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Environmental Technology Verification Report

NIPPON INSTRUMENTS CORPORATION DM-6/DM-6P MERCURY CONTINUOUS EMISSION MONITOR

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ETV Advanced Monitoring Systems Center

Nippon Instruments Corporation DM-6/DM-6P Mercury Continuous Emission Monitor

by
Thomas Kelly
Zachary Willenberg
Karen Riggs

Battelle
Columbus, Ohio 43201

and
(under the support of the U.S. Department of Energy)

James Dunn
Shaw Environmental, Inc.
Oak Ridge, Tennessee
Kristopher Kinder
Shaw Environmental, Inc.
Knoxville, Tennessee
James Calcagno
University of Tennessee
Knoxville, Tennessee

Notice

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Foreword

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

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

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

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List of Abbreviations

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

Chapter 1
Background

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

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

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of continuous emission monitors (CEMs) for mercury, including the Nippon Instruments Corporation DM-6/DM-6P 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 DM-6/DM-6P mercury CEM. Following is a description of the DM-6/DM-6P mercury CEM, based on information provided by the vendor. The information provided below was not subjected to verification in this test.

The DM-6/DM-6P mercury CEM is designed to provide continuous measurement of total vapor-phase mercury (Hg_T) in stack gases. Stack gas is pulled from the stack through a glass-lined probe maintained at 180°C (356°F) and a glass fiber particulate filter maintained at 200°C (392°F). The sample then passes through a catalyst bed that is heated to 160°C (320°F) to reduce oxidized mercury to elemental (Hg^o) mercury. The catalytic process is housed in a heater box that may be located either adjacent to the stack or remotely. If the catalyst is located remotely from the stack, a heated Teflon sample line is used to connect the catalyst heater box to the inlet probe and filter. After exiting the catalyst, the sample passes through a liquid/gas separator and is cooled to 2°C by a solid-state Peltier chip. The cooled sample gas is then filtered once again by a membrane filter before being transported to the detector. The detector is a cold vapor atomic absorption (CVAA) analyzer that reports total mercury.

The detector is factory calibrated, although an on-board permeation tube calibration source is available as an option for field calibration. The detector signal is zeroed automatically by passing sample gas over a gold trap to collect and remove mercury. The resulting zero gas is then introduced directly into the DM-6/DM-6P. The DM-6/DM-6P response to the zero gas is automatically adjusted to zero by the system. Figure 2-1 shows the DM-6/DM-6P installed in the CEM trailer at the base of the incinerator stack during this verification test. The DM-6/DM-6P does not require argon, compressed air, or other gas supplies for operation.

Figure 2-1. Nippon Instruments DM-6/DM-6P CEM

Chapter 3
Test Design and Procedures

3.1 Introduction

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

The performance of the DM-6/DM-6P was verified while monitoring emissions from the TSCAI that were generated from treating actual waste. The reference method for establishing the quantitative performance of the tested technologies was the Ontario Hydro (OH) method.(2)

