° Conc. (µg/m³)[a]	Pre-Test	Post Test	
		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.

CC19870, 19931, 20219, and 20291. 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 Lumex CEM was challenged in the first week of testing only with mercury standard cylinder number CC19931 and, in the second week, only with cylinder number CC20291. 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 19931, 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 two blank trains with a dilution of a commercial National Institute of Standards (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

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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 regent 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 pre-printed 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.

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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 µg/m^3, five showed levels of 0.5 to 1 µg/m^3, and two showed levels of 1.0 to 1.5 µg/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 Lumex CEM, 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 ($\mu g/m^3$)			
		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 ($\mu g/m^3$)			
		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

Date	Port Location	Total Hg (µg/m³)			
		Upstream		Downstream	
		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

Date	Port Location	Elemental Hg (µg/m³)			
		Upstream		Downstream	
		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/m³)			
		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/m³)			
		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 $\mu g/m^3$ at oxidized mercury levels of 1.2 to 1.3 $\mu g/m^3$. 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 $\mu g/m^3$, 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 water 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 Ontario Hydro Trains

Date	Train ID	Oxidized Hg	Hg^o (H$_2$O$_2$)	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 Audits

4.3.1 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.

4.3.2 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 4-4 summarizes the PE audits on several measurement devices at the RKIS; Table 4-5 summarizes the PE audit results from spiking OH trains.

Table 4-4 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 in simultaneous sampling of the flue gas. Duct temperature measurement was audited by

Table 4-4. Summary of PE Audits on Mercury CEM Verification

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

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 4-4 is for the 500-gram weight, which showed the greater percentage division.

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 4-5. 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 4-5 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 potassium permanganate 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. However, inadvertent pressurization caused a spillover between

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

Date	Train	Impinger[a] Number	Spike[b] (µg)	Analyses			Observed Agreement[c] (%)	Required Agreement (%)
				1st (µg)	2nd (µg)	Average (µg)		
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 $\times$ 100.

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.

4.3.3 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 Lumex CEM with respect to the elemental mercury results of the reference (OH) method was assessed by

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

where d refers to the arithmetic difference between corresponding OH and Lumex CEM results, and x corresponds to the OH result. S_d denotes the sample standard deviation of the differences, while t_{n-1}^{α} is the t value for the $100(1 - \alpha)$th percentile of the distribution with n-1 degrees of freedom. To calculate RA, the OH and corresponding Lumex CEM results were paired, and the differences between the paired results were calculated. Then, the absolute mean $|\bar{d}|$ and standard deviation (S_d) of those differences were calculated. The mean of the OH results $(\bar{x})$ was calculated, and the value of t_{n-1}^{α} 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 Lumex CEM 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 readings from the Lumex CEM were recorded, and the mean and standard deviations of those readings were calculated. Precision (*P*) was determined as

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

where *S* is the standard deviation of the readings and $\overline{X}$ 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

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

where $\overline{x}$ 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 Lumex CEM response when sampling elemental mercury standard gas through the entire Lumex CEM sample interface, compared to that when sampling the same gas directly at the Lumex CEM, expressed as a percentage of the response at the CEM. That is,

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

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

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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 Lumex CEM reading reached a level equal to 95% of that step change. Both rise time and fall time were determined. The Lumex CEM 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 Lumex CEM'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 Lumex CEM to determine low mercury concentrations was assessed by comparing responses at successive target levels of 0, 0.57, 1.13, 2.27, and 4.54 μg/m^3 of added mercury in the RKIS. 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 average elemental, oxidized, and total mercury results from the Lumex CEM during the period of each OH sampling run. Oxidized mercury is not measured directly by the Lumex CEM but is calculated from the difference in elemental and total mercury concentrations. These results may be compared to the OH results in Tables 4-1 and 4-2. Table 6-1 includes an indication of which data were obtained with the original CEM detectors and which with the substitute RA 915+ detectors.

In general, the Lumex CEM results were much lower than those of the OH method. The Lumex CEM did correctly indicate the approximate relative proportions of elemental and oxidized mercury in both weeks. However, throughout the verification test, the mercury results from the Lumex instruments were well below the corresponding OH results. In the first week, oxidized mercury results from the Lumex CEM were near zero in two runs and were reported as negative in two others. In the second week, the Lumex elemental mercury results were always very low. The total and oxidized mercury readings increased sharply on January 23 and 24, when the pyrolyzer in the CEM was set to a much higher temperature than earlier in the test. These results suggest that the pyrolyzer temperature was too low throughout much of the test. However, even with the increased pyrolyzer temperature, close agreement with the OH results in the last few OH runs was not obtained. Given the length and materials of construction of the inlet systems used with the Lumex instruments, loss of mercury species in the inlet likely also contributed to the generally low results obtained (see Section 6.5).

The results of the calculation of relative accuracy for the Lumex CEM are shown in Table 6-2, which provides separate relative accuracy results for the two weeks of testing for measuring elemental, oxidized, and total vapor-phase mercury. The relative accuracy for oxidized mercury in the first week was calculated both with and without the physically impossible negative results in OH Runs 2 and 5 (i.e., -0.54 and -0.05 $\mu g/m^3$, respectively, Table 6-1). In OH Run 2, the Lumex CEM showed unusual behavior in the form of abrupt changes in readings before and after brief zeroing intervals. In OH Run 5, the total mercury channel of the Lumex CEM showed a gradual downward drift that resulted in total mercury readings that were lower than those from the elemental mercury channel for the latter half of the OH run. As Table 6-2 indicates, excluding these results did not greatly improve the relative accuracy result for the Lumex CEM. Relative accuracy values of about 50 to over 100% were found for the various mercury species in the two weeks of sampling.

