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Environmental Technology Verification Report

APEX INSTRUMENTS
SORBENT-BASED MERCURY SAMPLING SYSTEM

Prepared by
Battelle

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

APEX INSTRUMENTS SORBENT-BASED MERCURY SAMPLING 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

agl	above ground level
AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
CEM	continuous emission monitor
cm ³ /min	cubic centimeter per minute
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
°F	degrees Fahrenheit
FGD	flue gas desulfurization
H ₂ O ₂	hydrogen peroxide
H ₂ SO ₄	sulfuric acid
Hg	mercury
HgCl ₂	mercuric chloride
Hg ^o	elemental mercury
Hg _T	total mercury
Hg _{OX}	oxidized 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
NIPSCO	Northern Indiana Public Service Company
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 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 Apex Instruments 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 Apex system. The following is a description of the system, based on information provided by the vendor. The information provided below was not verified in this test.

The Apex system tested in this program consisted of two Apex Instruments Model XC-60 Gas Sampling Consoles, an SGC 4000 Hg Stirling Gas Conditioner, and a 9-foot-long dual trap mercury sampling probe with a 25-foot-long heated sample line. Each XC-60 console incorporated a dry gas meter, rotameter flow meter, manual sample flow control valves, temperature indicators, vacuum gauge, and sampling pump. These consoles allow simultaneous sampling with two sorbent traps through the single probe, maintaining a constant sampling flow of about 500 cubic centimeters per minute (cm^3/min) through each trap. Pre- and post-run leak checks were conducted in each run. Sample gas drawn through the sorbent traps in the probe tip was transported through the heated sample line to the SGC 4000 Hg Stirling Gas Conditioner, where moisture was removed by condensation before the gas entered each XC-60 console. Sampling data were recorded manually every 15 minutes during each run and included stack, probe, console, and Stirling chiller temperatures; sample flow rates; and vacuum and pressure readings. Barometric pressure was documented for each run and used to correct results to standard conditions. Figure 2-1 shows the two XC-60 consoles, Figure 2-2 the SGC 4000 Hg Gas Conditioner, and Figure 2-3 the Apex sampling probe and heated line.

The cost of the Apex system as tested (i.e., a manually operated dual system) is \$10,000 to \$15,000, depending on options. As used in this test, the cost per sorbent trap sample was \$205, consisting of \$55 for the trap, \$60 for pre-spiking with mercury, and \$90 for analysis after sampling. The sorbent traps used with the Apex system in this test were prepared and analyzed by Ohio Lumex, Inc., of Twinsburg, Ohio.



Figure 2-1. Apex XC-60 Gas Sampling Consoles



Figure 2-2. Apex SGC 4000 Hg Stirling Gas Conditioner



Figure 2-3. Apex Dual Trap Sampling Probe and Heated Line

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⁾ Appendix K in Chapter 40 of the Code of Federal Regulations, Part 75 (40 CFR Part 75)⁽²⁾ 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 Apex system 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 Apex system is a sample collection system; the mercury results shown from the system in this report resulted from use of the system with sorbent traps prepared and subsequently analyzed for mercury by Ohio Lumex, Inc.

The Apex system 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.

Verification of the system was conducted 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.⁽³⁾ Specifically, the Apex system was used to sample stack gas from July 10 through July 13, 2006 and RA was determined by comparing the Apex 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 Apex system 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 Apex system were prepared for this test by Ohio Lumex. The traps included three sections of sorbent; the third section of each trap was spiked with 60 nanograms (ng) of mercury in the preparation process. After sampling, the sorbent traps were shipped to Ohio Lumex for analysis for mercury by an approach in which individual sorbent sections were pyrolyzed in a Lumex RP-91C pyrolysis attachment, thereby driving the collected mercury vapor into a Lumex RA-915+ Mercury Analyzer. The minimum reporting limit was 10 ng of mercury per sorbent section with this analytical approach, equivalent to approximately 0.15 micrograms per dry standard cubic meter of stack gas ($\mu\text{g}/\text{dscm}$) based on the sampling rate of $500 \text{ cm}^3/\text{min}$.