The DM-6/DM-6P performance parameters addressed included

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

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

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

3.2 Facility Description

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

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

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

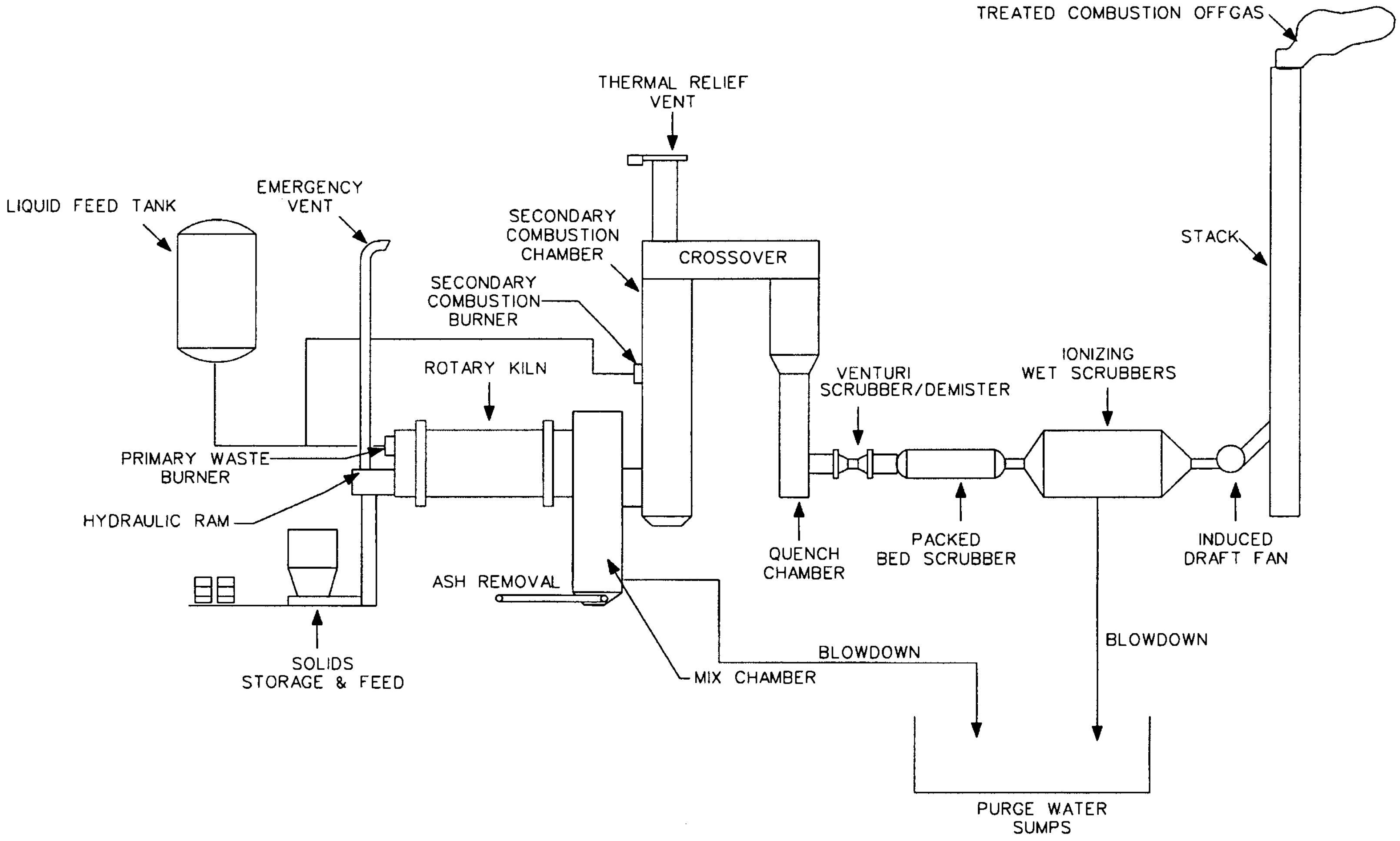

Figure 3-1. Schematic of the TSCAI and Off-Gas Cleaning System

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

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

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

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

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

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

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

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

3.3 Test Design

3.3.1 Equipment Setup

The DM-6/DM-6P was housed in the TSCAI Test Bed Mobile Laboratory Trailer located near the base of the TSCAI stack. A dedicated data acquisition system was placed inside the trailer for logging signals from the DM-6/DM-6P and other CEMs undergoing verification. The data logger was also connected to the facility Supervisory Control and Data Acquisition system through an Ethernet link to collect and log process parameters on the DM-6/DM-6P data logger.

At the lower of the two platforms on the TSCAI stack (i.e., about 30 feet above ground level), one sampling port was dedicated to a probe that extracts stack gas to be analyzed for CO, CO_2, and O_2 by the facility CEMs. Other ports at this level were used for the DM-6/DM-6P and other CEMs being tested.

For the DM-6/DM-6P, the vendor-supplied extractive sampling probe was connected to the CEM by means of a 1/4-inch outside diameter (0.156-inch inside diameter), heated PFA Teflon sample line. A vendor representative oversaw installation of the DM-6/DM-6P, which shared the heated Teflon sample line and extractive probe with another Nippon Instruments mercury CEM that was also undergoing verification. The source sample was withdrawn from the TSCAI stack through a glass-lined probe that was heated to 180°C (356°F). The sample then passed through a heated fiberglass filter located outside the stack in a heater box maintained at 200°C (392°F). For this verification, the heated mercury conversion catalyst was located in the trailer of the base of the TSCAI stack rather than mounted on the stack. A pump located near the instrument drew the sample gas through the 130-foot PFA Teflon sample line maintained at 180°C (356°) and into the thermal catalyst unit that converts oxidized mercury in the sample gas to Hg^o for detection (see Chapter 2). The total sample flow through the probe, filter, and Teflon line was approximately two liters per minute. Like all CEMs in this verification test, the Nippon DM-6/DM-6P sampled at a single (fixed) point in the stack. This CEM provides a continuous measurement of total vapor-phase mercury (Hg_T) (i.e., the sum of Hg° and oxidized [Hg_{OX}] mercury vapor), but does not determine particle-phase mercury. Verification of the performance of the DM-6/DM-6P was based on comparison with the corresponding Hg_T results from the OH reference method.

3.3.2 Test Schedule

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

The TSCAI was operated continuously during the first and last weeks of the test and was not shut down overnight. Such continuous round-the-clock operation is the standard mode of operation for the TSCAI. During the OH reference method sampling runs, the TSCAI burned aqueous,

Table 3-2. Mercury CEM Verification Test Schedule

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

solid, or a combination of aqueous and solid waste. The waste was characterized by chemical analysis before the test began, and some measure of control of the stack mercury concentration was achieved by varying the feed rate of aqueous waste and/or mixing solid and aqueous waste materials.

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

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

3.3.3 Reference Method Sampling

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

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

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

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

All OH trains were prepared, recovered, and analyzed in the same manner, with one exception. The particulate filters from trains designated “A” and used for sampling at the TSCAI stack were weighed before and after sampling to determine particulate matter loading in the flue gas,

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

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

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

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

whereas those from the trains designated “B” were not. The particulate loadings determined from the A trains ranged from 0.0012 to 0.0079 grain/dscf (2.68 to 18.2 mg/dscm). Particulate mercury was determined from the filter catch and probe rinse of both the A and B trains in all samples, but was never found at significant levels (i.e., maximum values of particulate Hg were less than 0.003 µg/dscm). Given this negligible amount of particulate mercury, the total vapor-phase mercury (Hg_T) determined by the OH method can be considered as the total mercury content of the stack gas.