Table 6-1. Average Mercury Results from the Lumex CEM During OH Sampling Runs

Date	OH Run Number	Lumex CEM Results ($\mu g/m^3$)		
		EM[a]	OM[a]	TM[a]
January 15	1	3.94	0.45	4.39
	2	3.81	-0.54	3.27
January 16	3	3.77	0.39	4.17
	4	3.56	0.02	3.57
January 17	5	2.14	-0.05	2.08
	6	3.45	0.03	3.48
January 22	7	1.36	15.4	16.8
	8	1.60	17.8	19.4
	9	1.87	15.4	17.2
January 23	10	1.38	18.4	19.7
	11	1.47	26.1	27.6
	12	1.37	39.8	41.2
January 24	13	1.07	50.4	51.5
	14	0.88	44.1	45.0
	15	1.66	58.2	59.8

[a] EM = elemental Hg, OM = oxidized vapor-phase Hg, TM = total vapor-phase Hg. Only data from OH Runs 1 through 6 were obtained with the Lumex CEM; all subsequent data obtained with the substitute RA 915+ detectors.

Table 6-2. Relative Accuracy Results for the Lumex CEM

Test Period[b]	Relative Accuracy (%)		
	Elemental Hg	Oxidized Hg	Total Hg
Week One	50.2	99.0[a]	58.2
Week Two	107	69.4	71.0

[a] Result shown excludes negative Lumex CEM values for oxidized Hg in OH Runs 2 and 5; with those values included relative accuracy = 110%.

[b] Week One data obtained with Lumex CEM; Week Two data obtained with RA 915+ detectors.

6.2 Correlation

The correlation of the Lumex CEM results with the OH reference method was calculated using the elemental, oxidized, and total mercury results shown in Table 6-1. Correlation plots of the Lumex and OH data from the first and second weeks of testing, and from 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 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 Lumex CEM Data with OH Results

	Coefficient of Determination (r^2)		
Test Period	**Elemental Hg**	**Oxidized Hg**	**Total Hg**
Week One	0.020	0.332[a,b]	0.001
Week Two	0.465	0.143	0.057
Both Weeks	0.052	0.631	0.621

[a] Result shown excludes negative Lumex CEM values for oxidized Hg in OH Runs 2 and 5; with those values included $r^2 = 0.014$.
[b] This r^2 value is based on a negative value of r.

The results in Table 6-3 show that r^2 values for elemental and total mercury were near zero in the first week of testing, and the corresponding value for oxidized mercury would also be near zero if the negative values in OH Runs 2 and 5 were not excluded. Note that, as indicated in the footnote to Table 6-3, the r^2 value for oxidized mercury in the first week results from a negative r value (i.e., anticorrelation with the OH results). In that week, the Lumex CEM oxidized mercury results gave a negative r value with respect to the OH results, whether the two negative Lumex CEM results from OH Runs 2 and 5 were included or not. These low values may be due largely to the limited range of mercury concentrations present in that first week (Table 4-1). In the second week, the r^2 value for elemental mercury was highest and that for total mercury the lowest. Both weeks combined provide the largest data set and the widest range of data, and consequently are most suitable for calculation of correlation. Table 6-3 shows that the r^2 value for elemental mercury based on both weeks of data is about 0.05, whereas r^2 for both oxidized and total mercury exceeds 0.6.

6.3 Precision

The precision of Lumex CEM 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 RSD of the elemental and total readings in each period. The mean and standard deviation of the readings are also shown.
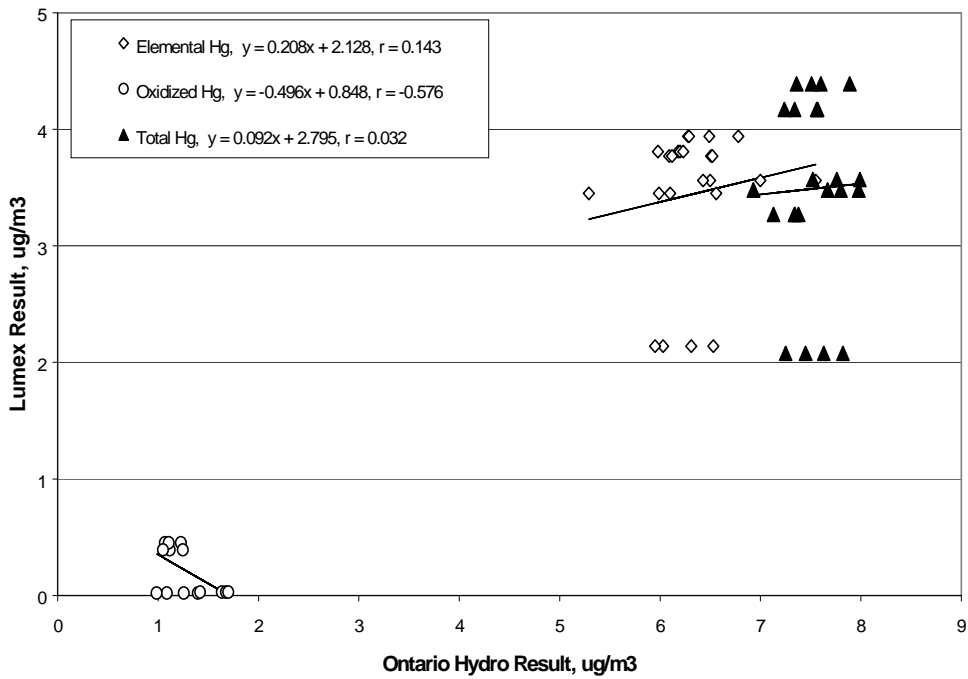
Figure 6-1a. Correlation Plot of Lumex and OH Results for Week One of Verification Testing
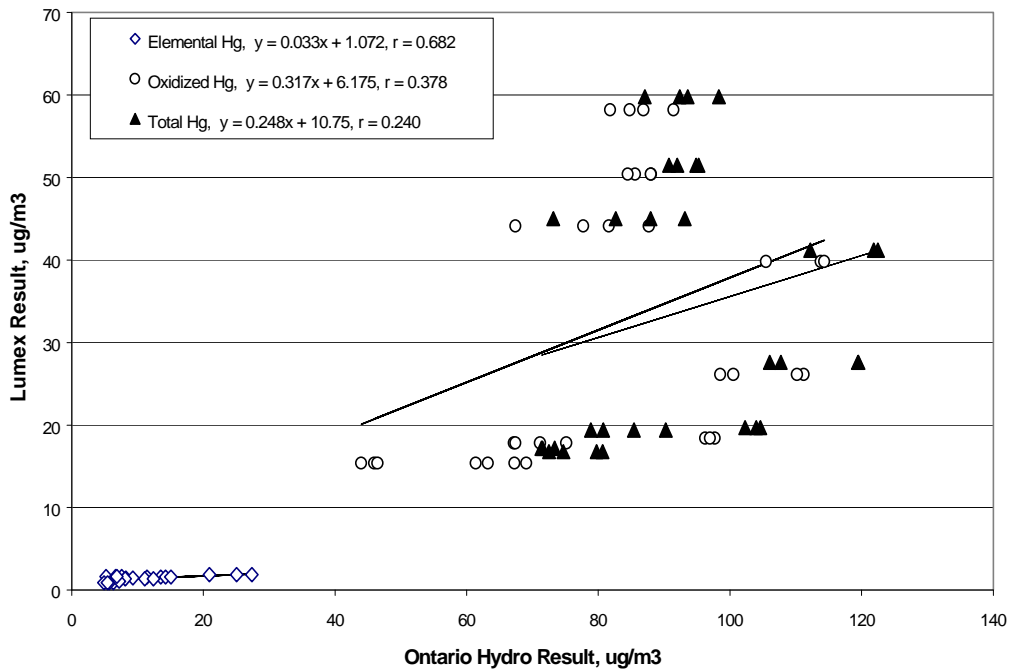

