February 2007

Environmental Technology Verification Report

ENVIRONMENTAL SUPPLY COMPANY
HG-324K SORBENT-BASED MERCURY SAMPLING SYSTEM

Prepared by
Battelle

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ETV ETV ETV

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ETV Advanced Monitoring Systems Center

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HG-324K SORBENT-BASED MERCURY SAMPLING SYSTEM

by
Thomas Kelly
Jan Satola
Zachary Willenberg
Amy Dindal

Battelle
Columbus, Ohio 43201

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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 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

agl	above ground level
AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
CEM	continuous emission monitor
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
°F	degrees Fahrenheit
FGD	flue gas desulfurization
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
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
L/min	liters per minute
MW	megawatt
µg/dscm	microgram per dry standard cubic meter
µg/mL	microgram per milliliter
mL	milliliter
NIST	National Institute of Standards and Technology
NO_x	nitrogen oxides
OH	Ontario Hydro
ppm	part per million
PE	performance evaluation
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RD	relative deviation

SO_2	sulfur dioxide
TSA	technical systems audit

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 the Environmental Supply Company's HG-324K sorbent-based mercury sampling 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 Environmental Supply Company's HG-324K mercury sampling system. The following is a description of the HG-324K, based on information provided by the vendor. The information provided below was not verified in this test.

The HG-324K system (Figure 2-1) was designed to sample mercury emissions from coal-fired sources as specified in Appendix K in Chapter 40 of the Code of Federal Regulations Part 75 (40 CFR Part 75).(1) The system consists of a dual heated probe, knockout and drying impingers to remove moisture, a connecting umbilical, and the HG-324K automated sampler. An integrated sample of vapor phase mercury is captured on two parallel and independent sorbent traps that are placed in the stack on the front of the sampling probe. Stack gas is drawn through each of the traps at a constant flow rate of approximately 500 cubic centimeters per minute. The traps and probe are heated to prevent condensation of moisture from the sample gas. After exiting the probe, the sample gas passes through the knockout and drying impingers to remove moisture and then is drawn into the HG-324K sampler for measurement of the sample volume. The HG-324K provides proportional, integral, derivative flow control of the dual samples; records all temperatures including the stack, probe, and condenser; controls the probe temperature; and measures the dry standard volume of sample gas.

Figure 2-1. HG-324K Sorbent Tube Mercury Sampling System

The mass of mercury is determined using cold vapor atomic fluorescence spectrometry as specified in EPA Method 1631.(2) For quality control, each trap has a breakthrough section and a spike and recovery section. The concentration of vapor phase mercury in the stack is determined based on the mass of mercury captured on the sorbent trap and the dry standard stack gas volume measured by the HG-324K.

The HG-324K is controlled using an industrial data acquisition and control system with a removable CompactFlash™ memory card for storing data files. The HG-324K may be connected to a plant network through wireless or direct connection to allow program control and remote data access. It comes in a watertight, corrosion proof case with 2-inch hard rubber transport wheels and a retractable extension handle. The outside dimensions are 24-5/8 inches long by 19-1/2 inches wide by 14 inches deep.

The list price for the automated sampler is $18,750. The sorbent traps used with the HG-324K in this test were prepared and analyzed by Frontier Geosciences, of Seattle, Washington. As used in this test, the cost per sorbent trap sample was about $500, including preparation of the trap, pre-spiking with mercury, and analyzing the trap for mercury after sampling.

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*.(3) Appendix K of 40 CFR Part 75(1) establishes sorbent-based sampling systems as an acceptable approach for determining mercury in the stack gas of utility generating stations. Such sorbent-based systems collect integrated samples of mercury from stack gas onto selective sorbent materials over extended time periods (from a few hours to several days). The collected samples are then analyzed for mercury, and the stack gas mercury concentration is calculated. Appendix K defines procedures for use of such systems to collect total vapor-phase mercury in combustion source emissions and requires the use of multi-stage sorbent traps pre-spiked with mercury as a quality assurance (QA) measure. In the test reported here, the HG-324K was verified for measurement of total vapor-phase mercury (Hg_T), which is the sum of elemental mercury (Hg^0) and oxidized mercury (Hg_{OX}) (which is primarily mercuric chloride [$HgCl_2$]) vapors. Note that the HG-324K is a sample collection system; the mercury results shown from the HG-324K in this report resulted from use of the HG-324K with sorbent traps prepared and subsequently analyzed for mercury by Frontier Geosciences.