3.3.4 Verification Procedures

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

Table 3-5. Data Used for DM-6/DM-6P Performance Evaluation

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

3.3.4.1 Relative Accuracy

The RA of the DM-6/DM-6P was verified using the OH reference method data for total mercury. The Hg_T readings of the DM-6/DM-6P during each OH sampling interval were averaged and compared with the average of the Hg_T results from the paired OH trains (see Section 4.2.1). The RA equation stated in Section 5.1 was applied to the averaged CEM data, using the OH data as the reference values. To optimize the comparability of the CEM and OH data, the OH sampling was coordinated with the CEM operations as noted in Section 3.3.3.

3.3.4.2 Correlation with Reference Method

The correlation of DM-6/DM-6P total mercury results with the OH results was based on the same data used to assess RA. No additional test procedures were needed to verify the correlation.

3.3.4.3 Precision

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

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

3.3.4.4 Sampling System Bias

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

3.3.4.5 Relative Calibration and Zero Drift

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

3.3.4.6 Response Time

Mercury CEM response time was also verified using zero gas and the commercial Hg^o standards. Response time was determined as the time required for the CEM to reach 95% of its final value, after switching from zero gas to the mercury gas standard, or vice versa. The former procedure was used to assess rise time, and the latter to assess fall time.

3.3.4.7 Data Completeness

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

3.3.4.8 Operational Factors

Throughout the field period of testing the mercury CEMs at the TSCAI (August 8 – September 19, 2002), the CEM vendors and TSCAI staff operating the CEMs recorded the repair, routine maintenance, and expendable needs of each CEM and noted operational issues such as the ease of use and calibration of the instruments. These observations are summarized for the DM-6/DM-6P in Section 6.7.

3.4 Materials and Equipment

3.4.1. High Purity Gases

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

3.4.2 Mercury Standard Gases

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

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

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

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

			Post-Test				
	March 1	August 8	October 7	November 5 & 6	November 6	November 13 & 21	
Cylinder Number	Initial Gas Vendor Certified Analysis (µg/m^3)	EPA-ORD Seefelder Analysis (µg/m^3)	EPA-ORD Seefelder Analysis (µg/m^3)	Method 101A Mini-Train Analysis (µg/m^3)	EPA-ORD Seefelder Analysis (µg/m^3)	Final Gas Vendor Certified Analysis (µg/m^3)	Difference Between Initial and Final Gas Vendor Certified Analyses (%)
CC133146	14.0	11.3	11.4	NA	NA	12.1	-13.3
CC133172	64.3	44.7	42.4	NA	NA	44.7	-30.4
CC133174	59.6	46.0	45.2	NA	NA	47.5	-20.3
CC133345	11.2	7.9	6.8	NA	NA	5.6	-50.0
CC133357	53.1	37.6	37.1	NA	NA	40.1	-24.6
CC133359	60.6	37.2	34.5	30.6	35.4	44.7	-26.2
CC133367	10.2	6.3	5.4	4.6	5.6	5.6	-45.4
CC133537	15.8	14.9	NA	NA	NA	NA	NA
CC133612	57.8	36.9	34.4	NA	NA	35.4	-38.7
CC133619	59.6	39.9	37.8	NA	NA	40.1	-32.8

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

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

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

Table 3-7. Precision of Elemental Mercury Standard Measurements

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

(a) Not applicable for one data point.

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

3.4.3 Mercury Spiking Standard

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

3.4.4 Sampling Trains

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

3.4.5 Analysis Equipment

Laboratory equipment for sample recovery and analysis was provided by STL. This included all chemicals and solutions for rinsing train components and recovering impinger samples, as well as cold vapor CVAA spectroscopy equipment for mercury determination.

Chapter 4
Quality Assurance/Quality Control

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

4.1 Facility Calibrations

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

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

4.2 Ontario Hydro Sampling and Analysis

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

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

4.2.1 Ontario Hydro Reproducibility

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

Inspection of Tables 4-1 and 4-2 shows that Hg^o composed most of the total mercury value, consistent with the extent of scrubbing of the TSCAI flue gas. The total mercury level was controlled to some extent by the choice of waste feed material and the waste feed rate entering the TSCAI. Total mercury was less than 1.7 µg/dscm in the first two OH runs and then was progressively increased throughout the rest of the first 10 OH runs (Table 4-1), peaking at about 200 µg/dscm in OH Run 16. In the eight OH runs conducted during the final week of the test (Table 4-2), total mercury ranged from about 23 to 85 µg/dscm. All the CEMs tested produced readings of Hg_T that generally paralleled this progression of mercury levels during the two weeks of OH method sampling. Hg_{OX} was typically about 1% of the total mercury, and in 17 of the 18 OH runs, the Hg_{OX} results from both OH trains were less than 2 µg/dscm. The one exception was the Hg_{OX} level of about 15 µg/dscm observed with the peak mercury levels in OH Run 16, when Hg_{OX} was about 7% of Hg_T.