Figure 6-1b. Correlation Plot of Lumex and OH Results for Week Two of Verification Testing
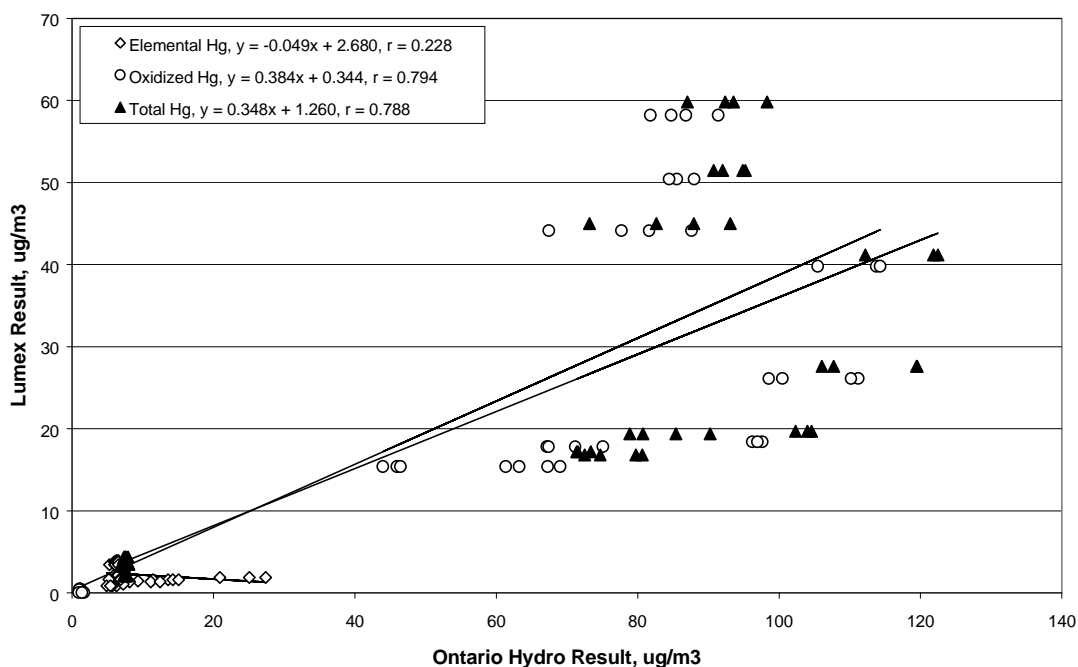
Figure 6-1c. Correlation Plot of Lumex and OH Results from Both Weeks of Verification Testing

The purpose of this test was to assess the precision of the Lumex CEM 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 calculating the percent RSD.

The results in Table 6-4 indicate that the precision of the Lumex instruments for elemental mercury was within 10% RSD in five of the 15 OH sampling periods, and within 15% RSD in eight periods. The very low elemental mercury results reported in week two often exhibited relatively high percent RSD values. For total mercury, the Lumex instruments exhibited precision within 10% RSD in eight of the 15 OH sampling periods, and within 15% in 11 of the periods. The results in Table 6-4 indicate that the Lumex CEM and RA 915+ detectors are capable of precision within 10% RSD. Note that modifications made by Lumex staff to their system during testing may have contributed to the variability observed. For example, during OH Run 14, a large increase in total mercury response was observed, and is thought to result from adjustments made to the pyrolyzer temperature in this period.

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Table 6-4. Precision Results for the Lumex CEM

Date	OH Run Number	Elemental Mercury Mean (Std. Dev.)	% RSD	Total Mercury Mean (Std. Dev.)	% RSD
1/15	1	3.94 (0.46)	11.6	4.39 (0.88)	19.9
	2	3.81 (0.89)	23.3	3.27 (0.88)	27.0
1/16	3	3.77 (0.12)	3.2	4.17 (0.20)	4.7
	4	3.56[a] (0.33)	9.3	3.56[a] (0.28)	7.9
1/17	5	2.14[a] (0.14)	6.5	2.08[a] (0.35)	16.8
	6	3.45 (0.18)	5.2	3.48 (0.49)	14.1
1/22	7	1.36 (0.36)	26.3	16.8 (0.73)	4.4
	8	1.60 (0.55)	34.4	19.4 (1.15)	5.9
	9	1.79[a] (0.53)	29.7	17.0[a] (1.92)	11.3
1/23	10	1.38 (0.15)	10.7	19.8 (0.87)	4.4
	11	1.31[a] (0.10)	7.8	27.8[a] (2.90)	10.4
	12	1.37 (0.16)	12.0	41.2 (1.05)	2.5
1/24	13	1.07 (0.43)	39.7	51.5 (1.65)	3.2
	14	0.88 (0.27)	30.4	45.0 (12.1)	27.0
	15	1.66 (0.42)	25.3	59.8 (2.7)	4.5

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

6.4 Calibration/Zero Drift

The daily Lumex 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. Table 6-5 includes readings for both elemental and total mercury.

