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Environmental Technology Verification Report

TEKRAN INSTRUMENTS CORPORATION
SERIES 3300 MERCURY CONTINUOUS EMISSIONS
MONITORING SYSTEM

Prepared by
Battelle

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

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SERIES 3300 MERCURY CONTINUOUS EMISSIONS
MONITORING SYSTEM**

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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 permittees, 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. Under a cooperative agreement, Battelle has received EPA funding 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

AC	alternating current
agl	above ground level
AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
°C	degrees Celsius
CEM	continuous emission monitor
CFR	Code of Federal Regulations
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
°F	degrees Fahrenheit
FGD	flue gas desulfurization
ft ³	cubic foot
H ₂ O ₂	hydrogen peroxide
H ₂ SO ₄	sulfuric acid
HCl	hydrogen chloride
Hg	mercury
HgCl ₂	mercuric chloride
Hg ⁰	elemental mercury
Hg _{OX}	oxidized mercury
Hg _T	total mercury
HNO ₃	nitric acid
ICCI	Illinois Clean Coal Institute
KCl	potassium chloride
klb/hr	thousands of pounds per hour
KMnO ₄	potassium permanganate
LE	linearity error
L/min	liter per minute
µg/dscm	microgram per dry standard cubic meter
µg/L	microgram per liter
mL	milliliter
MW	megawatt
NIST	National Institute of Standards and Technology
NO _x	nitrogen oxides

OH	Ontario Hydro
ppm	parts per million
PE	performance evaluation
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RA	relative accuracy
%RD	percent relative deviation
SO ₂	sulfur dioxide
TSA	technical systems audit
UV	ultraviolet
V	volt

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 permittees; 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 the Tekran Instruments Corporation Series 3300 Mercury Continuous Emissions Monitoring (CEM) System for determining mercury in stack gas at a coal-fired power plant. This evaluation was carried out in collaboration with the Illinois Clean Coal Institute and with the assistance of the Northern Indiana Public Service Company.

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 report provides results for the verification testing of the Tekran Series 3300 Mercury CEM. The following is a description of the Series 3300, based on information provided by the vendor. The information provided below was not verified in this test.



Figure 2-1. Tekran Series 3300 CEM

The Series 3300 (Figure 2-1) measures total mercury (Hg_T), elemental mercury (Hg^0), and oxidized mercury (Hg_{OX}) in combustion sources. It has a dual channel stack gas conditioner with selective scrubbing. The system is designed to separate mercury into elemental and oxidized species, while removing interfering acid gases, and provide real-time feedback to optimize mercury reduction technologies. It is designed to be insensitive to the presence of sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide, hydrogen chloride (HCl), and other common combustion by-products and can operate unattended for extended periods. In this verification the Series 3300 was programmed to report a reading of mercury concentration every 2.5 minutes. The CEM alternated measurements of Hg_T and Hg^0 , providing two successive readings of Hg_T , followed by two of Hg^0 , two of Hg_T , etc.

The Series 3300 consists of a sampling probe, a heated umbilical line, a sample conditioner, a mercury analyzer, a saturated Hg^0 vapor calibrator, and a control system. It uses a stack-mounted inertial probe to minimize mercury measurement artifacts due to filtering. The sample flow is then diluted and sent at a high rate through a heated line to the sample conditioning module. The probe performs automated filter blowback, multi-point calibrations, and standard additions of mercury into the sample matrix. The conditioning module speciates the mercury into elemental and oxidized forms, without using chemical reagents or solid sorbents. The diluted sample is split into two streams. In the first stream, a thermal conditioner unit converts all mercury forms into Hg^0 . Tekran's patented thermal conditioner/scrubber system is designed to avoid recombination by the quantitative removal of HCl and other gases. The second pathway removes oxidized (water soluble) mercury, leaving only the Hg^0 to pass through to the converter. This stream is then subjected to additional conditioning to remove acid gases and excess humidity from the sample. The two conditioned streams are analyzed using a Tekran Model

2537A mercury vapor analyzer. The analyzer uses gold preconcentration combined with atomic fluorescence detection.

A calibration source of Hg^0 allows both multi-point calibrations and standard additions to be automatically initiated. Both these operations are performed through the entire CEM path, including all probe filters. The calibration unit generates concentrations of Hg^0 by using a saturated mercury vapor source. Precision mass flow controllers dilute the output of this source to the desired value. The computer provides full control of each module within the system. All temperatures, flows, and pressures are displayed by the application program and may be set by authorized users. The system features remote operation and problem diagnosis. The Series 3300 can be audited by introduction of mercury calibration gas standards, which can be delivered directly to the probe inlet by the umbilical line.

The Series 3300 component rack system (Figure 2-1) is approximately 67 inches high by 31.5 inches deep by 23 inches wide. The associated air purification system occupies a wall-mountable panel 24 inches by 24 inches in size.

The cost of the Series 3300 CEM as tested was approximately \$125,000, excluding the umbilical line, installation, and training.

Chapter 3 Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Continuous Emission Monitors (CEMs) and Sorbent-Based Samplers for Mercury at a Coal-Fired Power Plant*.⁽¹⁾ CEMs for mercury are designed to determine total and/or chemically speciated vapor-phase mercury in combustion source emissions. Performance requirements for mercury CEMs are contained in Chapter 40 of the Code of Federal Regulations, Part 75 and Part 60 (40 CFR Parts 75 and 60)⁽²⁾ and require assessment of the performance of newly installed mercury CEMs only for their determination of Hg_T. This total is the sum of vapor-phase mercury in all chemical forms in the combustion gas, including Hg⁰ and Hg_{OX} (which is primarily mercuric chloride [HgCl₂]) vapors. In this test the Series 3300 was verified for its measurement of vapor-phase Hg⁰, Hg_{OX}, and Hg_T.

The Series 3300 was verified by evaluating the following parameters:

- Relative accuracy (RA)
- Linearity
- Seven-day calibration error
- Cycle time
- Data completeness
- Operational factors such as ease of use, maintenance and data output needs, power and other consumables use, reliability, and operational costs.

Verification of the Series 3300 was conducted in a field test that lasted from June 12 to July 25, 2006, and that included two separate four-day periods of reference mercury measurements carried out by ARCADIS Inc., under subcontract to Battelle, using American Society for Testing and Materials (ASTM) D 6784-02, the “Ontario Hydro” (OH) method.⁽³⁾ RA was determined by comparing CEM vapor-phase mercury results to simultaneous results from the OH method. RA of the Series 3300 was determined for Hg_T and Hg⁰. Linearity was determined based on Series 3300 responses to Hg⁰ standards. Calibration error was evaluated by comparing Series 3300 readings on mercury standard and zero gases performed once each day over a consecutive seven-day period. Cycle time was evaluated in terms of the response of the Series 3300 when switching from a zero gas or upscale Hg⁰ standard gas, supplied at the Series 3300 inlet, to sampling of stack gas. Data completeness was assessed as the percentage of maximum data return achieved by the Series 3300 over the test period. Operational factors were

evaluated by means of observations during testing and records of needed maintenance, vendor activities, and expendables use.

3.2 Test Facility

The host facility for the Series 3300 verification was the R. M. Schahfer Generating Station, located near Wheatfield, Indiana, approximately 20 miles south of Valparaiso, Indiana. The Schahfer plant consists of four units (designated 14, 15, 17, and 18), with a total rated capacity of about 1,800 megawatts (MW). The Series 3300 verification was conducted at Unit 17, which burns pulverized Illinois sub-bituminous coal and has an electrostatic precipitator and a wet flue gas desulfurization (FGD) unit. Unit 17 has a typical capacity of about 380 MW. The unit was operated near this capacity for most of the test period, although the typical daily pattern of operation was to reduce load substantially for a few hours between late evening and early morning.