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

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

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

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

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

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

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

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

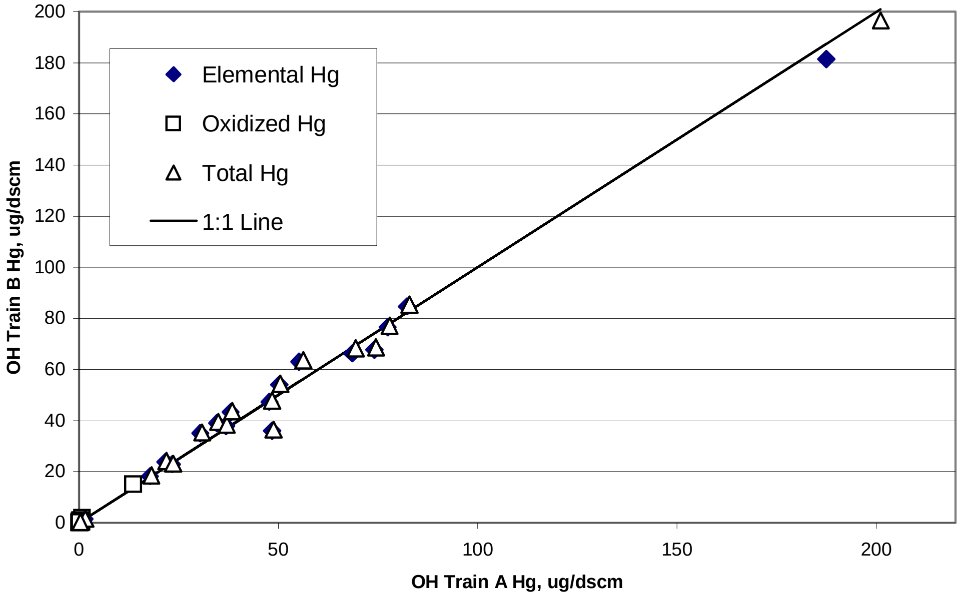

Figure 4-1. Plot of Ontario Hydro Train B Results vs. Train A Results

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

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

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

4.2.2 Ontario Hydro Blank and Spike Results

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

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

4.3 Audits

4.3.1 Technical Systems Audit

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

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

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

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

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

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

4.3.2 Performance Evaluation Audits

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

Table 4-4. Summary of PE Audits

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

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

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

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

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

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

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

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

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

4.3.3 Data Quality Audit

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

Chapter 5
Statistical Methods

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

5.1 Relative Accuracy

RA was verified by comparing the DM-6/DM-6P results against the reference results for total mercury. The average of the paired OH train results was used as the reference value for each OH run. The CEM readings in each OH run were averaged for comparison to the reference data.

The RA of the DM-6/DM-6P with respect to the reference method was calculated using

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

Where

$\left|\overline{d}\right|$ = the absolute value of the arithmetic mean of the differences, d, of the paired DM-6/DM-6P reference method results

$\overline{X}_{RM}$ = arithmetic mean of the reference method result

n = number of data points

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

SD = standard deviation of the differences between the paired DM-6/DM-6P and reference method results.

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

5.2 Correlation with Reference Method

Correlation of the DM-6/DM-6P with the OH method was calculated using the same data used to assess RA. The coefficient of determination (r^2) was calculated to determine the degree of correlation of the DM-6/DM-6P Hg_T results with the reference method results. This calculation was conducted using data from the first week, the last week, and both weeks of OH reference method sampling.

5.3 Precision

As described in Section 3.3.4.3, precision was assessed based on the individual readings provided by the DM-6/DM-6P over the duration of OH method sampling Runs 9 and 12. Precision of the DM-6/DM-6P was determined by calculating the percent relative standard deviation (RSD) of a series of DM-6/DM-6P measurements made during stable operation of the TSCAI in these OH runs. The %RSD is the ratio of the standard deviation of those readings to the mean of the readings, expressed as a percentage:

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

where

SD = standard deviation of the DM-6/DM-6P readings
$\overline{X}$ = mean of the DM-6/DM-6P readings.

The calculated precision values from Equation 2 include the variability of the TSCAI stack gas mercury concentration, as well as the variability of the DM-6/DM-6P itself. To estimate the precision of the DM-6/DM-6P, it was assumed that the two sources of variability combine in root-mean-square fashion, with the variability of the TSCAI mercury concentration represented by the variability of the aqueous waste feed rate. Consequently, the CEM precision was estimated in terms of a %RSD by means of Equation 3:

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

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

5.4 Sampling System Bias

Sampling system bias (*B*) reflects the difference in DM-6/DM-6P response when sampling Hg^o standard gas through the DM-6/DM-6P's entire sample interface, compared with that when sampling the same gas directly at the DM-6/DM-6P's mercury analyzer, i.e.:

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

where

R_i = DM-6/DM-6P reading when the standard gas is supplied at the sampling inlet
R_a = DM-6/DM-6P reading when the standard is supplied directly to the analyzer.