Table 6-6 summarizes the calibration/zero drift results, in terms of the mean, standard deviation, percent 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. Because of the substitution of detectors that took place on January 18 with the Lumex CEM, Table 6-6 shows averaged zero and standard gas responses for the different detectors in different time periods.

Tables 6-5 and 6-6 show that the Lumex CEM and RA 915+ detectors gave near-zero readings on zero gas in almost all cases. However, the Lumex CEM gave widely varying responses with the standard gas in the first week. Responses to the standard gas varied by about a factor of three over the three days in which the Lumex CEM was operational. This variability resulted in percent RSD values for the standard gas response of about 50% in that period (Table 6-6). This variability is probably caused by the CEM itself, not by the mercury standard (cylinder CC 19931), based on the long-term stability of all the mercury standards (Section 3.4.1) and daily observations with the other standards used in this verification. Only a few analyses of this standard were conducted after the substitution of the RA 915+ detectors on January 18. Those few results show better consistency of response than did the Lumex CEM results.

Tables 6-5 and 6-6 also show that the RA 915+ detectors gave consistent readings on the standard gas (cylinder CC 20291) used in the second week of verification. The average values of the standard gas readings from the two RA 915+ detectors (55.3 and 58.3 $\mu g/m^3$, respectively) agree within about 5%, and the two detectors show percent RSD values of 5.4 and 6.1%, respectively. These observations show the stability of the Lumex detection approach, and also support the utility of the elemental mercury standards for confirmation of CEM stability. The mercury concentrations in the gas standards are not known absolutely, but the average mercury standard concentrations determined by the Lumex CEM and RA 915+ detectors in the first week (14.7 to 15.7 $\mu g/m^3$, and 11.7 to 13.2 $\mu g/m^3$, respectively) are all within a range of +11 to -17% of the nominal concentration of 14.1 $\mu g/m^3$ stated by the manufacturer (Section 3.4.1). Similarly, the average standard concentrations determined by the RA 915+ detectors in the second week (55.3 and 58.3 $\mu g/m^3$) are within 11% and 17%, respectively, of the manufacturer's nominal value of 49.8 $\mu g/m^3$.

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Table 6-5. Zero and Standard Gas Responses of the Lumex CEM

	Date	Elemental Mercury Response[a]		Total Mercury Response[b]	
		Zero Gas (μg/m^3)	Standard Gas (μg/m^3)	Zero Gas (μg/m^3)	Standard Gas (μg/m^3)
Week One	1/15/01	-0.29	10.9[c]	-0.20	13.5[c]
		0.37	27.1	0.18	22.9
	1/16/01	-0.02	20.1	-0.01	20.3
		-0.04	13.7	-0.02	14.0
	1/17/01	0.00	8.4	-0.04	8.6
		0.05	9.3	0.05	7.5
	1/18/01	0.00	13.6	NA	NA
		-0.01	12.9	-0.01	9.6
	1/19/01	0.00	13.2	0.15	13.8
Week Two	1/22/01	-0.06	54.8	0.02	55.4
		0.04	56.6	-2.45	57.2
	1/23/01	0.02	54.7	0.02	52.1
		0.05	58.0	-0.06	60.1
	1/24/01	0.14	58.6	-0.04	60.9
		0.04	54.8	0.42	61.8
	1/25/01	0.17	49.6	0.74	60.6

[a] Readings through 1/17/01 obtained with Lumex CEM; readings after that obtained with RA 915+ detector No. 167.

[b] Readings through 1/17/01 obtained with Lumex CEM; readings after that obtained with RA 915+ detector No. 164.

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

NA = Not available.

Table 6-6. Summary of Calibration /Zero Drift Results for the Lumex CEM

	Result	Elemental Mercury Response		Mercury Response	
		Zero Gas ($\mu g/m^3$)	Standard Gas ($\mu g/m^3$)	Zero Gas ($\mu g/m^3$)	Standard Gas ($\mu g/m^3$)
Week One	Mean[a]	0.01	15.7[b]	0.001	14.7[b]
	Std. Dev[a].	0.21	7.9	0.001	6.9
	% RSD[a]	NA	50.3	NA	46.7
	Maximum[a]	0.37	27.1	0.18	15.8
	Minimum[a]	-0.29	8.4	-0.20	14.6
	Mean[c]	0.00	13.2	0.07	11.7
	Std. Dev.[c]	0.01	0.35	0.10	3.0
	% RSD[c]	NA	2.7	NA	25.4
	Maximum[c]	0.00	13.6	0.15	13.8
	Minimum[c]	-0.01	12.9	-0.01	9.6
Week Two	Mean[d]	0.01	55.3	-0.19	58.3
	Std. Dev.[d]	0.10	2.98	1.04	3.55
	% RSD[d]	NA	5.4	NA	6.1
	Maximum[d]	0.14	58.6	0.74	61.8
	Minimum[d]	-0.17	49.6	-2.45	52.1

[a] Based on data from Lumex CEM through 1/17/01.
[b] Excludes first standard gas result from 1/15/01; delivery procedure for elemental mercury standard gas not properly equilibrated.
[c] Based on data from RA 915+ No. 167 (elemental mercury) and RA 915+ No. 164 (total mercury) on 1/18 and 1/19/01.
[d] Based on data from RA 915+ No. 167 (elemental mercury) and RA 915+ No. 164 (total mercury) in the second week of testing.
NA = not applicable.

6.5 Sampling System Bias

Table 6-7 shows the results of providing the elemental mercury gas standards directly to the RA 915+ detectors, and at different locations in the Lumex sampling probes, on January 19 and 25, 2001. Shown are the final stable readings on the zero gas and the mercury standard, when the respective gas was provided at the detector inlet, at the inlet of the ice bath condenser in the sample line, and at the inlet of the flue gas probe (i.e., through the entire sample inlet system).