Flue gas from Unit 17 feeds into a free-standing concrete chimney with an internal liner. The top of the stack is 499 feet above ground level (agl). Emission test ports and penetrations in the concrete chimney and liner are located at a platform approximately 8 feet wide that encircles the outside of the stack at 370 feet agl. The stack diameter at the platform level is 22 feet 6 inches, so the total flow area is 397.6 square feet. The last flow disturbance is at the FGD connection to the stack liner at 128 feet agl. Thus, the emission test ports were over 10 stack diameters downstream from the last flow disturbance and nearly six diameters upstream from the stack exit. Four emission test ports were located at 90° intervals around the circumference of the stack about 4 feet above the platform at 370 feet agl and were standard 4-inch ports with #125 flanges. No traversing was done during sampling; both the OH method and the Series 3300 CEM sampled from a single fixed point inside the inner liner of the stack at their respective port locations. This arrangement is justified by the absence of stratification observed for SO₂ and NO_x at this sampling location.

Table 3-1 summarizes key operating and stack gas conditions that characterize Schahfer Unit 17 during the field period, showing the range and average values of key parameters and constituents. Stack gas pressure was slightly positive at the sampling location.

Table 3-1. Operating and Stack Gas Conditions at Schahfer Station Unit 17

Parameter	Average	Range
Unit 17 Load ^a	334 MW	140–391
Coal Feed Rate ^a	297 klb/hr ^c	140–374
Temperature ^a	130°F	118–140
Moisture ^b	15.5 %	13.3–16.7
NO _x ^a	97 ppm ^d	61–165
SO ₂ ^a	193 ppm	104–316
Hg _T vapor ^b	0.91 µg/dscm ^e	0.73–1.22

a: Values calculated from hourly data recorded routinely at the R.M. Schahfer facility, June 12 to July 25, 2006.

b: Values based on measurements made during OH reference sampling periods June 12–15 and July 10–13, 2006.

c: klb/hr = thousands of pounds per hour.

d: ppm = parts per million.

e: µg/dscm = micrograms per dry standard cubic meter.

3.3 Test Procedures

Following are the test procedures used to evaluate the Series 3300 mercury CEM.

3.3.1 Relative Accuracy

The RA of the Series 3300 CEM was evaluated by comparing its mercury results to simultaneous results obtained by sampling stack gas with the OH reference method. The OH method is the currently accepted reference method for mercury measurements in stack gas and employs dual impinger trains sampling in parallel through a common probe to determine oxidized and elemental vapor-phase mercury by means of appropriate chemical reagents.⁽³⁾ In each of two separate weeks of the field test period, ARCADIS conducted a series of 12 OH runs, each of two hours in duration, as described in Sections 3.5 and 4.1. The Hg⁰, Hg_{OX}, and Hg_T determined by the OH reference method were compared to corresponding results from the Series 3300, by averaging the successive Series 3300 readings over the period of each OH run. A Tekran vendor representative operated the Series 3300 throughout all OH sampling.

The OH trains were dismantled for sample recovery in the field by ARCADIS staff, and all collected sample fractions were logged and stored for transfer to the ARCADIS analytical laboratory. All sample handling, quality assurance/quality control (QA/QC) activities, and mercury analyses were conducted by ARCADIS. Subsequent to mercury analysis, ARCADIS reviewed the data and reported final mercury results from all trains in units of µg/dscm. The results from the paired OH trains were checked relative to the duplicate precision requirement for use of the OH data,^(3,4) and qualified OH results were averaged to produce the final reference data used for comparison to the Series 3300 results. RA was calculated as described in Section 5.1 for Hg_T and Hg⁰ for each of the two sets of OH reference data. In addition, the averages of the Series 3300 results for Hg_T, Hg⁰, and Hg_{OX} were compared to the corresponding averages from the OH reference method, for each of the two sets of OH data.

3.3.2 Linearity

Linearity was evaluated by challenging the Series 3300 with three concentrations of Hg⁰ standard gases using a calibration source built into the Series 3300. These standards were supplied to the Series 3300 in non-repetitive triplicate through the Series 3300's inlet filter at a rate that exceeded the Series 3300's inlet flow rate. Each challenge was maintained long enough to achieve a stable response before moving to the next challenge gas. The triplicate responses of the Series 3300 at each challenge concentration were averaged, and the average values were then compared to the known mercury level of the standards. The three challenge concentrations were initially set at about 4, 8, and 16 µg/dscm, but the linearity test was later repeated at about 1, 2.5, and 4.5 µg/dscm, as these concentrations were judged more appropriate given the relatively low mercury level in the Unit 17 stack gas.

3.3.3 Seven-Day Calibration Error

At programmed 24-hour intervals over the period of July 18 to July 24, the Series 3300 was challenged with zero gas and an Hg⁰ standard concentration of about 4.5 µg/dscm, using the Series 3300 calibration source. These challenge gases were supplied through the Series 3300's inlet filter at a rate that exceeded the Series 3300's inlet flow rate. Each such challenge was maintained long enough to achieve a stable response. Deviation of the Series 3300 zero and calibration readings from the expected zero or calibration value was assessed to determine calibration error in the CEM readings.

3.3.4 Cycle Time

Cycle time was determined by monitoring the Series 3300 readings while switching from sampling of zero gas to sampling of stack gas, and from sampling an Hg⁰ standard to sampling of stack gas. The former procedure determined the upscale response (or rise) time, and the latter the downscale response (or fall) time. In each case, the response time was determined as the time needed to achieve 95% of the change from one stable reading to the next.

3.3.5 Data Completeness

No additional test procedures were carried out specifically to address data completeness. This parameter was assessed based on the overall data return relative to the total amount of data return possible for the technology being tested.

3.3.6 Operational Factors

Operational factors such as maintenance needs, data output, consumables use, and ease of use were evaluated based on observations by Battelle and Schahfer facility staff. A laboratory record book was maintained at the host facility and was used to enter daily observations on these factors. Examples of information recorded in the record books are the daily status of diagnostic indicators for the Series 3300, use or replacement of any consumables, the effort or cost associated with maintenance or repair, vendor effort (e.g., time on site) for repair or maintenance, the duration and causes of any down time or data acquisition failure, and operator observations about ease of use of the Series 3300.

3.4 CEM Installation

The Series 3300 rack system, argon gas cylinder, and deionized (DI) water container were installed in an air-conditioned laboratory trailer placed at the base of the Unit 17 stack. The rack components drew electrical power from two 120V/15A AC circuits inside the trailer.

Compressed air (110 pounds per square inch gauge) was supplied from a compressor located near the trailer to a wall-mountable air purification panel provided by Tekran and located inside the trailer. The rack system was connected to the sampling probe on the stack by a heated umbilical approximately 480 feet in length. Heating of the umbilical was powered by a separate 240V transformer located near the trailer at ground level. The dilution sampling probe was powered by two additional 120V/15A circuits located near the Series 3300's sampling port on the platform at 370 feet agl.

Installation of the Series 3300 was conducted by two Tekran field engineers; the more senior of the two trained the other in the installation procedures as the installation was carried out. The more junior field engineer then remained on site to conduct instrument checkout and calibration procedures, and trained Battelle and Schahfer facility staff in routine operation of the Series 3300. That Tekran field engineer operated the Series 3300 CEM during both periods of OH reference method sampling.

The Series 3300 umbilical and needed utility supplies were in place by June 7, 2006, and the Series 3300 was first connected to the stack and began sampling stack gas on June 8. However, the slightly recessed position of the flange on the sampling port was found to prevent the opening of doors on the CEM's sampling probe, so a port extension was installed that allowed the doors to clear the port opening on the side of the stack. The use of this extension caused the sampling point for the Series 3300 probe to be 2.45 feet from the inner wall of the stack, rather than 3.28 feet (1 meter) as prescribed in the test/QA plan.⁽¹⁾ Thus, the Series 3300 sampled stack gas from a point 10 inches closer to the stack wall than did the OH reference method. This difference is not expected to affect the comparison of CEM and OH data in Section 6.1 because of the lack of stratification observed in the Unit 17 stack for other gases (SO₂ and NO_x).

As noted below, the field verification began with collection of a series of 12 OH samples from June 12 to 15. The Series 3300 then continued to monitor stack gas continuously until July 25, a time period that included completion of a second series of 12 OH measurements over the period of July 10 to 13, 2006.

3.5 Verification Schedule

The Series 3300 was verified between June 12 and July 25, 2006, in a field effort that also evaluated two sorbent-based mercury sampling systems and one other mercury CEM. The Series 3300 sampled stack gas at Unit 17 throughout that entire period. Table 3-2 shows the weekly activities conducted prior to and during the field period. Flue gas mercury was sampled using the OH reference method during the first and fifth weeks of the test period, and the other weeks were used for routine monitoring by the Series 3300.