The HG-324K was verified by evaluating the following parameters:

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

The HG-324K was verified during part of 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.(4) Specifically, the HG-324K was used to sample stack gas from June 12 through June 15, 2006, and RA was determined by comparing HG-324K vapor-phase mercury results to simultaneous results from 12 two-hour sampling runs with the OH method. Data completeness was assessed as the percentage of maximum data return achieved by the HG-324K over its test period. Operational factors were evaluated by means of operator observations and records of needed maintenance, vendor activities, and expendables use.

The sorbent traps used with the HG-324K for this verification were prepared, and subsequently analyzed for mercury after sampling, by Frontier Geosciences. The traps each contained four separate sections of sorbent. The first section collected mercury from the flue gas; the second collected any breakthrough from the first section; the third was spiked, as required by Appendix K(1), with mercury before sampling; and the fourth collected any mercury lost from the third section during sampling. Trap preparation included spiking the third sorbent section of each trap with nominally 100 ng of mercury. Spike recovery determinations were not based on this nominal value, however. Frontier Geosciences determined the true value of the mercury spike amount as 98.47 ng, by retaining a subset of spiked traps in the laboratory, and determining the amount of mercury on the spiked section of the traps at the same time that the collected samples from this field verification of the HG-324K were analyzed. The mercury analysis by Frontier Geosciences included measurement of mercury on each of the four sorbent stages in each trap, analysis of blank traps, analysis of a mercury Standard Reference Material® (National Institute of Standards and Technology [NIST] 1641d), assessment of analytical spike recovery and replicate analysis precision, and analysis of initial and continued calibration blank and continued calibration verification samples.

3.2 Test Facility

The host facility for the HG-324K 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 HG-324K was verified 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 90º 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 HG-324K sampled from a single fixed point one meter inside the inner liner of the stack at their respective port locations. This arrangement was justified by the absence of stratification observed for sulfur dioxide (SO_2) and nitrogen oxides (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]	14.8 %	13.3–15.3
NO_x[a]	97 ppm[d]	61–165
SO_2[a]	193 ppm	104–316
Total mercury vapor[b]	0.81 µg/dscm[e]	0.73–0.93

a: Values calculated from hourly data recorded by R.M. Schahfer staff June 12 to July 25, 2006.
b: Values based on measurements made during OH reference sampling periods June 12–15, 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 HG-324K.

3.3.1 Relative Accuracy

The RA of the HG-324K was evaluated by comparing its Hg_T results to simultaneous results obtained by sampling stack gas with the OH 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.(4) Over the period of June 12 to 15, ARCADIS conducted a series of 12 OH runs on the Unit 17 stack, each two hours in duration, using paired OH trains. The Hg_T concentration determined by the OH reference method in each run was compared to the corresponding result from paired HG-324K traps sampled over exactly the same time period as the OH run.

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 (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 criterion required of the OH method,(5) and qualified OH results were averaged to produce the final reference data. The paired sorbent trap samples collected using the HG-324K were sent to Frontier Geosciences in Seattle, Washington, for mercury analysis. The mercury results from the paired HG-324K sorbent traps were reviewed for spike recovery and duplicate precision relative to Appendix K requirements.(1) RA was calculated as described in Section 5.1, and in addition the average of all HG-324K results was compared to the average of all OH results.

3.3.2 Data Completeness

No additional test procedures were carried out specifically to address data completeness of the HG-324K. This parameter was assessed by comparing the overall data return to the total possible data return.

3.3.3 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. Examples of information used to assess operational factors were the 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 observations about ease of use of the HG-324K.

3.4 Verification Schedule

The HG-324K was verified in a field effort that took place from June 12 to July 25, 2006, that also evaluated two mercury CEMs and one other sorbent-based system. The HG-324K was installed at the Unit 17 stack on June 11 and removed on June 16, 2006, during which period it was operated by a vendor representative. Twelve successive OH reference method runs were carried out in this period for comparison to the HG-324K results.