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Table 6-7. Results of Sampling System Bias Test of the Lumex CEM[a]

Date	Gas To:	Elemental Mercury Response			Total Mercury Response		
		Zero ($\mu g/m^3$)	Standard ($\mu g/m^3$)	Bias[b] %	Zero ($\mu g/m^3$)	Standard ($\mu g/m^3$)	Bias[b] %
1/19/01	Analyzer	0.00	13.2	--	0.15	13.8	--
	Condenser	0.04	12.9	-2.6	NT	NT	NT
	Probe Inlet	0.23	7.56	-44.5	0.05	8.75	-36.3
1/25/01	Analyzer	-0.17	49.6	--	0.74	60.6	--
	Condenser	0.28	55.3	10.5	0.45	58.9	-2.4
	Probe Inlet	0.18	51.2	2.5	0.63	48.2	-20.5

[a] Lumex CEM operated with substitute RA 915+ detectors on both January 19 and 25; RA 915+ No. 167 (elemental mercury) and RA 915+ No. 164 (total mercury)

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

NT = not tested.

Both elemental and total mercury readings are shown in Table 6-7. The resulting bias in transport of the elemental mercury standard is also shown in each case.

Table 6-7 shows that, in the test with the elemental mercury detector on January 25, positive sampling system biases (i.e., delivery efficiencies greater than 100%) were obtained. This result is probably due to an error in the measurement of the standard gas delivered at the analyzer. However, the test was not repeated, and those test results are disregarded. Considering the other results, the bias in transport of elemental mercury through the Lumex condensers and to the analyzers was minimal: -2.6% in the one test made with the lower level mercury standard, and -2.4% in one test with the higher level standard. On the other hand, when elemental mercury was sampled through the entire Lumex inlet systems, relatively large biases were obtained, i.e., from -20.5 to -44.5%. These results clearly suggest that the Lumex inlets caused loss of elemental mercury in sampling of flue gas. Given the ease with which oxidized forms of mercury are adsorbed on surfaces, these results also suggest that negative biases in sampling oxidized mercury were similarly large. Note that the Lumex inlets were composed in part of stainless steel tubing, whereas Teflon, other plastics, and glass may be preferable materials. These findings indicate that the relative accuracy values found for the Lumex CEM (Section 6.1) may have been at least partly due to inefficient transfer of mercury from flue gas to the mercury detectors.

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. Figures 6-2a and b illustrate the elemental and total mercury response, respectively, of the Lumex CEM with RA 915+ detectors 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 6-2a shows that neither 500 ppm NO nor 500 ppm CO had any effect on the readings of the Lumex elemental mercury channel (RA 915+ detector No. 167). However, elemental mercury readings decreased from about 6 to about 4 $\mu g/m^3$ upon the addition of 2,000 ppm sulfur dioxide, before stabilizing at about 5 $\mu g/m^3$. Addition of 250 ppm hydrogen chloride to the duct caused a sharp decrease in elemental mercury readings. Replacement of the hydrogen chloride with 10 ppm of chlorine further decreased the elemental mercury readings, to less than 1 $\mu g/m^3$. Addition of nitric oxide along with the chlorine caused the elemental mercury readings to rise only slightly. When all the interferants were added at once, the Lumex elemental mercury readings remained near 1 $\mu g/m^3$, i.e., a small fraction of the initial elemental mercury level. Unfortunately, data were not recorded for elemental mercury for the last portion of this test, in which only elemental mercury was once more present in the duct.

The corresponding results from the Lumex total mercury channel (RA 915+ detector No. 164) are shown in Figure 6-2b. When 500 ppm of nitric oxide was added to the duct, the Lumex instrument showed a large and broad peak in total mercury response, before settling back to the original total mercury reading. Addition of 500 ppm carbon monoxide and then 2,000 ppm sulfur dioxide had no significant effect on total mercury response. [Note that in this time period the total mercury channel (Figure 6-2b) read lower than the elementary mercury channel (Figure 6-2a).] Adding 250 ppm hydrogen chloride reduced the total mercury readings by nearly half, and replacing the hydrogen chloride with 10 ppm of chlorine reduced total mercury readings still further, though not to as great an extent as was observed for elementary mercury. Adding nitric oxide with the chlorine partly restored the total mercury response, but no further increase was seen when all the interferants were introduced together. When only mercury was once more present in the duct, the total mercury reading was close to that observed before any interferant gases were introduced.