Table 3-2. Weekly Test Activities During the Field Period

Week of	Test Activity
May 15	Battelle trailer arrived at Schahfer facility
May 22	Electric power and other utilities established at Schahfer facility
May 29	Series 3300 equipment arrived at site
June 5	Series 3300 installed; trial operations conducted
June 12	First OH reference method sampling period
June 19	Routine operation
June 26	Routine operation
July 3	Routine operation
July 10	Second OH reference method sampling period
July 17	Routine operation
July 24	Routine operation concluded; Series 3300 shut down and removed from Battelle trailer

Table 3-3 shows the actual schedule of OH reference method sampling completed by ARCADIS in the week of June 12, and Table 3-4 shows the corresponding schedule of OH sampling completed in the week of July 10. The OH sampling proceeded efficiently, with three runs conducted on each of four successive days in each week. In all cases, Tekran personnel and other participating vendors were informed of the planned start time of each OH run and, in few instances, the start time of a run was delayed slightly to assure that the technologies being tested were fully ready to obtain data during the OH run. All OH runs were of exactly two hours duration, and Tekran personnel were notified as the ending time of each run approached.

Table 3-3. Schedule of OH Method Sampling in the Week of June 12, 2006

Run Number	Date	Start Time	End Time
1	6/12/06	09:15	11:15
2	6/12/06	12:15	14:15
3	6/12/06	15:40	17:40
4	6/13/06	08:15	10:15
5	6/13/06	11:10	13:10
6	6/13/06	14:05	16:05
7	6/14/06	08:10	10:10
8	6/14/06	11:25	13:25
9	6/14/06	14:30	16:30
10	6/15/06	08:20	10:20
11	6/15/06	11:05	13:05
12	6/15/06	13:45	15:45

Table 3-4. Schedule of OH Method Sampling in the Week of July 10, 2006

Run Number	Date	Start Time	End Time
1	7/10/06	9:00	11:00
2	7/10/06	11:50	13:50
3	7/10/06	14:55	16:55
4	7/11/06	8:30	10:30
5	7/11/06	11:15	13:15
6	7/11/06	14:00	16:00
7	7/12/06	8:30	10:30
8	7/12/06	11:40	13:40
9	7/12/06	14:15	16:15
10	7/13/06	8:20	10:20
11	7/13/06	11:10	13:10
12	7/13/06	13:45	15:45

Chapter 4

Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the Quality Management Plan (QMP) for the AMS Center⁽⁵⁾ and the test/QA plan for this verification test.⁽¹⁾ QA/QC procedures and results are described below.

One deviation from the test/QA plan occurred due to the inability to position the Series 3300 sampling point at 1 meter inside the inner wall of the stack (see Section 3.4). A deviation form was prepared and approved noting this occurrence.

4.1 OH Reference Method

This verification test included a comparison of the Series 3300 results to those of the OH reference method for flue gas mercury.^(3,4) The quality of the reference measurements was assured by adherence to the requirements of the OH method, including requirements for solution and field blanks, spiked samples, and continuing calibration standards. All OH reference measurements were made with paired trains, and the percent relative deviation (%RD = the difference between the paired train results divided by the sum of those results, expressed as a percentage) of each data pair was required to be $\leq 10\%$ (at mercury levels $>1.0 \mu\text{g/dscm}$) or $\leq 20\%$ (at mercury levels $\leq 1.0 \mu\text{g/dscm}$).⁽⁴⁾ Data not meeting this criterion were excluded from comparison with the Series 3300 results. The following sections present key data quality results from the OH method.

4.1.1 OH Reproducibility

The mercury results of the OH stack gas samples are shown in Tables 4-1 and 4-2, for the initial (June 12–15) and final (July 10–13) weeks of OH method sampling, respectively. Each table indicates the OH run number and lists the average vapor phase Hg_{OX} , Hg^0 , and Hg_{T} results from the paired OH trains in each run and the %RD of each pair of results. All mercury results are in $\mu\text{g/dscm}$, i.e., adjusted to 20°C (68°F) and one atmosphere pressure.

Inspection of Tables 4-1 and 4-2 shows that Hg_{T} in the Unit 17 stack ranged from 0.727 to 0.933 $\mu\text{g/dscm}$ in the OH runs conducted in the June 12–15 period, and from 0.787 to 1.215 $\mu\text{g/dscm}$ in the OH runs conducted in the July 10–13 period. The average Hg_{T} values in these periods were 0.815 and 1.008 $\mu\text{g/dscm}$, respectively (note that one OH result for Hg_{T} is excluded from the latter average because of inadequate dual train precision, as described below).

Hg⁰ comprised the great majority of the Hg_T, consistent with the scrubbing of the Schahfer Unit 17 flue gas. Hg_{OX} never exceeded about 0.09 µg/dscm, and was typically about 5% of the Hg_T.

The %RD values in Tables 4-1 and 4-2 show generally close agreement between the paired OH train results for all three mercury fractions. The %RD values are less than about 6.5% in almost all runs for both Hg⁰ and Hg_T. The only exceptions were the results for OH Run #8 in the second set of runs (Table 4-2). The Hg_T result from that run is excluded from calculations of RA because the %RD value is outside the 10% criterion for values >1.0 µg/dscm. (Note that the Hg⁰ result from that run is not similarly excluded because its %RD value is within the 20% criterion for values <1.0 µg/dscm.) The %RD values for Hg_{OX} are slightly higher than those for Hg_T and Hg⁰, presumably due to the low Hg_{OX} concentrations, with two %RD values from the second data set exceeding 20%. RA was not calculated using the Hg_{OX} data, so no Hg_{OX} values need be excluded based on %RD.

Table 4-1. OH Results from June 12–15, 2006, Sampling Period

OH Run	Mercury Concentration (µg/dscm) and % RD of Paired Train Results ^a					
	Hg _{OX}	%RD	Hg ⁰	%RD	Hg _T	%RD
1	0.022	15.3	0.762	3.6	0.783	3.0
2	0.037	6.8	0.822	3.8	0.859	3.4
3	0.038	3.9	0.821	1.1	0.859	0.9
4	0.058	3.4	0.875	2.0	0.933	1.7
5	0.053	6.6	0.795	0.6	0.848	0.1
6	0.048	11.4	0.684	4.9	0.732	5.3
7	0.072	1.2	0.739	2.1	0.811	2.0
8	0.060	0.5	0.690	4.3	0.750	3.9
9	0.055	5.0	0.819	1.9	0.874	1.5
10	0.054	0.2	0.766	3.9	0.820	3.6
11	0.037	2.5	0.691	1.1	0.727	0.9
12	0.032	1.8	0.748	2.4	0.781	2.4

a: %RD = difference between paired train results divided by sum of paired train results.

Table 4-2. OH Results from July 10–13, 2006, Sampling Period

OH Run	Mercury Concentration ($\mu\text{g}/\text{dscm}$) and %RD of Paired Train Results ^a					
	Hg _{OX}	%RD	Hg ⁰	%RD	Hg _T	%RD
1	0.033	10.1	0.902	0.8	0.935	0.4
2	0.037	2.9	0.823	1.4	0.860	1.2
3	0.040	3.7	0.929	1.1	0.969	0.9
4	0.066	52.3	0.886	1.4	0.952	4.9
5	0.029	11.6	0.757	0.3	0.787	0.1
6	0.038	2.0	1.018	6.5	1.056	6.4
7	0.028	5.7	1.055	1.2	1.083	1.3
8	0.084	7.2	0.997	12.6	1.081 ^b	11.0
9	0.090	6.3	1.126	0.7	1.215	0.2
10	0.093	0.6	0.982	0.1	1.074	0.1
11	0.092	0.9	1.014	2.0	1.107	1.8
12	0.037	22.7	1.015	0.6	1.053	0.2

a: %RD = difference between paired train results divided by sum of paired train results.

b: This data point excluded from calculation of RA because %RD value exceeds acceptance criterion.