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

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

5.5 Relative Calibration and Zero Drift

Calibration and zero drift were reported in terms of the mean, relative standard deviation, and range (maximum and minimum) of the readings obtained from the DM-6/DM-6P in the repeated sampling of the same Hg^o standard gas and of zero gas. The relative standard deviation of standard gas or zero gas readings was calculated as according to Equation 2 above. This calculation, along with the range of the data, indicates the variation in zero and standard gas readings.

The DM-6/DM-6P was challenged with three Hg^o gas standards in this test, cylinders CC133359, CC133367, and CC133172, which had nominal average Hg^o concentrations of 36.5, 5.5, and 43.9 $\mu g/m^3$, respectively. These nominal averages are based on all analyses of the gas standards from August 8, 2002, through November 21, 2002 (Table 3-7), i.e., excluding the vendor's initial pre-test analysis of the standards in March 2002.

5.6 Response Time

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

5.7 Data Completeness

Data completeness was assessed by comparing the data recovered from the DM-6/DM-P with the amount of data that would be recovered upon completion of all portions of these test procedures.

5.8 Operational Factors

Maintenance and operational needs were documented qualitatively, both through observation and through communication with the vendor during the test. Factors noted included the frequency of scheduled maintenance activities, the down time of the DM-6/DM-6P, and the staff time needed for maintaining it during the verification test.

Chapter 6
Test Results

The results of the verification test of the DM-6/DM-6P are presented below for each of the performance parameters.

6.1 Relative Accuracy

Tale 6-1 lists the OH reference method results and the corresponding DM-6/DM-6P results, for Hg_T in all 18 OH sampling runs. The OH results are the averages of the Hg_T results from the paired A and B trains in each run; the DM-6/DM-6P results are the averages of the DM-6/DM-6P readings over the period of each OH run.

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

		Hg_T, µg/dscm	
Date	**OH Run**	**OH**	**DM-6/DM-6P**
8/8/2002	7	1.65	1.64
	8	0.36	0.66
8/9/2002	9	18.4	13.1
	10	37.2	28.9
8/10/2002	11	42.6	42.8
	12	48.1	37.3
	13	37.8	30.6
8/11/2002	14	41.1	28.6
	15	68.9	52.0
	16	198.8	158.0
9/16/2002	18	71.6	74.3
	19	77.5	86.2
9/17/2002	20	84.1	85.5
	21	52.5	50.2
9/18/2002	22	23.1	22.7
	23	33.1	33.8
9/19/2002	24	23.4	22.7
	25	60.0	62.3

Table 6-1 shows that, during the first week of the verification test (OH Runs 7-16), the DM-6/DM-6P readings were often somewhat lower than the corresponding OH results. In the last week of the test (OH Runs 18-25), the DM-6/DM-6P readings agreed more closely with the OH results. This observation is reflected in the RA results for the DM-6/DM-6P, shown in Table 6-2. The RA for the second week of OH sampling was substantially improved relative to that for the first week, and an overall RA of 20.3% was found for the entire data set.

Table 6-2. Relative Accuracy Results for the DM-6/DM-6P

Test Period	Relative Accuracy (%)
First Week (n = 10)	38.2
Last Week (n = 8)	8.1
Overall (n = 18)	20.3

6.2 Correlation with Reference Method

The correlation of the DM-6/DM-6P readings with the OH results for Hg_T was calculated using the data shown in Table 6-1. To illustrate the correlation, Figure 6-1 shows a linear regression plot of the DM-6/DM-6P Hg_T results against the corresponding OH results. The linear regression equation and r^2 are shown on the graph. Table 6-3 shows the coefficients of determination (r^2) for the first and last weeks of OH sampling and for the two periods combined. All the r^2 values in Table 6-3 exceed 0.95, with an overall r^2 of 0.953.