These results indicate that the pyrolytic approach to total mercury measurement used in the Lumex CEM did not provide stable total mercury measurements in the presence of the interferant gases. The presence of hydrogen chloride and/or chlorine caused a reduction in the total mercury readings. This result may be due to loss of oxidized mercury species in the Lumex inlet systems: the observed transfer efficiencies for elemental mercury of about 55 to 80% (Section 6.5) suggest that losses of the more easily adsorbed oxidized mercury may be large. In addition, it should be noted that at the time of this interference test the temperature of the pyrolyzer in the Lumex CEM was relatively low. Poor conversion of oxidized to elemental mercury may have resulted from the low pyrolyzer temperature.
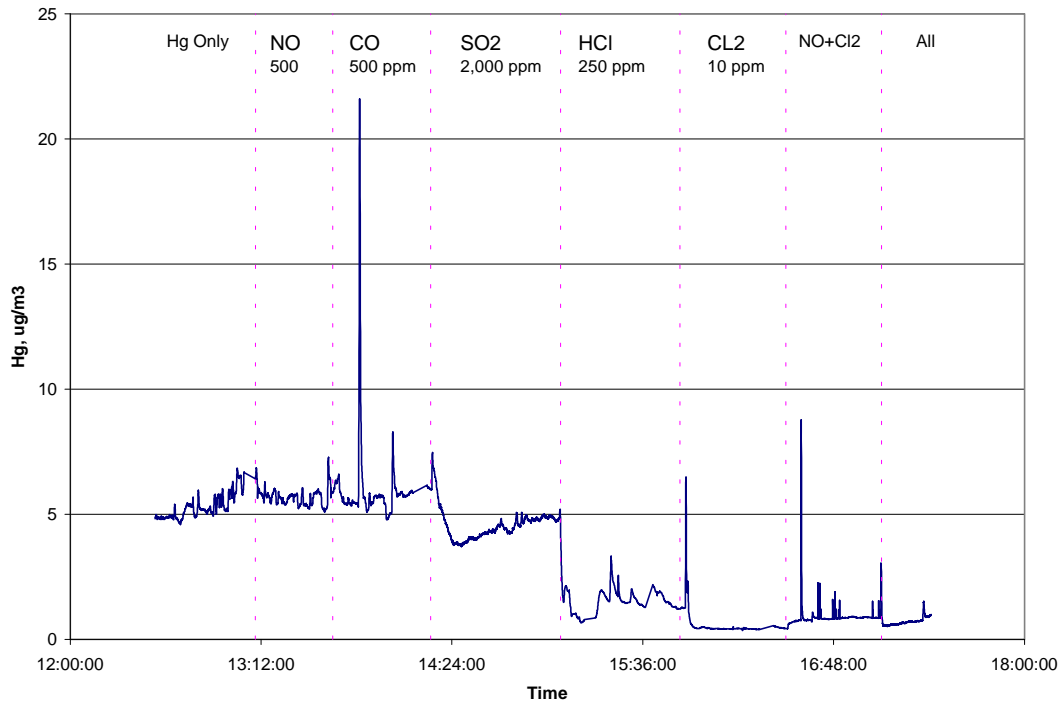
Figure 6-2a. Lumex CEM Elemental Mercury Response in Interference Test, January 18, 2001
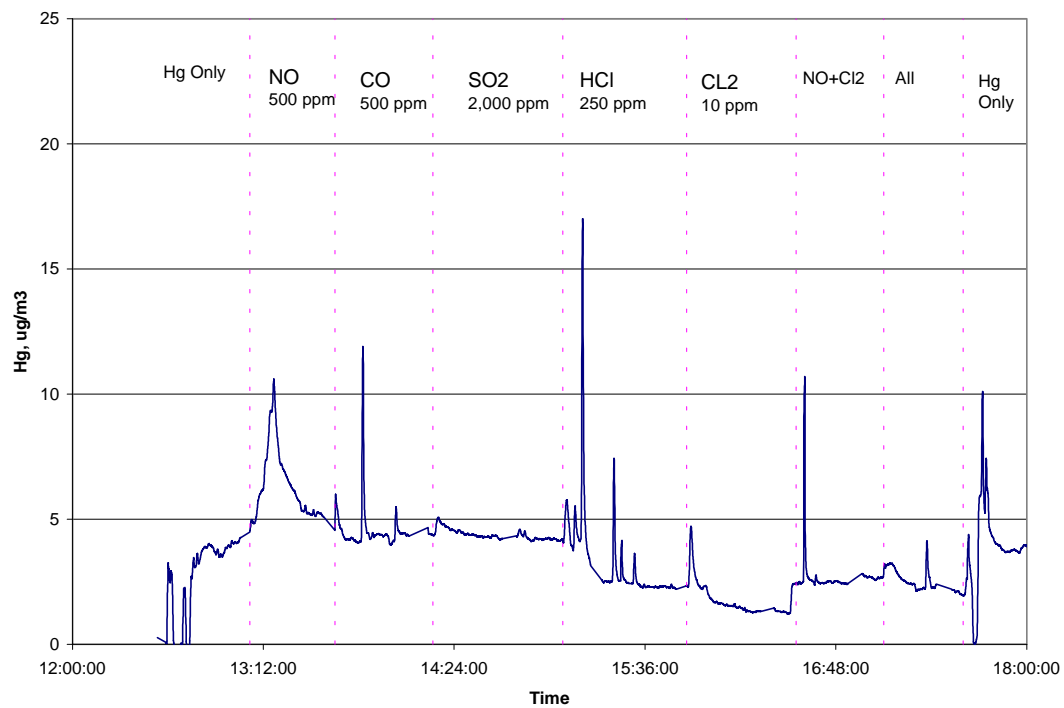

Figure 6-2b. Lumex CEM Total Mercury Response in Interference Test, January 18, 2001

6.7 Response Time

The rise and fall times of the Lumex CEM 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 summarizes the resulting response times, listing the rise and fall times (in seconds) found for both the elemental and total mercury channels of the Lumex instrument. Note that, from January 18 on, the RA 915+ detectors were used in place of the detectors originally used in the Lumex CEM.

Table 6-8 shows that there was considerable variability in the observed response times of the Lumex instruments. Rise and fall times varied from 20 seconds to nearly 150 seconds, with most results between abut 30 and 100 seconds. The reason for this variability is not known; the zero and span gases were always introduced in the same manner, and the small variability in starting and stopping those gases cannot account for so wide a range of response times. As noted above, the Lumex inlet systems were modified during the course of this test, and those modifications may contribute to the variability observed. In any case, Table 6-8 shows that the Lumex CEM generally exhibited response times of about one minute or less.

6.8 Low-Level Response

Figures 6-3a and b illustrate the response of the Lumex CEM to low levels of mercury injected into the duct, as described in Section 3.3.8. Figure 6-3a shows the elemental mercury response of the Lumex RA 915+ No. 167, during the low level response test on January 19. Figure 6-3b shows the corresponding total mercury response of the RA 915+ No. 164. The dashed vertical lines in each figure indicate the time periods during which each indicated mercury level was introduced.

Figures 6-3a and b show that the Lumex CEM responded to all mercury concentrations injected, producing a clearly observable response above the flue gas background even with the injection of as little as 0.57 µg/m^3 of Hg. The added mercury was detected largely in the form of elemental mercury. The primary observation from these data is that the Lumex CEM is sensitive enough to detect mercury at levels below 1 µg/m^3. However, the increases in response were not in quantitative agreement with the nominal mercury levels injected. For example, with a nominal total mercury concentration of 4.54 µg/m^3 added to the duct, the Lumex total mercury response was only about 2.5 µg/m^3 above flue gas background (Figure 6-3b). When the Lumex total mercury responses at each mercury level are averaged, a regression of average Lumex response *vs.* nominal mercury level gives the equation Lumex response = 0.55 × (Hg, µg/m^3) + 0.11 µg/m^3, with r^2 = 0.992. Other sources of information confirm that the mercury levels in the duct were close to the nominal values, so these regression results indicate that the Lumex CEM reported substantially low in this test. This result is consistent with the generally low readings provided by the Lumex CEM and RA 915+ instruments in comparison to the OH results (Section 6.1). The relatively large bias caused by the Lumex sampling inlets (Section 6.5) is undoubtedly a factor in the low-level response results. In fact, the slope of the regression noted above is consistent with the biases found in transfer of elemental mercury, shown in Table 6-7.