4.1.2 OH Blank and Spike Results

Analyses were conducted on 18 total samples collected at the Schahfer site from the blank reagents used in the OH method. Only four of those samples showed detectable mercury, with concentrations ranging from 0.003 to 0.006 micrograms per liter ($\mu\text{g}/\text{L}$). These blank reagent concentrations are negligible in comparison to the mercury in impinger solutions recovered from trains after stack sampling. Those recovered sample concentrations were typically about 0.1 $\mu\text{g}/\text{L}$, 0.2 $\mu\text{g}/\text{L}$, and 3 to 4 $\mu\text{g}/\text{L}$ in potassium chloride (KCl) solution, hydrogen peroxide (H_2O_2) solution, and potassium permanganate (KMnO_4) solution, respectively.

Blank OH sampling trains were prepared and taken to the sampling location on the Unit 17 stack on three occasions in each week of OH sampling, and were 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. For the June 12 to 15 sampling period, the total amounts of mercury recovered from the three blank trains ranged from 0.126 to 0.144 μg , equivalent to approximately 7% of the typical total amount of mercury recovered from an OH train after stack gas sampling in that period. Those blank train results correspond to stack gas mercury concentrations of less than 0.06 $\mu\text{g}/\text{dscm}$. For the July 10–13 sampling period, the total amounts of mercury recovered from the three blank trains ranged from 0.193 to 0.250 μg ,

equivalent to less than 10% of the typical total amount of mercury recovered from a train after stack gas sampling in that period. Those blank train results correspond to stack gas mercury concentrations of less than 0.1 µg/dscm.

All initial and continuing blank and calibration values from laboratory analysis of the OH samples met the requirements of the OH method. The recovery of mercury spiked into each reagent solution recovered from blank and sampled OH trains was also evaluated during laboratory analysis. Those spike recoveries ranged from 85 to 117% and averaged 97%. The recovery of mercury spiked into blank train samples as part of the performance evaluation (PE) audit also met the prescribed criteria, as described in Section 4.2.1.

4.2 Audits

Three types of audits were performed during the verification test: a PE audit of the reference method, a technical systems audit (TSA) of the verification test procedures, and a data quality audit. Audit procedures are described further below.

4.2.1 Performance Evaluation Audits

PE audits of the OH method were carried out through procedures implemented at the Schahfer plant during the field period. Table 4-3 summarizes the procedures and results of the PE audits of the OH reference method, showing the parameter audited, the date of the audit, the OH and reference values, the observed agreement, and the target agreement. The OH method incorporates dual sampling trains, and the equipment used by ARCADIS to carry out the OH sampling included dual Model 522 Source Sampler meter boxes (Apex Instruments, Fuquay-Varina, North Carolina) designated by their serial numbers as #2007 and #2008. As a result, for some parameters Table 4-3 includes results for both meter boxes or for both of the dual OH trains.

Four PE audits were conducted:

- A Fluke Model 52 II digital thermometer (Serial No. 80730162) was used to audit the probe temperature measurements made by the #2007 meter box and the stack temperature measurements made by the #2008 meter box. For this comparison, the appropriate thermocouple was disconnected from the meter box and connected to the Fluke thermometer.
- A BIOS International Corporation DryCal National Institute of Standards and Technology-(NIST)-traceable flow measurement standard (Model DC2-B, Serial No. 103777, vendor-calibrated on May 9, 2006) was used to audit the sample gas flow rate with each of the two OH meter boxes.
- A set of weights (Rice Lake Weight Set, Serial No. 1JXA) calibrated to ASTM Class 3 standards was used to audit the electronic balance (AND FP-6000, Serial No. 6402118) used for weighing the OH method impingers.
- Recovery of mercury from OH trains was audited by spiking impingers containing KCl, H₂O₂/nitric acid (HNO₃), and KMnO₄/sulfuric acid (H₂SO₄) reagents in two blank OH impinger trains, with 1 milliliter (mL) of a prepared mercury solution, in each of the two

separate periods of OH sampling. The mercury spiking solution was 2.5 µg/mL Hg in 1% HNO₃ and was prepared by dilution of a NIST-traceable 1,000-ppm (i.e., 1,000-µg/mL) standard (Aa34n-1, Accustandards, Inc.). In the first week of OH sampling, Impingers 2, 4, and 5 of Blank Trains 8L and 8R were spiked; and, in the final week of OH sampling, Impingers 2, 4, and 6 of Blank Trains 7L and 7R were spiked.

Table 4-3 shows that all the PE audit results were within the target tolerances set in the test/QA plan.⁽¹⁾

Table 4-3. Summary of PE Audit Results

Parameter	Date	OH Result	Reference Value	Agreement with Standard	Target Agreement	
OH temperature measurement	6/14/06 probe T stack T	228°F ^a	230°F	0.29%	2% absolute T	
		127°F ^b	129°F	0.31%		
OH sample flow measurement	7/11/06	15.02 L/min ^a	14.56 L/min	3.2%	5%	
		14.58 L/min ^b	14.35 L/min	1.6%		
Impinger weighing	6/14/06	199.72	200 grams	0.14%	Greater of 1% or 0.5 gram	
		499.27	500 grams	0.15%		
Mercury spike recovery	6/14/06 train 8L	imp 2	2.48 µg	2.5 µg	0.8%	25%
		imp 4	2.02 µg	2.5 µg	19.2%	25%
		imp 5	2.08 µg	2.5 µg	16.8%	25%
	train 8R	imp 2	2.47 µg	2.5 µg	1.2%	25%
		imp 4	1.97 µg	2.5 µg	21.2%	25%
		imp 5	2.10 µg	2.5 µg	16.0%	25%
	7/12/06 train 7L	imp 2	2.24 µg	2.5 µg	10.4%	25%
		imp 4	2.12 µg	2.5 µg	15.2%	25%
		imp 6	2.38 µg	2.5 µg	4.8%	25%
	train 7R	imp 2	2.27 µg	2.5 µg	9.2%	25%
		imp 4	2.33 µg	2.5 µg	6.8%	25%
		imp 6	2.39 µg	2.5 µg	4.4%	25%

a: #2007 meter box.

b: #2008 meter box.

L/min = liters per minute; T = temperature; imp = impinger.

4.2.2 Technical Systems Audit

A Battelle Quality Management representative conducted a TSA at the Schahfer test site on June 14 to ensure that the verification test was being conducted in accordance with the test/QA plan⁽¹⁾ and the AMS Center QMP.⁽⁵⁾ As part of the TSA, test procedures were compared to those specified in the test/QA plan,⁽¹⁾ and data acquisition and handling procedures, as well as the reference standards and method, were reviewed. The Quality Management representative

observed OH method sampling and sample recovery processes, interviewed ARCADIS personnel, and observed the PE audit procedures noted above, except for the OH sample flow and second OH train spiking audits, which were conducted at a later date. Observations and findings from the TSA were documented and submitted to the Battelle Verification Test Coordinator for response. None of the findings of the TSA at the Schahfer site required corrective action. In addition, an internal TSA was conducted in the laboratory charged with analyzing the OH samples. This TSA was conducted by the ARCADIS independent QA Officer in the laboratory on-site at EPA in Research Triangle Park, North Carolina, on July 19 and July 27, 2006. None of the findings of this laboratory TSA required corrective action. Records from both TSA efforts are permanently stored with the Battelle Quality Manager.

4.2.3 Data Quality Audit

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.3 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.⁽⁵⁾ Once the audit reports were prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were submitted to the EPA.

4.4 Data Review

Records generated in the verification test received a one-over-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5

Statistical Methods

The statistical methods used to evaluate the performance factors listed in Section 3.1 are presented in this chapter. Qualitative observations were also used to evaluate verification test data.