Table 3-2 shows the actual schedule of OH reference method sampling completed by ARCADIS between June 12 and 15, 2006. The OH sampling proceeded efficiently, with three runs conducted on each of four successive days. In all cases, the HG-324K vendor representative was informed of the planned start time of each OH run; and, in a 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.

Table 3-2. 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

Following the field sampling effort, all HG-324K sorbent trap samples were shipped by Environmental Supply Company to Frontier Geosciences for analysis. Frontier Geosciences returned an analysis data file that included results of blank, replicate analysis, and other QA/QC results, along with the calculated stack gas mercury concentrations from each sorbent trap both uncorrected and corrected for mercury spike recovery.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(6) and the test/QA plan for this verification test.(3) QA/QC procedures and results are described below.

4.1 OH Reference Method

This verification test included a comparison of HG-324K results to those of the OH reference method for flue gas mercury.(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 initial and continuing blanks and calibration standards. In addition, all OH reference measurements were made with paired trains, and the percent relative deviation (%RD) of each data pair was required to be ≤ 10% (at mercury levels >1.0 µg/dscm) or ≤ 20% (at mercury levels ≤ 1.0 µg/dscm) (%RD = difference between the paired train results divided by sum of those results, expressed as a percentage).(5) 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 Table 4-1 for the June 12 to 15 period of OH method sampling. The 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 percent relative deviation of each pair of results. All mercury results are in micrograms of mercury per dry standard cubic meter (µg/dscm).

Inspection of Table 4-1 shows that Hg_T in the Unit 17 stack ranged from 0.73 to 0.93 µg/dscm in the OH runs conducted in the June 12–15 period. The average Hg_T value was 0.81 µg/dscm. Hg^0 comprised the great majority of the Hg_T, consistent with the scrubbing of the Schahfer Unit 17 flue gas. Hg_{OX} never exceeded about 0.07 µg/dscm and was typically about 5% of the Hg_T.

Table 4-1 shows close agreement between the paired OH train results for all three mercury fractions. The %RD values in Table 4-1 are less than about 5% in all 12 runs for both Hg^0 and Hg_T. The %RD values for the relatively very low Hg_{OX} concentrations are slightly higher, with

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

OH Run	Average 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.

two values exceeding 10%. The applicable acceptance criterion for all the paired OH results is %RD < 20%, because all OH mercury results from this set of OH runs were less than 1 µg/dscm.(5) All results in Table 4-1 met that criterion, even for the Hg_{OX} fraction, which was present at very low concentrations.

4.1.2 OH Blank and Spike Results

Analyses were conducted on eight total samples collected at the Schahfer site from the blank reagents used in the OH method between June 12 and 15. Only two of those samples showed detectable mercury, with concentrations of 0.004 µg/L. This blank reagent concentration is negligible compared to the mercury in impinger solutions recovered from trains after stack sampling. Those recovered sample concentrations were typically about 0.1 µg/L, 0.2 µg/L, and 3 µg/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 the period 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 range from 0.126 to 0.144 µg, equivalent to approximately 7% of the typical total amount of mercury recovered from a train after stack sampling at the Schahfer plant. Those blank train results correspond to stack gas mercury concentrations of less than 0.06 µg/dscm under typical sampling conditions in this verification.

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 112%, and averaged 93%. 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 OH reference method, a technical systems audit (TSA) of the verification test performance, 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 4-2 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 serial number as #2007 and #2008. As a result, for some parameters, Table 4-2 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 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. Note that this audit was conducted during a second period of OH sampling carried out in this verification test in July 2006, rather than in the June 12 to15 period used for verification of the HG-324K.