Table 6-8. Results of Response Time Tests on the Lumex CEM

Date	Elemental Mercury		Total Mercury	
	Rise Time	**Fall Time**	**Rise Time**	**Fall time**
1/15/01 a.m.	97[a]	42	96	41
1/15/01 p.m.	79	NA	36	NA
1/16/01 a.m.	51	48	50	47
1/16/01 p.m.	108	104	67	96
1/17/01 a.m.	NA	96	NA	66
1/17/01 p.m.	57	NA	122	NA
1/18/01 a.m.	66	20	NA	NA
1/18/01 p.m.	NA	NA	34	90
1/19/01 a.m.	NA	NA	NA	NA
1/22/01 a.m.	105	39	148	34
1/22/01 p.m.	136	82	133	NA
1/23/01 a.m.	39	74	110	76
1/23/01 p.m.	92	64	32	31
1/24/01 a.m.	49	42	31	30
1/24/01 p.m.	55	47	31	31
1/25/01 a.m.	35[b]	33[b]	31[b]	31[b]
1/25/01 p.m.	31	33	NA	NA
	44[b]	39[b]	37[b]	NA
	47[c]	45[c]	NA	NA

[a] All rise and fall times in seconds; and all results are for gases provided at the analyzer inlet, unless otherwise noted.
[b] Data with gas supplied to inlet of the ice bath condenser.
[c] Data with gas supplied through entire CEM inlet system.
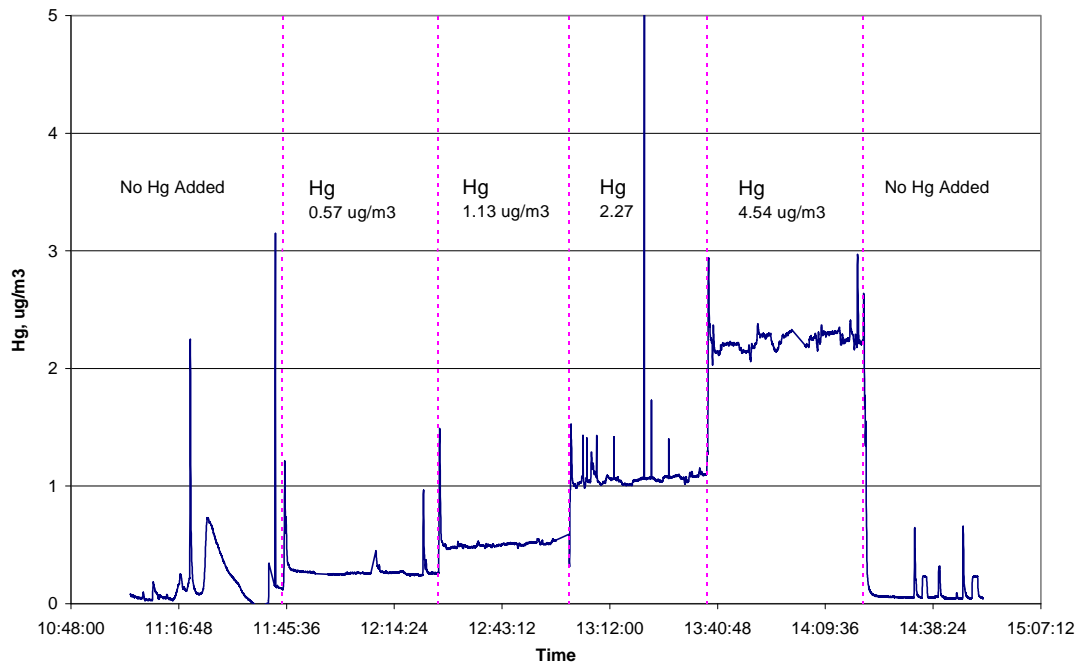NA=not available.

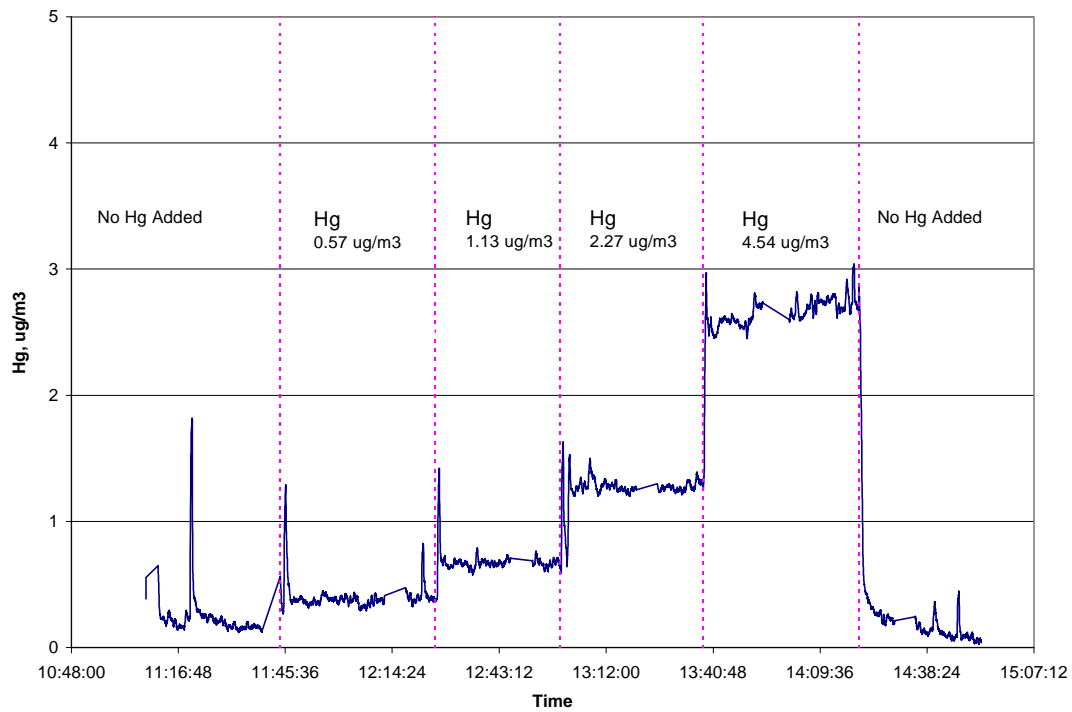**Figure 6-3a. Lumex Elemental Mercury Response During Low-Level Response Test, January 19, 2001**