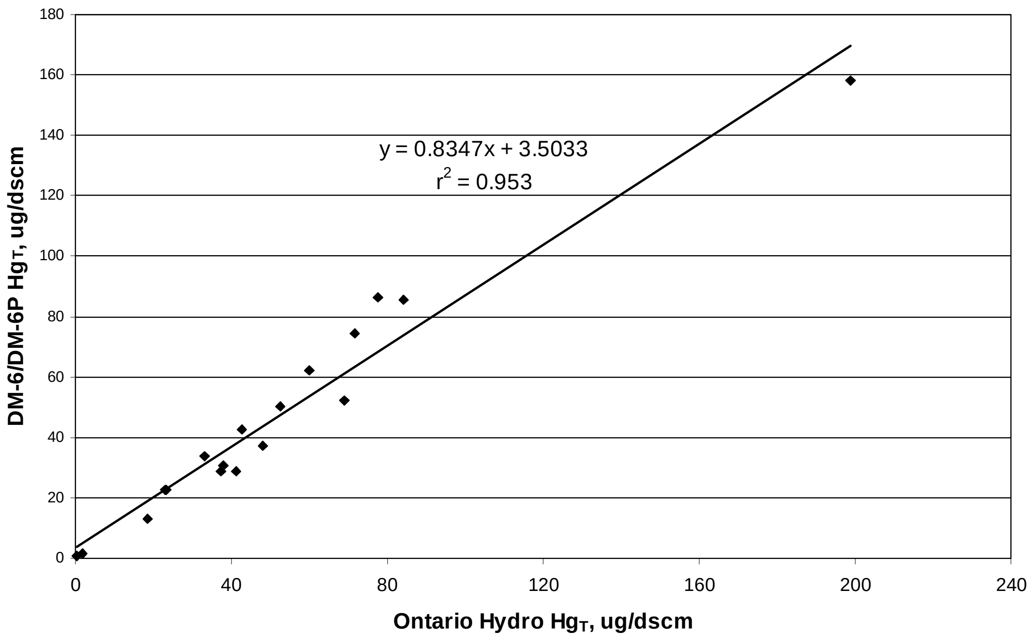

Figure 6-1. Linear Regression Plot of DM-6/DM-6P Hg_T Results Against OH Results

Table 6-3. Coefficients of Determination (r^2) for DM-6/DM-6P Hg_T with OH Results

Test Period	r^2
First Week (n = 10)	0.994
Last Week (n = 8)	0.990
Overall (n = 18)	0.953

6.3 Precision

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

Table 6-4. Precision of the DM-6/DM-6P During OH Runs 9 and 12

OH Run Number	Aqueous Feed Rate Variability (%RSD_{WF})	DM-6/DM-6P Readings (%RSD_R)	Maximum CEM Variability (%RSD_{CEM})
9	2.4	11.2	10.9
12	13.9	16.6	9.1

The results in Table 6-4 show that the DM-6/DM-6P readings exhibited variability of about 11 to 17%RSD under conditions of relatively stable mercury feed into the TSCAI. The maximum variability attributable to the DM-6/DM-6P was 10.9%RSD in OH Run 9 and 9.1%RSD in OH Run 12.

6.4 Sampling System Bias

On eight occasions during the verification test, an Hg^o gas standard was supplied directly to the analyzer of the DM-6/DM-6P and then to the inlet of the sampling system on the TSCAI stack. In five of these tests, a relatively low concentration mercury standard was used, and in three a relatively high concentration standard was used. Table 6-5 shows the date, the mercury standard, and the DM-6/DM-6P readings obtained for each of these sampling system bias checks. The last column in Table 6-5 also shows the sampling system bias, calculated according to Equation 4 in Section 5.4.

Table 6-5. Sampling System Bias Test Results

Date	Hg° Standard[a]	Response at Inlet (R_i) (µg/m^3)	Response at Analyzer (R_a) (µg/m^3)	Bias[b] %
8/8/02	CC133367	7.5	8.1	7.4
8/9/02	CC133367	7.0	8.1	13.6
8/10/02	CC133367	8.6	8.6	0.0
9/18/02	CC133367	7.0	7.3	4.1
9/19/02	CC133367	7.2	7.5	4.0
9/17/02	CC133359	44.4	45.4	2.2
9/18/02	CC133359	43.9	45.6	3.7
9/19/02	CC133359	44.7	46.5	3.9

[a] See Section 3.4.2 for information on mercury standard gases.
[b] Calculated according to Equation 4, Section 5.4.

Table 6-5 shows that the sampling system bias was 7.4 to 13.6% in the first two bias checks, and 0.0 to 4.1% in the last six checks. After August 10, a sampling system bias of about 4% or less was characteristic of the Nippon inlet system, with both the low and high mercury gas standards.

6.5 Relative Calibration and Zero Drift

Mercury gas standards and zero gas (high-purity nitrogen) were analyzed by the DM-6/DM-6P periodically throughout the verification test to assess the drift in calibration and zero response of the DM-6/DM-6P. The results of these analyses are shown in Table 6-6, which lists the date of each analysis and the DM-6/DM-6P readings on zero gas and on the mercury standards. Also shown in Table 6-6 are the mean, standard deviation, %RSD, and range of the DM-6/DM-6P readings.

Table 6-6 shows that the zero gas readings of the DM-6/DM-6P averaged -0.01 µg/m^3 over the duration of the verification test, with a standard deviation of 0.35 µg/m^3. These results indicate minimal drift of the zero readings of the CEM. The results for the three mercury standard gases also show consistent responses. The 25 analyses of the lowest concentration standard (CC133367) took place over a period of about six weeks and exhibit an RSD of 7.1%. The seven analyses of the middle concentration standard (CC133359), over a four-day period, show an RSD of 2.7%. Finally, the 12 analyses of the highest concentration standard (CC133172) over a one-month period resulted in an RSD of 1.7%.