5.1 Relative Accuracy

The RA of the Series 3300 with respect to the OH reference method results was assessed as a percentage, using Equation 1:

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

where d refers to the difference between the OH reference mercury concentration and the average Series 3300 reading over the OH sampling period, and x corresponds to the OH reference mercury concentration. S_d denotes the sample standard deviation of the differences, while t_{n-1}^{α} is the t value for the 100(1 - α)th percentile of the distribution with $n-1$ degrees of freedom. The RA was determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). RA was calculated separately for Hg_T and Hg^0 , and was calculated separately for the two periods of OH reference method sampling. All paired OH data meeting the method quality criteria were eligible for inclusion in the calculation of RA. However, for each of the OH sampling periods, if more than nine OH results met the acceptance criteria, then selected OH results could be omitted and RA recalculated. At least nine results were always included in the calculation. An RA of less than 20% is considered acceptable.⁽²⁾ Alternatively, when the mean reference mercury level is less than 5.0 $\mu\text{g/dscm}$ (as in this test), agreement of the overall mean Series 3300 CEM value within 1.0 $\mu\text{g/dscm}$ of the mean OH value is also considered acceptable.⁽²⁾

5.2 Linearity

The linearity of the Series 3300 response was assessed by comparing its responses to the Hg^0 standard concentrations, using Equation 2:

$$LE = \frac{|R - A|}{R} \times 100 \quad (2)$$

where LE is the linearity error at each concentration, R is the reference mercury concentration supplied to the Series 3300, and A is the average of the triplicate readings at each concentration. LE within 10% is considered acceptable.⁽²⁾

5.3 Seven-Day Calibration Error

The assessment of calibration error was based on the difference between the Series 3300 responses and the known mercury content of the zero or standard gas. Calibration error was calculated from the Series 3300 responses to both the zero and calibration gases for each of the seven consecutive days of this test. Specifically, calibration error was calculated using Equation 3:

$$CE = \frac{|R - A|}{S} \times 100 \quad (3)$$

where CE is the calibration error as a percentage of the Series 3300 span value, R is the reference mercury concentration supplied to the CEM, A is the Series 3300 response to the reference gas, and S is the span value of the instrument. Acceptable calibration error is within 5%.⁽²⁾ However, for this verification, a span value of 10 $\mu\text{g/dscm}$ was assumed and, therefore, the secondary acceptance criterion of 1.0 $\mu\text{g/dscm}$ (10% of span) applies.⁽²⁾ The absolute value of the differences ($R - A$) were also reported.

5.4 Cycle Time

The upscale and downscale cycle times (essentially the rise and fall times) of the Series 3300 response were determined as the elapsed time needed to achieve 95% of the final stable reading after switching from zero gas to stack gas and from a high mercury standard to stack gas, respectively. The slower (i.e., longer) of the two response times was reported as the cycle time of the Series 3300. Cycle times not exceeding 15 minutes are acceptable under Part 75.⁽²⁾

5.5 Data Completeness

Data completeness was calculated as the percentage of the total possible data return that was achieved by the Series 3300 over the entire field period. This calculation used the total hours of data recorded divided by the total hours of data in the entire field period. The field period began at the start of the first OH method run on June 12 and ended at the shutdown of the CEM on July 25. For this calculation, no distinction was made between data recorded during stack gas monitoring and that recorded during calibration or zeroing, or in performance of linearity, cycle time, and seven-day calibration error testing. The causes of any substantial incompleteness of data were established from operator observations or vendor records.

Chapter 6 Test Results

The results of the verification tests of the Tekran Series 3300 Mercury CEM are presented below for each of the performance parameters. To illustrate the overall results for this CEM, Figure 6-1 shows all of the Tekran CEM's stack gas Hg_T readings for the entire test, which spanned over 43 days, from June 12 (designated as Day 0) to July 25 (Day 44). Figure 6-1 shows that the Hg_T readings of the Series 3300 were usually below $1 \mu\text{g}/\text{dscm}$, with most readings centered around $0.8 \mu\text{g}/\text{dscm}$. A frequent daily pattern of Hg_T readings is evident, in that lower Hg_T values were reported in the early morning hours when the load was reduced on Unit 17. Figure 6-1 also shows the occurrence of frequent readings of $0 \mu\text{g}/\text{dscm}$ for Hg_T from the Tekran CEM between days 15 and 30 (June 27 to July 12). This period includes part of the second set of OH reference method samples (the x-axis label in Figure 6-1 defines the OH sampling periods).

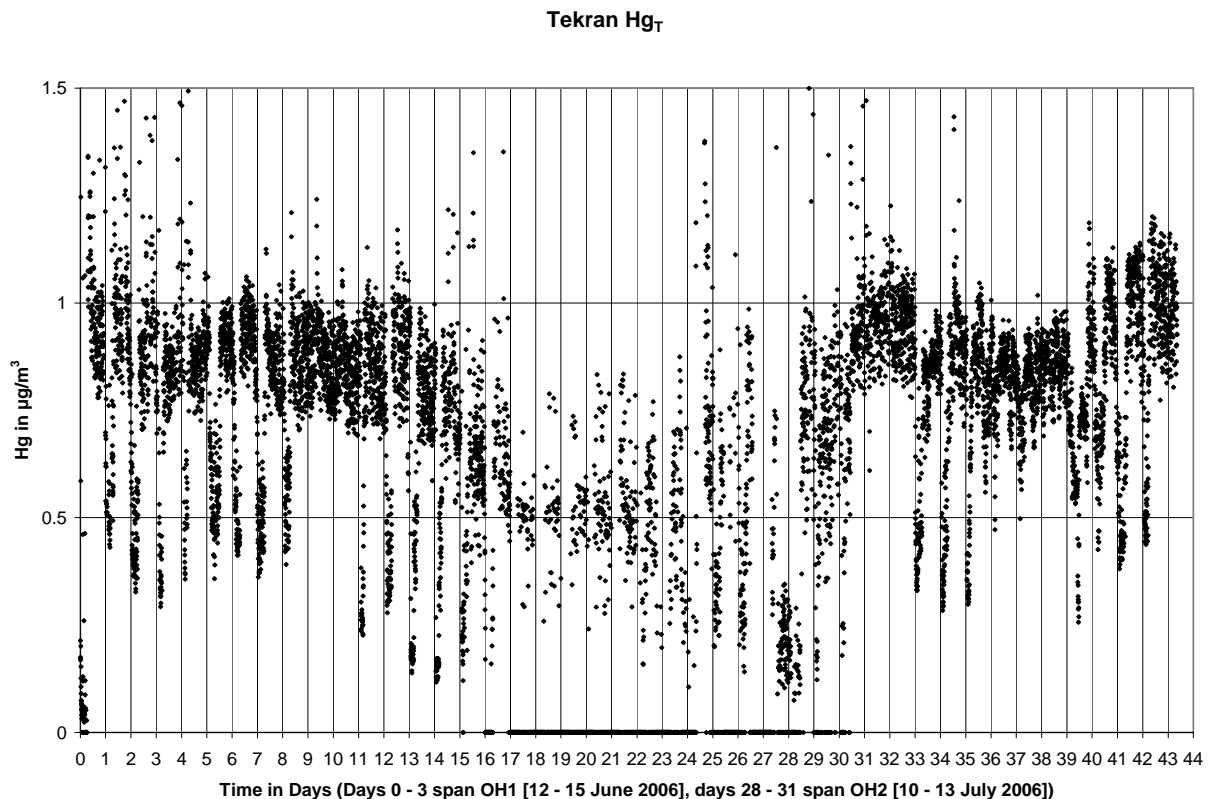


Figure 6-1. Hg_T Readings from the Tekran Series 3300 CEM During the Field Test

6.1 Relative Accuracy

The RA of the Series 3300 with respect to the OH results for Hg_T and Hg^0 was calculated using Equation 1 in Chapter 5. Table 6-1 lists the Tekran results for Hg_T , Hg^0 , and Hg_{OX} for those time periods corresponding to each of the OH sampling runs (see Tables 4-1 and 4-2). The Tekran Hg_T and Hg^0 results in Table 6-1 are each the averages of 24 2.5-minute readings over the 2-hour period of each OH run. The Tekran Hg_{OX} values were determined as the difference between the average Hg_T and Hg^0 readings for each 2-hour OH run. Note that the OH result for Hg_T from run #8 in the July 10–13 sampling period was excluded from the calculation because the %RD value exceeded the acceptance criterion (see Section 4.1.1).