- 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, H_2O_2/nitric acid (HNO_3), and $KMnO_4$/sulfuric acid (H_2SO_4) 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% HNO_3 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 4-2 shows that all the PE audit results were within the target tolerances set in the test/QA plan.(3)

Table 4-2. Summary of PE Audit Results

Parameter	Date	OH Result	Reference Value	Observed Agreement	Target Agreement
OH temperature measurement	6/14/06				
	probe T	228°F(a)	230°F	0.29%	2% absolute T
	stack T	127°F(b)	129°F	0.31%	
OH sample flow measurement	7/11/06	15.02 L/min(a) 14.58 L/min(b)	14.56 L/min 14.35 L/min	3.2% 1.6%	5%
Impinger weighing	6/14/06	199.72 499.27	200 grams 500 grams	0.14% 0.15%	Greater of 1% or 0.5 gram
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(3) and the AMS Center QMP.(6) As part of the TSA, test procedures were compared to those specified in the test/QA plan,(3) 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.(6) 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 quantitative 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 HG-324K with respect to the OH reference method results was assessed as a percentage, using Equation 1:

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

where *d* refers to the difference between the OH reference mercury concentration and the HG-324K result 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^{α}_{n-1} 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 only for total vapor-phase mercury. All paired OH data meeting the method quality criteria were eligible for inclusion in the calculation of RA. All 12 OH runs met the quality criteria and were included in the RA calculation for the HG-324K. A RA of less than 20% is considered acceptable.(1) Alternatively, when the mean reference mercury level is less than 5.0 µg/dscm (as in this test), agreement of the overall average HG-324K value within 1.0 µg/dscm of the mean OH value is also considered acceptable.(1)

5.2 Data Completeness

Data completeness was calculated as the percentage of the total possible data return that was achieved by the HG-324K over its several days of operation in the field. The primary form of data completeness was the number of OH runs (out of 12) for which HG-324K produced valid data. In addition, any down time when the HG-324K would not have been available to carry out a measurement was judged as incomplete data. 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 HG-324K sorbent-based sampling system are presented below for each of the performance parameters.

6.1 Relative Accuracy

The RA of the HG-324K with respect to the OH results for Hg_T was calculated using Equation 1 in Chapter 5. The primary calculation of RA was conducted using the data from all collected HG-324K sorbent samples. In addition, RA was calculated after applying the acceptance criteria and spike recovery correction required under Appendix K(1) to the HG-324K sorbent trap results. These additional calculations were made to illustrate the impact on RA results if these criteria were applied.

Table 6-1 summarizes the results obtained from the HG-324K sorbent sampling system. Table 6-1 lists the date, run number, and trap number of each HG-324K sorbent sample; the blank-corrected Hg_T concentration in stack gas determined by each of the sorbent traps; and the corresponding average concentration of each pair of traps. Also shown are the spike recovery percentage found for each trap; the Hg_T concentration that results from applying the spike recovery correction to each trap as indicated in Appendix K;(1) the corresponding average spike-corrected concentration of each pair of traps; and the percent relative difference of the spike-corrected paired trap results.

Table 6-1 shows that the Hg_T results from paired sorbent traps were generally closely similar, with the exception of the results from Run 8. In that run the HG-324K post-test leak check failed, and thus the results from Run 8 are excluded from comparison to the OH results. Table 6-1 also shows the spike recovery percentage for each trap, and indicates that this percentage was outside the acceptable range of 75 to 125% for three traps. The results from those traps are also excluded from comparisons of the spike-corrected HG-324K results to the OH results, in Section 6.1.2. It is noteworthy that those paired traps exhibiting substantial differences in mercury spike recovery did not exhibit comparable differences in the measured Hg_T concentration in the stack before correction for spike recovery (see Runs 1, 3, and 10 in Table 6-1).

The amount of mercury found on the second sorbent section of each HG-324K trap never exceeded 2% of the amount found on the corresponding first sorbent section. As a result, all the HG-324K samples met the 5% mercury breakthrough criterion stated in Appendix K.(1)