Table 6-6. Calibration and Zero Drift Results

	DM-6/DM-6P Readings (µg/m^3)			
Date	**Zero Gas[a]**	**Mercury Standard CC133367[b]**	**Mercury Standard CC133359[b]**	**Mercury Standard CC133172[b]**
8/8/02	0.1	8.1		
8/9/02	0.0	8.1		
8/10/02	0.4	8.6		
8/11/02	0.1	7.7		
8/12/02	0.2	8.4		
8/14/02	0.2	7.9		
8/14/02	0.3	8.4		60.6
8/15/02	0.6			60.7
8/24/02	-1.5	6.0		
8/28/02	0.1	7.5		59.9
8/29/02	-0.4	7.7		62.0
9/4/02	-0.2	7.3		60.7
9/5/02	0.0	8.1		62.1
9/11/02	0.2	7.7		61.7
9/12/02	0.1	8.0		61.9
9/13/02	-0.2	7.1		61.6
9/14/02	-0.1	7.3		62.2
9/15/02	-0.2	7.1		60.0
9/15/02	-0.1			59.0
9/16/02	-0.1	7.1		60.4
9/16/02	0.0		43.0	
9/16/02	0.0	7.5	45.0	
9/17/02	0.0	7.2	44.5	
9/17/02	0.1	7.5	45.4	
9/18/02	-0.1	7.3	45.6	
9/18/02	0.1	7.6	46.5	
9/19/02	0.0	7.5	46.5	
9/19/02	0.1	7.7		
Mean	-0.01	7.62	45.2	61.0
Std. Dev.	0.35	0.54	1.22	1.01
%RSD	--	7.1%	2.7%	1.7%
Range	-1.5 – 0.6	6.0 – 8.6	43.0 – 46.5	59.0-62.2

[a] High purity nitrogen used for zero checks.

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

6.6 Response Time

Response time of the DM-6/DM-6P was determined using zero gas and two mercury standard gases in a test conducted on September 18, 2002. These gases were supplied sequentially to the inlet of the sampling system shared by the DM-6/DM-6P and another Nippon Instruments CEM, and the response of the DM-6/DM-6P was recorded. Table 6-7 lists the data from this test, showing the date and time of each reading, the indicated concentration from the DM-6/DM-6P, and the resulting percent rise or fall in successive readings.

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

Date	Time	Zero/Span Gas	DM-6/DM-6P Response (ug/m^3)	Result
9/18/02	11:11:56	Z	0.0	
	11:12:56	Z	-0.1	
	11:13:56	CC133367	2.5	
	11:14:56	CC133367	6.9	98.6% rise in two minutes
	11:15:56	CC133367	7.0	
	11:16:56	CC133367	7.0	
	11:17:56	CC133367	7.0	
	11:18:56	Z	4.5	
	11:19:56	Z	0.2	97.1% fall in two minutes[a]
	11:23:42	Z	0.6	
	11:24:42	CC133359	24.7	
	11:25:42	CC133359	42.5	96.8% rise in two minutes
	11:26:42	CC133359	43.3	
	11:27:42	CC133359	43.7	
	11:27:59	CC133359	43.9	
	11:31:00	CC133359	43.4	
	11:32:00	CC133359	5.8	
	11:33:00	Z	0.6	98.6% fall in two minutes[a]

[a] Fall time calculations assume that final response would be 0.0 if data recording was continued.

Table 6-7 shows that the DM-6/DM-6P readings rose to more than 95% of their final readings in two minutes in both test cases, with the test gases supplied to the inlet of the DM-6/DM-6P's sampling system. Thus the DM-6/DM-6P rise time was two minutes. The fall in DM-6/DM-6P readings was over 95% within two minutes in the two cases, indicating a fall time of two minutes. The DM-6/DM-6P data were not recorded for long after the mercury standard was removed from the inlet. These fall time results are based on assuming that the CEM response would have returned to a reading of 0.0 ug/m^3 if data recording had continued.

6.7 Data Completeness and Operational Factors

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

The operation and maintenance activities listed in Table 6-8 include only those that were not required by the test/QA plan(1) (e.g., time required to conduct zero and standard gas checks was not considered down time) and that were responsible for either CEM down time or for operator intervention. As Table 6-8 shows, maintenance on the DM-6/DM-6P included replacing the sampling pump, repairing the inlet line, installing a new transformer, and reconnecting the condensate drain line. The longest period of down time (12 hours) was experienced on August 29, 2002, when the laptop data logger was found to be not working properly and had to be restarted. The second longest period of down time (3.5 hours) occurred on September 13, 2002, when the vendor replaced the read-only-memory in the analyzer to facilitate easier time keeping. The total down time experienced during the six-week test period was 1,500 minutes (25 hours); the down time includes a total required service time of 1,020 minutes (17 hours). The total down time amounted to about 2.5% of the duration of the field period (August 8 through September 19), so that data completeness was 97.5%.

The cost of the DM-6/DM-6P also was considered as an operational factor. The approximate purchase cost of the DM-6/DM-6P as tested was $44,000.