Table 6-1. Results from Tekran Series 3300 CEM for Each OH Sampling Run

Date	OH Run	Mercury ($\mu\text{g}/\text{dscm}$)		
		Hg_T	Hg^0	Hg_{OX}
6/12/2006	1	1.027	0.946	0.081
6/12/2006	2	0.977	0.903	0.074
6/12/2006	3	0.900	0.844	0.056
6/13/2006	4	1.016	0.914	0.102
6/13/2006	5	0.982	0.887	0.095
6/13/2006	6	0.958	0.864	0.094
6/14/2006	7	0.860	0.773	0.087
6/14/2006	8	0.876	0.835	0.041
6/14/2006	9	0.931	0.872	0.059
6/15/2006	10	0.877	0.829	0.049
6/15/2006	11	0.821	0.760	0.061
6/15/2006	12	0.851	0.757	0.094
7/10/2006	1	0.077	0.040	0.037
7/10/2006	2	0.734	0.683	0.051
7/10/2006	3	0.800	0.711	0.090
7/11/2006	4	0.700	0.584	0.116
7/11/2006	5	0.608	0.536	0.072
7/11/2006	6	0.609	0.489	0.120
7/12/2006	7	0.640	0.533	0.107
7/12/2006	8	0.910	0.799	0.111
7/12/2006	9	0.908	0.795	0.112
7/13/2006	10	0.943	0.843	0.099
7/13/2006	11	0.967	0.830	0.138
7/13/2006	12	0.945	0.838	0.108

The Tekran and OH results are shown graphically in Figure 6-2 for the June 12–15 OH sample set, and in Figure 6-3 for the July 10–13 sample set.

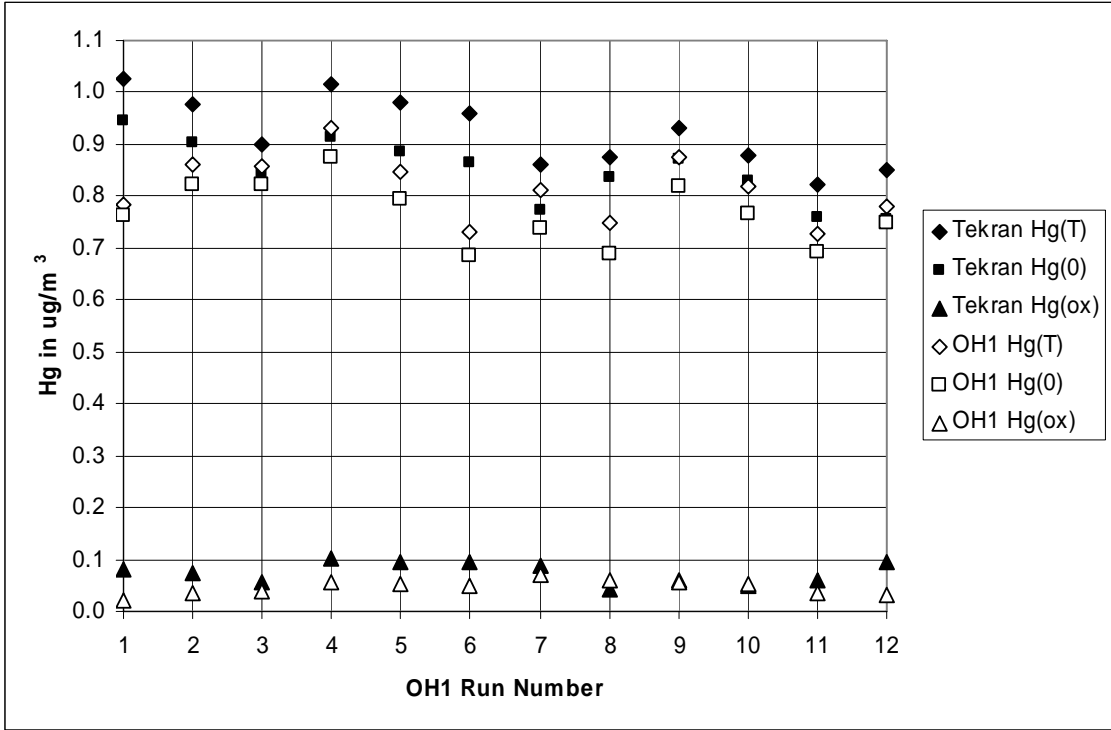


Figure 6-2. Tekran Series 3300 and OH Mercury Results, June 12–15, 2006

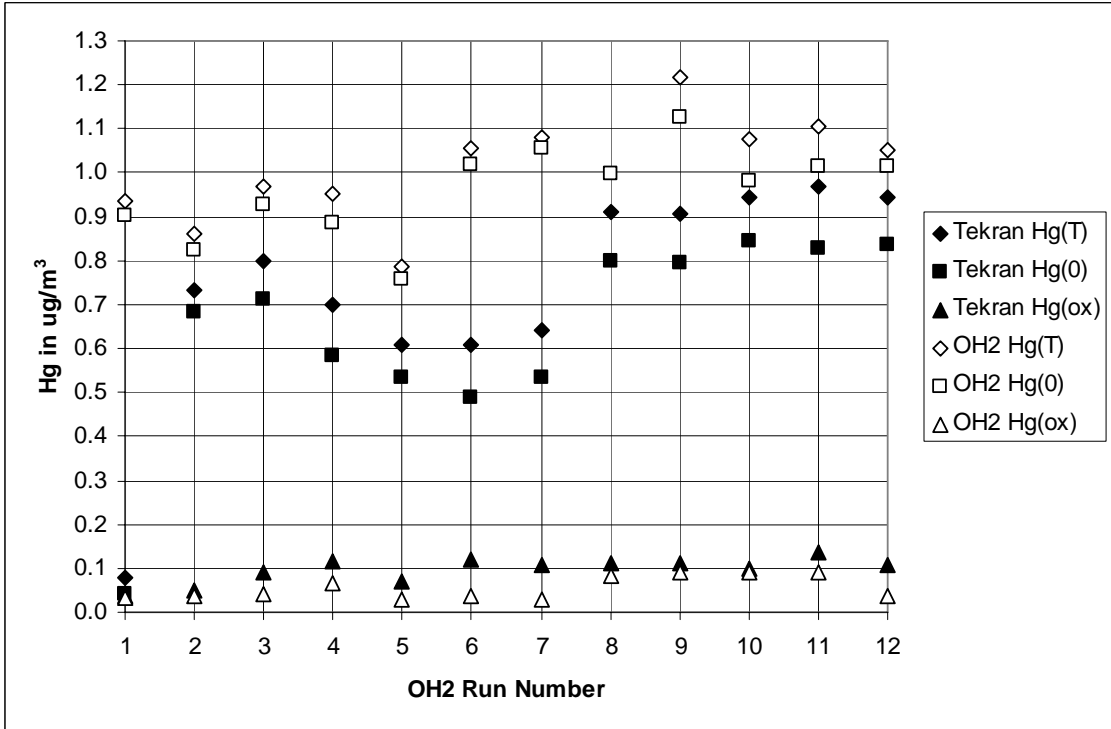


Figure 6-3. Tekran Series 3300 and OH Mercury Results, July 10–13, 2006

The RA results for the Tekran Series 3300 CEM for Hg_T and Hg^0 are shown in Table 6-2, for both of the two OH data sets. RA values within 20% were achieved by the Series 3300 CEM for both Hg_T and Hg^0 in comparison to the June 12–15 OH data set, but not when compared to the July 10–13 OH data set. The cause for the latter result appears to be the relatively low readings obtained from the Series 3300, including readings of 0 $\mu\text{g}/\text{dscm}$ for stack gas mercury, over portions of the test (see Figure 6-1). The Tekran field engineer noted the severely low readings from the Series 3300 CEM during the first OH run on July 10 (see Figure 6-3) and requested that that run be excluded from the calculation of RA with the July 10–13 OH data set. He then made adjustments to the Series 3300 before the start of the second OH run on that day. Consistent with the application of the equation for RA (Section 5.1), additional Series 3300 data points were also excluded, so that the RA calculation with the July 10–13 OH data set was performed with the minimum nine data points for Hg_T and for Hg^0 . The additional data points excluded were those with the poorest agreement between the Series 3300 and OH results. For Hg_T the one additional data point excluded was from run #6 (note that run #8 was already excluded because of its %RD value). For Hg^0 the two data points excluded were from runs #6 and #7. Table 6-2 shows that omission of these data points and use of the minimum nine data points resulted in RA values of 28.7% for Hg_T and 27.8% for Hg^0 in comparison to the July 10–13 OH data set.