Figure 6-3b. Lumex Total Mercury Response During Low-Level Response Test, January 19, 2001

6.9 Data Completeness

The Lumex mercury CEM operated reliably for the first few days of verification testing, achieving 100% data recovery over that period, but then was damaged in operation and was not repairable. The substitute RA 915+ detectors operated reliably for the rest of the verification test. However, modifications were made to the Lumex pyrolyzer and the inlet systems during the test. In conjunction with the change in mercury detectors, these modifications prevent any firm conclusions about the reliability of a single Lumex CEM over the course of the test. In addition, small periods of Lumex data were lost from a few OH runs, due to truncation or loss of the electronic data files, apparently due to operator error.

6.10 Setup and Maintenance

The Lumex CEM and RA 915+ detectors were set up and operated by four representatives of Lumex Ltd., and from three to five Lumex representatives were present throughout the verification test. The Lumex CEM and RA 915+ detectors were easily set up and were ready to sample flue gas within about two hours. Because of problems with the Lumex CEM, substantial effort was spent in maintenance and modification of the instruments. However, routine scheduled maintenance was minimal, consisting essentially of replenishing the ice in the ice bath condensers used to remove water from the sampled gas. The Lumex CEM requires no gas supplies and uses no liquid reagents or other consumables.

6.11 Cost

No estimate of the purchase price of the Lumex CEM was available.

Chapter 7
Performance Summary

This verification report presents the results of testing the Lumex CEM and substitute Lumex RA 915+ detectors that were put into operation after the CEM was damaged. The Lumex CEM was new at the time of this verification, and modifications were made to the Lumex pyrolyzer system and inlet systems during the test. As a result of these factors, the verification results summarized below must be considered to apply to the Lumex technologies and approaches in general, rather than to the Lumex CEM specifically.

During the first week of verification testing, the Lumex CEM provided accuracy relative to the OH method of 58.2% for total mercury, at total mercury levels of about 7 to 8 µg/m^3. Testing showed relative accuracy of 50.2% for elemental mercury and 99% for oxidized mercury, at elemental mercury levels of approximately 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, the Lumex instruments provided relative accuracy of 71% for total mercury, at total mercury levels of about 70 to 120 µg/m^3. Relative accuracy of 107% for elemental mercury and 69.4% 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. These RA results were caused primarily by a consistent underestimation of all mercury concentrations by the Lumex CEM, which may have been due to both losses of mercury in the inlet systems, and low pyrolyzer temperatures for much of the test.

The coefficient of determination (r^2) of the Lumex and OH elemental mercury results was 0.052, based on the data from both weeks of verification. The corresponding r^2 values for oxidized mercury and total mercury were 0.631 and 0.621, respectively.

Precision of the Lumex 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 Lumex response for elemental mercury was within 10% in five of the 15 periods, and within 15% in eight of the periods. For total mercury, precision was within 10% RSD in eight of the 15 periods and within 15% in 11 of the periods. These precision results include both variability in the test facility and in the Lumex instruments.

Calibration and zero drift were determined by repeated analysis of zero gas and elemental mercury standard gases. The failure of the Lumex CEM and subsequent substitution of the RA 915+ detectors interrupted the continuity of this portion of the test. Both the Lumex CEM and the RA 915+ detectors gave consistent readings on zero gas in both weeks of testing. Six analyses of

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a mercury standard gas with the Lumex CEM in the first week of verification gave average responses of 15.7 ($\pm$ 7.9) and 14.7 ($\pm$ 6.9) $\mu g/m^3$ for elemental and total mercury, respectively. These values equate to percent RSD's of 50.3% and 46.7%, respectively. Three analyses of the same standard with the RA 915+ detectors in the first week gave 13.2 ($\pm$ 0.35) and 11.7 ($\pm$ 3.0) $\mu g/m^3$, respectively, for percent RSD values of 2.7% and 25.4%. Seven analyses of a different standard by the RA 915+ detectors in the second week of verification gave readings of 55.3 ($\pm$ 2.98) and 58.3 ($\pm$ 3.55) $\mu g/m^3$ for elemental and total mercury, respectively. These standard gas results equate to percent RSD values of 5.4% and 6.1%, respectively. The Lumex CEM exhibited rise and fall times that varied substantially, usually ranging between about 30 seconds and 100 seconds.

Sampling system bias of the inlet systems used with the Lumex CEM and RA 915+ detectors was determined using elemental mercury gas standards. The bias in transport of elemental mercury through the entire inlet systems ranged from -20.5 to -44.5%.

Elevated levels of sulfur dioxide, nitrogen oxides, and carbon monoxide had little effect on Lumex response to elemental or oxidized mercury in flue gas. However, the presence of hydrogen chloride or chlorine reduced elemental mercury readings from about 5 $\mu g/m^3$ to less than 1 $\mu g/m^3$, and the total mercury readings were also reduced by half or more in the presence of these species. When these gases were all present at once in the flue gas, the Lumex elemental mercury readings remained below 1 $\mu g/m^3$, and the total mercury readings were only about 60% of those with the same mercury level but no interferants present.

The Lumex CEM (with RA 915+ detectors in place) responded to as little as 0.57 $\mu g/m^3$ of mercury in flue gas, but the response to concentrations of 0.57 to 4.5 $\mu g/m^3$ averaged only about 55% of the nominal mercury concentration. Loss of mercury in the CEM's inlet system is one possible cause for the low response at low mercury levels.

The setup and operation of the Lumex instruments was relatively simple, and the pyrolysis approach requires no chemical reagents or solutions and no external gas supplies. Routine maintenance was limited to that required for the ice bath condensers in the sampling inlets. However, failure of the Lumex CEM required substitution of the RA 915+ detectors to continue the verification. Data completeness cannot be estimated well because of the changes in detectors used and the modifications made to Lumex inlet systems and the pyrolysis unit during the test.

Chapter 8
References

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