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

Date	Down Time [(a)]	Service Time [(b)]	Activity
8/10/02	1 hour (hr)	1 hr	The DM-6 sample pump was weaker than the DM-5 pump. Since both analyzers were connected to the same sample line, the vendor suspected that the DM-5 pump affected the absorption cell pressure in the DM-6 analyzer.
8/11/02	45 min	20 min	Analyzer stopped responding. Had to stop and restart analyzer.
8/12/02	45 min	15 min	Adjusted the range for reporting mercury measurements.
8/13/02	3 hr	3 hr	Installed PC communications software for data transfer. Installed a new transformer and supplied power through the new transformer.
8/13/02	1 hr	1 hr	Tested a higher capacity sample pump, but returned to original pump.
8/14/02	1 1/2 hr	1 1/2 hr	Higher capacity sample pump installed. Removed moisture filter from analyzer to reduce pressure loss.
8/25/02	NA(c)	1 hr	Discovered that the heated sample line was not working due to failed fuse in the heater controller.(d) Disconnected the analyzer from the sample line. The analyzer remained on while sampling ambient air from the room while the problem with the sample line was investigated.
8/26/02	NA	30 min	Local vendor representative reset the date and time to correct the date stamp on the laptop computer. (The date was apparently incorrectly entered on 8/22/02 at the analyzer touch pad as 8/17/02. The mercury measurements made between 8/22/02 and 8/26/02 were recovered from the data files.) Vendor representative also completed instrument checks.

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

Date	Down Time [a]	Service Time [b]	Activity
8/27/02	NA	2 hr	Fuse failure in heater controller was traced to the fuse holder. It is believed that there may have been a loose connection at the fuse holder, which allowed heat to buildup over time, causing the fuse holder to deform and the fuse to fail. A new fuse holder was installed and tested overnight.
8/28/02	NA	1 hr	Sample line was at temperature and working properly since installing and testing the new fuse holder on 8/27/02. Disconnected sample line at the probe and purged line with nitrogen for five minutes. Reconnected sample line at probe and at analyzer and began sampling flue gas. Probe filter was inspected and was clean.
8/29/02	12 hr	NA	Found the laptop data logger was not working. The windows that had been tracking the mercury measurements were closed, and a system error was displayed. The error occurred at 20:47 on 8/28/02. The analyzer was in good working order.
8/29/02	1 hr	1 hr	Consulted with the vendor and followed instructions to turn off the laptop computer and restart it. The trend windows were restored, and the data logging was reinitiated.
8/29/02	NA	20 min	Drain pipe for draining condensate from flue gas had become disconnected from tygon tubing drain line, and a puddle of water had collected on the countertop surface. Wiped up water and reconnected the line.
8/30/02	NA	5 min	Found drain line disconnected from drain pipe. Wiped up water and reconnected the line with tie-wrap.
9/13/02	3 1/2 hr	3 1/2 hr	Vendor representative came to site to check instrument before starting OH reference method testing. Routine maintenance and operation of DM-6/DM-6P returned to vendor. Replaced ROM in the analyzer. With the new ROM, there is no need to adjust the clock when performing measurements of standard gases. Replaced the probe filter.

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

Date	Down Time [a]	Service Time [b]	Activity
9/15/02	30 min	30 min	Replaced calibration inlet Teflon tubing with a short section of heated Teflon tubing to prevent condensate from being aspirated into the analyzer. Reinstalled moisture filter in analyzer (that was removed on 8/14/02).
TOTAL	1,500 min	1,020 min	97.5% availability and 17 service man-hours [e]

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

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

[c] NA = not applicable.

[d] Failure of the heated sample line did not affect operation of the analyzer. Therefore, the time that the analyzer was not sampling the flue gas was not included in the calculation of availability.

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

Chapter 7
Performance Summary

The RA of the DM-6/DM-6P for measuring Hg_T was verified by comparison to the results of 18 sampling runs using dual trains of the OH reference method at Hg_T levels from <1 to 200 µg/dscm. When all 18 OH runs were included in the comparison, an overall RA of 20.3% was found.

Correlation of the DM-6/DM-6P Hg_T results with the OH results showed an r^2 value of 0.953.

Precision of the DM-6/DM-6P was estimated using two OH sampling periods having relatively stable introduction of mercury in aqueous waste into the TSCAI. The maximum variability attributable to the DM-6/DM-6P itself was 9.1% and 10.9% RSD for these two periods.

The bias introduced by the DM-6/DM-6P sampling system was evaluated by introducing Hg^o standard gas both at the CEM analyzer and at the inlet to the sampling system. In the first two days of the verification test, sampling system bias results of 7.4% and 13.6% were found, at an Hg° level of about 8 µg/m^3. In six subsequent evaluations through the end of the verification, sampling system bias results of 0.0 to 4.1% were found, at Hg° levels of about 7 to 45 µg/m^3.

Repeated analysis of zero gas and Hg^o standards was used to assess the zero and calibration drift of the DM-6/DM-6P over the six-week field period. Twenty-five analyses of an approximately 5.5 µg/m^3 Hg° standard over six weeks resulted in an RSD of 7.1%. Seven analyses of an approximately 36.5 µg/m^3 Hg° standard over four days resulted in an RSD of 2.7%. Thirteen readings of an approximately 43.9 µg/m^3 Hg° standard over four weeks resulted in an RSD of 1.7%.

Rise and fall times of the DM-6/DM-6P were determined at times of switching between zero and mercury standard gases. The 95% rise time and fall time of the DM-6/DM-6P were both two minutes.

The DM-6/DM-6P operated reliably throughout the verification period, with the result that data completeness was 97.5%. The longest period of down time was when the laptop data logger was not working properly, and the second longest period of down time was when the vendor replaced the read-only-memory in the analyzer to facilitate easier time keeping.

Chapter 8
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