Table 6-2. RA Results for Tekran Series 3300 CEM

OH Reference Method Sampling Period	RA (%)	
	Hg_T	Hg^0
June 12–15	18.5	15.4
July 10–13 ^a	28.7	27.8

a: Results shown based on RA calculation using nine data points.

In addition to the calculation of RA, the mean values of Hg_T , Hg^0 , and Hg_{OX} from the OH method and the Series 3300 CEM were compared for each of the two OH data sets. That comparison is shown in Table 6-3. For the June 12–15 data set, the comparison in Table 6-3 is based on all 12 OH and Tekran results. For the July 10–13 data set, the comparison is based on the nine OH and Tekran results used to calculate RA, as described above. The nine runs used for the RA calculation were not all the same for different mercury fractions, so the sum of Hg^0 and Hg_{OX} averages in Table 6-3 may not exactly equal the corresponding Hg_T average. Table 6-3 shows that the Tekran Series 3300 mean values differed from the OH mean values by 0.027 to 0.213 $\mu\text{g}/\text{dscm}$. All of these differences are well within the 1.0 $\mu\text{g}/\text{dscm}$ acceptable difference from the mean OH value.⁽²⁾

6.2 Linearity

The linearity of the Tekran Series 3300 CEM was evaluated over concentration ranges of 4 to 16 $\mu\text{g}/\text{dscm}$ and 1 to 4.5 $\mu\text{g}/\text{dscm}$. Table 6-4 shows the results of the linearity tests. Shown in the table are the dates of the tests, the Hg^0 standard concentrations, the triplicate CEM responses to each mercury standard, the mean of the triplicate sets of responses, the difference between that mean and the standard value, and the resulting LE, calculated using Equation 2 (Section 5.2). As shown in Table 6-4, the LE of the Series 3300 CEM was within 7% at all three points in both concentration ranges.

Table 6-3. Mean Mercury Values from Tekran Series 3300 CEM and OH Method

OH Sampling Period	Species	OH Mean ($\mu\text{g/dscm}$)	Tekran Mean ($\mu\text{g/dscm}$)	Difference ($\mu\text{g/dscm}$)
June 12–15	Hg _T	0.815	0.923	0.108
	Hg ⁰	0.768	0.849	0.081
	Hg _{OX}	0.047	0.074	0.027
July 10–13 ^a	Hg _T	1.011	0.805	0.206
	Hg ⁰	0.948	0.735	0.213
	Hg _{OX}	0.060	0.098	0.038

a: Results based on nine OH results.

Table 6-4. Tekran Series 3300 Linearity Test Results

Linearity Test Date	Hg ⁰ Standard ($\mu\text{g/dscm}$)	Tekran Responses ($\mu\text{g/dscm}$)	Tekran Mean ($\mu\text{g/dscm}$)	Difference ($\mu\text{g/dscm}$)	LE (%)
June 14–15	3.969	4.251	4.196	0.227	5.7
		4.053			
		4.285			
June 14–15	7.937	8.291	8.221	0.284	3.6
		7.887			
		8.484			
June 14–15	15.86	15.96	16.12	0.26	1.6
		15.83			
		16.58			
June 28	1.034	1.447	0.970	0.064	6.2
		0.821			
		0.640			
June 28	2.412	2.556	2.246	0.166	6.9
		2.096			
		2.087			
June 28	4.478	4.375	4.268	0.210	4.7
		4.294			
		4.136			

6.3 Seven-Day Calibration Error

Calibration error of the Tekran Series 3300 CEM was determined based on zero and calibration responses obtained on each of seven consecutive days. Table 6-5 summarizes the results, listing the zero and calibration responses and the resulting calibration error, calculated according to Equation 3 (Section 5.3) and expressed as a percentage of the 10 $\mu\text{g/dscm}$ span value. Table 6-5 shows that the Series 3300 exhibited zero readings up to 1.455 $\mu\text{g/dscm}$ (14.6% of span), and differences from the 4.478 $\mu\text{g/dscm}$ standard of up to 0.314 $\mu\text{g/dscm}$ (3.14% of span). All the Series 3300 calibration results are within the 5% of span acceptance criterion in Part 75, and well within the alternate 1 $\mu\text{g/dscm}$ acceptance criterion for a span range of 10 $\mu\text{g/dscm}$.⁽²⁾ However, the zero readings of the Tekran CEM all exceeded the 5% acceptance criterion, and the result from July 24 even exceeded the 1 $\mu\text{g/dscm}$ tolerance.

Table 6-5. Results of Zero/Calibration Stability Tests for Tekran Series 3300 CEM

Date	Zero Readings (µg/dscm)	Difference from Standard^a (µg/dscm)	Zero Error (%)^b	Calibration Readings (µg/dscm)	Difference from Standard^c (µg/dscm)	Calibration Error (%)^b
July 18	0.814	0.814	8.14	4.251	0.227	2.27
July 19	0.575	0.575	5.75	4.393	0.085	0.85
July 20	0.895	0.895	8.95	4.544	0.066	0.66
July 21	0.679	0.679	6.79	4.265	0.214	2.14
July 22	0.738	0.738	7.38	4.327	0.151	1.51
July 23	0.976	0.976	9.76	4.559	0.081	0.81
July 24	1.455	1.455	14.6	4.792	0.314	3.14

a: Relative to standard concentration of zero.

b: Relative to span value of 10 µg/dscm.

c: Relative to standard concentration of 4.478 µg/dscm.

6.4 Cycle Time

The cycle time of the Tekran Series 3300 CEM was assessed by inspection of periods when the CEM was switched between sampling of calibration or zero gas and sampling of stack gas. This assessment was complicated by the automated sequencing of the Series 3300 in continuous monitoring, which alternated between two readings of Hg_T and two of Hg⁰; by the integrated sampling mode of the Series 3300, which produced new mercury readings at 2.5-minute intervals; and by noise in the CEM readings at the low stack gas mercury levels observed. However, data were sufficient to allow an estimate of cycle time. Table 6-6 presents the data from periods used to assess the cycle time of the Series 3300, showing the date, time, and value of the Tekran Series 3300 readings in µg/dscm; the readings chosen as the initial and final readings, and readings near the 95% change level; and the estimate of cycle time (either fall time from calibration gas to stack gas or rise time from zero gas to stack gas).

Table 6-6 shows that the Tekran Series 3300 Hg_T cycle time (both fall and rise time) was estimated to be 7.5 to 10 minutes. The Series 3300 response actually rose slightly for one reading upon switching from calibration gas to stack gas, and similarly the Series 3300 reading initially overshot the stack gas Hg_T level upon switching from zero gas to stack gas. These readings are apparently artifacts of the switching of gases supplied to the Series 3300 probe.

Table 6-6. Assessment of Cycle Time of the Tekran Series 3300 CEM

Date	Time	Tekran Reading (µg/dscm)	Comments	Cycle Time Estimate
6/13/06	17:35:01	17.47 ^a	Initial Hg _T reading	
	17:37:31	17.84 ^a		
	17:40:01	10.06 ^a		
	17:42:31	2.35 ^a	93.5% decrease	
	17:45:01	1.39 ^b		Fall time 7.5 to 10 minutes (3 to 4 measurement intervals)
	17:47:31	1.21 ^b		
	17:50:01	1.51 ^a	98.7% decrease	
	17:52:31	1.47 ^a		
	17:55:01	1.11 ^b		
	17:57:31	1.00 ^b		
18:00:01	1.25 ^a			
18:02:31	1.30 ^a	Final Hg _T reading		
7/11/06	21:42:31	0.00 ^a	Initial Hg _T reading	
	21:45:01	1.15 ^a		
	21:47:31	0.90 ^a		
	21:50:01	0.76 ^a	93.8% increase	Rise time 7.5 to 10 minutes (3 to 4 measurement intervals)
	21:52:31	0.73 ^a		
	21:55:01	0.51 ^b		
	21:57:31	0.76 ^b		
	22:00:01	0.85 ^a	105% increase	
22:02:31	0.81 ^a	Final Hg _T reading		

a: Hg_T
b: Hg⁰

6.5 Data Completeness

The total duration of the field test was from the start of the first OH sampling run on June 12 to the shutdown of the CEMs on July 25, a total of 43.4 days. The Tekran CEM operated for all of that period, and suffered minimal down time or loss of data, recording 24,955 readings. The maximum number of 2.5-minute readings possible was 24,977, so the Series 3300 achieved 99.9% data recovery. However, not all of the Tekran CEM readings were valid measurements of stack gas mercury. A more detailed breakdown of the Series 3300 operational activity is shown in Table 6-7.