Table 6-1. HG-324K Hg_T Results

Date/Run/Trap	Hg_T[a] (µg/dscm)	Pair Avg Hg_T (µg/dscm)	% Spike Recovery	Spike-Corrected Hg_T (µg/dscm)[b]	Pair Avg Spike-Corrected Hg_T (µg/dscm)	%RD[c]
6/12/06 R1 T1	1.045	1.085	67.7%	d	1.209	e
6/12/06 R1 T2	1.125		93.1%	1.209		
6/12/06 R2 T1	1.021	1.049	95.1%	1.074	1.087	1.2%
6/12/06 R2 T2	1.076		97.9%	1.100		
6/12/06 R3 T1	1.071	1.081	64.1%	d	1.081	e
6/12/06 R3 T2	1.092		101.0%	1.081		
6/13/06 R4 T1	1.178	1.215	99.2%	1.188	1.210	1.8%
6/13/06 R4 T2	1.252		101.6%	1.232		
6/13/06 R5 T1	1.082	1.082	102.8%	1.053	1.081	2.6%
6/13/06 R5 T2	1.082		97.6%	1.110		
6/13/06 R6 T1	1.095	1.019	96.3%	1.138	1.036	9.8%
6/13/06 R6 T2	0.943		100.9%	0.934		
6/14/06 R7 T1	0.918	0.906	94.2%	0.974	0.936	4.1%
6/14/06 R7 T2	0.895		99.8%	0.897		
6/14/06 R8 T1	1.453	f				
6/14/06 R8 T2	0.875					
6/14/06 R9 T1	0.962	0.953	87.0%	1.107	1.077	2.8%
6/14/06 R9 T2	0.944		90.2%	1.047		
6/15/06 R10 T1	0.932	0.901	73.8%	d	0.912	e
6/15/06 R10 T2	0.869		95.3%	0.912		
6/15/06 R11 T1	0.793	0.827	79.7%	0.995	1.013	1.8%
6/15/06 R11 T2	0.860		83.4%	1.031		
6/15/06 R12 T1	0.825	0.927	84.9%	0.972	1.063	8.5%
6/15/06 R12 T2	1.029		89.2%	1.154		

a: Results corrected for average blank trap Hg result.
b: Spike-corrected result = (Hg_T/% Spike Recovery) x 100.
c: %RD (percent relative deviation) = 100 x absolute value of (T1-T2)/(T1+T2).
d: Spike recovery less than 75%, data excluded per Appendix K.
e: Only one valid result, %RD not calculated.
f: Post-check leak test failed, data excluded.

6.1.1 Relative Accuracy: Uncorrected Data

Table 6-2 lists the Hg_T results in µg/dscm from the OH method (see Table 4-1) and the HG-324K (see Table 6-1, third column), for OH runs 1 through 7 and 9 through 12; Run 8 is excluded because of the failed leak test. The RA of the HG-324K based on 11 runs using the uncorrected data is 29.5 %. Also for these 11 runs, the overall average Hg_T value from the OH reference method is 0.821 µg/dscm, whereas the uncorrected HG-324K average is 1.004 µg/dscm, a difference of 0.183 µg/dscm.

Table 6-2. Data Used for Comparison of OH and HG-324K Hg_T Results

Date	OH Run No.[a]	OH Hg_T (µg/dscm)	HG-324K Hg_T, (µg/dscm)
6/12/06	1	0.783	1.085
6/12/06	2	0.859	1.049
6/12/06	3	0.859	1.081
6/13/06	4	0.933	1.215
6/13/06	5	0.848	1.082
6/13/06	6	0.732	1.019
6/14/06	7	0.811	0.906
6/14/06	9	0.874	0.953
6/15/06	10	0.820	0.901
6/15/06	11	0.727	0.827
6/15/06	12	0.781	0.927

a: Run 8 excluded from calculation because HG-324K failed post-sampling leak check in that run.

6.1.2 Relative Accuracy: Spike-Corrected Data

Table 6-3 lists the Hg_T results in µg/dscm from the OH method (see Table 4-1) and the spike-corrected results in µg/dscm from the HG-324K (see Table 6-1), for OH runs 1 through 7 and 9 through 12; Run 8 is excluded because of the failed leak test. Table 6-3 also notes which three HG-324K results are from a single trap, as opposed to the average of paired traps, due to low spike recovery on one trap. The RA of the HG-324K based on these 11 runs using the spike-corrected data is 37.0 %. Also for these 11 runs, the overall average Hg_T value from the OH reference method is 0.821 µg/dscm, whereas the spike-corrected HG-324K average is 1.064 µg/dscm, a difference of 0.243 µg/dscm.

Table 6-3. Data Used for Comparison of OH and Spike-Corrected HG-324K Hg_T Results[a]

Date	OH Run No.[a]	OH Hg_T (µg/dscm)	Spike-Corrected HG-324K Hg_T (µg/dscm)
6/12/06	1	0.783	1.209[b]
6/12/06	2	0.859	1.087
6/12/06	3	0.859	1.081[b]
6/13/06	4	0.933	1.210
6/13/06	5	0.848	1.081
6/13/06	6	0.732	1.036
6/14/06	7	0.811	0.936
6/14/06	9	0.874	1.077
6/15/06	10	0.820	0.912[b]
6/15/06	11	0.727	1.013
6/15/06	12	0.781	1.063

a: Run 8 excluded from calculation because HG-324K failed post-sampling leak check in that run.
b: Low spike recovery from one trap; therefore, this result from a single trap; all others from paired traps.

The paired trap precision requirement of <10% RD stated in Appendix K(2) was met in the eight valid HG-324K runs in which spike-corrected paired trap results were obtained (see Table 6-1, last column). However, eight runs is below the nine values needed to calculate RA, so that calculation was not done using only the spike-corrected paired trap results.

6.2 Data Completeness

The HG-324K sampled during all 12 of the OH runs conducted June 12-15, 2006, with no delays, breakdowns, or sampling interruptions. All sorbent traps were recovered after sampling, with no broken traps. However, after OH Run 8, the post-test leak check failed; and, as a result, only 11 of the 12 sampling runs (91.7%) were suitable for comparison to the OH reference results.

6.3 Operational Factors

The HG-324K was installed quickly at the Schahfer Unit 17 stack on June 11 and was operated by one vendor representative without serious problems for the subsequent four days of OH reference method sampling. A single failed post-test leak check was the only difficulty encountered over all 12 OH runs. Ease of use was not investigated with a newly trained operator, as the vendor operated the HG-324K during the test period. The sorbent traps obtained from Frontier Geosciences were rugged and uniform in construction, so that no breakage occurred; and no problems were encountered in placing the traps into the end of the sampling probe or recovering them after sampling. The sampling probe used with the HG-324K was simple and relatively light in weight, and was handled by the one vendor operator in all sampling. The HG-324K sorbent sampling system incorporated the usual capabilities of a stack sampling box, but also included data acquisition and transfer capabilities. Those capabilities included wireless communication with a personal computer over distances up to several hundred feet, which allowed review and transfer of the sampling data at any time without interrupting the sampling itself. Data were recorded on magnetic card media in the HG-324K, providing a readily transportable and reliable means of data storage.

Chapter 7
Performance Summary

The RA of the HG-324K for determining $\mathrm{Hg_T}$ based on 11 OH runs was 29.5%, when the comparison was based on HG-324K results corrected for trap blanks but not corrected for mercury spike recovery. For those 11 runs, the overall average $\mathrm{Hg_T}$ value from the OH reference method was 0.821 µg/dscm, whereas that from the HG-324K was 1.004 µg/dscm, a difference of 0.183 µg/dscm. When comparing HG-324K results corrected for mercury spike recovery, the RA for 11 OH runs was 37.0%, and the OH and HG-324K average values were 0.821 µg/dscm and 1.064 µg/dscm, respectively, a difference of 0.243 µg/dscm.

The HG-324K sampled during all 12 OH runs conducted over four days with no delays, breakdowns, broken traps, or sampling interruptions. The only problem encountered was that after Run 8 the post-test leak check failed. As a result, only 11 of the 12 sampling runs (91.7% data completeness) were suitable for comparison to the OH reference results.

The HG-324K was installed quickly and was operated by a vendor representative without serious problems. A failed post-test leak check in one sampling run was the only difficulty encountered. The sorbent traps were rugged and uniform in construction, so that no breakage occurred; no problems were encountered in placing the traps into the end of the sampling probe or recovering them after sampling. The sampling probe used with the HG-324K was simple and relatively light in weight, and was handled by the one vendor operator in all sampling. The HG-324K sorbent sampling system incorporated data acquisition and transfer capabilities, including magnetic card recording media and wireless communication.

The cost of the HG-324K system as tested is $18,750. The cost of each sorbent trap sample was about $500, including preparation and pre-spiking of the trap, and analysis for mercury after sampling.

Chapter 8
References

1. *Code of Federal Regulations,* 40 CFR part 75, including Appendices A through K, July 2005.

2. EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA-821-R-02-019, August 2002.

3. *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.

4. *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.

5. *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.

6. *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.