Table 6-7. Tekran Series 3300 CEM Operational Activities During the Field Test

Activity	Number of Measurements	Days	Percent of Time
Stack Gas Monitoring (Stack Gas Readings of 0 µg/dscm)	21,953 (4,643) ^a	38.1 (8.1)	87.9% (18.6%)
Filter Blowback	622	1.1	2.5%
Calibration/Zeroing/Other Checks	2,380	4.1	9.5%
Totals	24,955 ^b	43.3	99.9%

a: These readings are a subset of the 21,953 total stack gas readings.

b: Maximum number of 2.5-minute readings was 24,977.

Table 6-7 shows that operational activities for the Tekran CEM during this test consisted of 38.1 days (87.9% of the field period) of routine monitoring of stack gas mercury; 1.1 days (2.5%) conducting or re-stabilizing after programmed filter blowback; and 4.1 days (9.5%) in calibration, zeroing, and other programmed QC procedures. However, for 8.1 days of the routine stack gas monitoring (18.6% of the total field time), the Tekran Series 3300 produced erroneous readings of “0” µg/dscm on stack gas. Thus, non-zero stack gas mercury readings were achieved for at most 69.3% of the field period.

6.6 Operational Factors

The Tekran Series 3300 CEM used high purity argon gas at a rate of about 200 cubic centimeters per minute, consuming one standard cylinder of argon (i.e., approximately 200 cubic feet [ft³] of gas) in about one month of continuous operation. This CEM also used DI water at a rate of about 3 L per day. The Series 3300 required both 240 and 120V AC power, and required power connections both at the ground and aloft at the stack sampling port. Facility compressed air was also required. The Series 3300 used software that controlled all monitoring, calibration, and data acquisition functions and provided a detailed display of current readings and activity that was valuable in the field. For example, it was possible to tell at a glance what the most recent mercury reading was; whether it was of Hg_T or Hg⁰; and whether a zero, calibration, blowback, or other QA activity was in progress. A running plot of mercury data could also be displayed. This software is accessible by means of an analog phone line through a modem built into the Series 3300’s computer, and the vendor frequently used this means of access. The data system automatically recorded a detailed record of all measurements and operations conducted over each day of monitoring (midnight to midnight).

The Tekran CEM operated reliably throughout the test period, in the sense of having negligible down time. However, several problems did require substantial attention by Tekran representatives over the course of test. These included adjustments to the internal filter temperature, probe dilution ratio, and duration of daily zeroing and replacement of the ultraviolet (UV) lamp in the mercury analyzer. The most recurring problem was the occurrence of low or zero readings for mercury. Tekran was first notified of this issue on June 27 after the problem was noticed by

Unit 17 field staff. Efforts to diagnose the problem via modem connection were unsuccessful, and Tekran personnel then suspected a plug in the sampling probe. In early July, efforts were made to clean the probe, culminating with the probe being pulled from the stack on July 9 and reinstalled at a slight downward angle. At this time the voltage of the UV lamp was also adjusted from 14 V to about 8 V. However, the erroneous low readings persisted, and on July 10 the Tekran representative concluded that the photomultiplier voltage also should have been adjusted when the lamp voltage was adjusted. The Tekran CEM readings during the first OH run on July 10 were severely low, and the Tekran representative requested that this run be omitted from calculation of RA. He continued to work on the problem, but it was apparently not corrected until the UV lamp was again replaced on July 12. After that date, the erroneous zero readings were not seen again in the Tekran data (see Figure 6-1).

Tekran representatives spent a total of about 21 man-days at the Schahfer Unit 17 test site during the field test and controlled the Series 3300 CEM remotely via modem in other periods. Most of the on-site days were during the initial installation and startup, when two Tekran representatives were on site.

Chapter 7

Performance Summary

The RA of the Tekran Series 3300 Mercury CEM was 18.5% for Hg_T and 15.4% for Hg^0 , based on comparison to 12 OH reference results obtained at the start of the six-week field test. The overall average Hg_T , Hg^0 , and Hg_{OX} values from that first set of OH data were 0.815, 0.768, and 0.047 $\mu\text{g/dscm}$, whereas those from the Series 3300 were 0.923, 0.849, and 0.074 $\mu\text{g/dscm}$, with resulting differences of 0.108, 0.081, and 0.027 $\mu\text{g/dscm}$, respectively. The RA of the Series 3300 was 28.7% for Hg_T and 27.8% for Hg^0 , based on comparison to nine OH reference results obtained at the end of the six-week field test. The overall average Hg_T , Hg^0 , and Hg_{OX} values from that set of OH data were 1.011, 0.948, and 0.060 $\mu\text{g/dscm}$, whereas those from the Series 3300 were 0.805, 0.735, and 0.098 $\mu\text{g/dscm}$, with resulting differences of 0.206, 0.213, and 0.038 $\mu\text{g/dscm}$, respectively.

The LE of the Series 3300 was 4.7 to 6.9% when tested over the range of about 1 to 4.5 $\mu\text{g/dscm}$ and 1.6 to 5.7% when tested over a range of about 4 to 16 $\mu\text{g/dscm}$.

The seven-day calibration error of the Series 3300 was evaluated with zero gas and with a calibration gas of about 4.5 $\mu\text{g/dscm}$ Hg^0 . Error in zero readings ranged from 5.75 to 14.6% of span, and error in calibration gas readings from 0.66 to 3.14% of span, in both cases relative to an assumed 10 $\mu\text{g/dscm}$ span value.

Cycle time of the Series 3300 was estimated to be 7.5 to 10 minutes, in switching from either zero gas or span gas to sampling of stack gas. The Series 3300 provided a mercury reading every 2.5 minutes, so the cycle time was estimated as a multiple of this integration time.

Data completeness of the Series 3300 was 99.9% over the six-week field test, in the sense that the CEM operated with minimal down time and provided readings at 2.5-minute intervals throughout the test. However, not all readings were valid measurements of stack gas mercury. Frequent erroneous readings of 0 $\mu\text{g/dscm}$ were reported by the Series 3300 in a portion of the field period, amounting to 8.1 days of such readings (18.6% of the field test duration).

The Series 3300 used one standard cylinder of argon (about 200 ft^3 of gas) in about one month of continuous operation. The Series 3300 also used DI water at a rate of about 3 L per day; required both 240 and 120V AC power, with connections for the latter both at the ground and aloft at the stack sampling port; and required connection to facility compressed air. The Series 3300 is controlled by software that can be accessed locally or remotely and provides rapid control of all instrument operations and detailed information on mercury results and instrument functions. The

only recurring problem with the Series 3300 was the frequent reporting of 0 µg/dscm for stack gas mercury over approximately two weeks of the field period. This problem apparently was related to the UV lamp in the mercury analyzer of the Series 3300 and was ultimately solved by replacement of the lamp and proper adjustment of lamp voltage.

The cost of the Tekran Series 3300 Mercury CEM as tested was approximately \$125,000, excluding the umbilical line, installation, and training.

Chapter 8 References

1. *Test/QA Plan for Verification of Continuous Emission Monitors and Sorbent-Based Samplers for Mercury at a Coal-Fired Power Plant*, Battelle, Columbus, Ohio, May 18, 2006.
2. *Code of Federal Regulations*, 40 CFR Part 75, including Appendices A through K, and Part 60, July 2005.
3. *Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-fired Stationary Sources (Ontario Hydro Method)*, ASTM D 6784-02, American Society for Testing and Materials, West Conshohocken, PA, June 2002.
4. *Performance Specification 12A – Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources*, 40 CFR Part 60 Appendix B, July 2005.
5. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 6.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, November 2005.