3.2 Test Facility

The host facility for the Apex system 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 Apex system 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 Apex 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	16.2 %	15.7–16.7
NO _x ^a	97 ppm ^d	61–165
SO ₂ ^a	193 ppm	104–316
Total mercury vapor ^b	1.01 µg/dscm ^e	0.79–1.22

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 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 Apex system.

3.3.1 Relative Accuracy

The RA of the Apex system 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.⁽³⁾ Over the period of July 10 to 13, 2006 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 was compared to the corresponding result from paired Apex 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,⁽⁴⁾ and qualified OH results were averaged to produce the final reference data. The paired sorbent trap samples collected using the Apex system were sent to Ohio Lumex, in Twinsburg, Ohio, for mercury analysis. The mercury results from the paired Apex sorbent traps were reviewed for spike recovery and duplicate precision relative to Appendix K requirements.⁽²⁾ RA was calculated as described in Section 5.1, and in addition the average of all Apex sorbent system 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 Apex sorbent system. 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 Apex system.

3.4 Verification Schedule

The Apex system was verified in a field effort that also evaluated two mercury CEMs and one other sorbent-based system. The Apex system was installed at the Unit 17 stack on July 9 and removed on July 13, 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 Apex results.

Table 3-2 shows the actual schedule of OH reference method sampling completed by ARCADIS between July 10 and 13, 2006. The OH sampling proceeded efficiently, with three runs conducted on each of four successive days. In all cases the Apex 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 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

Following the field sampling effort, all sorbent trap samples were turned over by Apex Instruments to Ohio Lumex for analysis. Ohio Lumex returned an analysis data file that included results for collected mercury on the first two sorbent sections of each trap, the spike recovery from the third section, and the spike-corrected stack gas mercury results for both individual traps and paired trap averages. Battelle staff used information from this analysis file also to calculate stack gas mercury concentrations uncorrected 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⁽⁵⁾ and the test/QA plan for this verification test.⁽¹⁾ QA/QC procedures and results are described below.

4.1 OH Reference Method

This verification test included a comparison of Apex sorbent sampler results to those of the OH reference method for flue gas mercury.⁽³⁾ 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 $\leq 10\%$ (at mercury levels $>1.0 \mu\text{g/dscm}$) or $\leq 20\%$ (at mercury levels $\leq 1.0 \mu\text{g/dscm}$) (%RD = difference between the paired train results divided by sum of those results, expressed as a percentage).⁽⁴⁾ Data not meeting this criterion were excluded from comparison with the Apex 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 Table 4-1 for the July 10–13 period of OH method sampling. The table indicates the OH run number, and lists the average vapor phase Hg_{OX} , Hg^0 , and total Hg 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 ($\mu\text{g/dscm}$).

Inspection of Table 4-1 shows that Hg_{T} in the Unit 17 stack ranged 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} value was 1.008 $\mu\text{g/dscm}$ (note that one OH result for Hg_{T} is excluded from the average because of inadequate dual train precision, as described below). 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 0.09 $\mu\text{g/dscm}$, and was typically about 5% of the Hg_{T} .

Table 4-1. OH Results from July 10–13, 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	0.033	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	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.

Table 4-1 shows generally close agreement between the paired OH train results for all three mercury fractions. The %RD values in Table 4-1 are less than 7% in all 12 runs for both Hg⁰ and Hg_T, with the exception of Run 8, for which %RD exceeded 10% for both Hg_T and Hg⁰. The %RD values for Hg_{OX} are slightly higher, with four values exceeding 10%, probably due to the low Hg_{OX} concentrations. The only %RD values in Table 4-1 which do not meet the acceptance criteria for paired OH results are the value of 11.0% RD for Hg_T in run 8, and the values of 22.7 and 52.3 %RD for Hg_{OX} in Runs 12 and 4, respectively. Because of the %RD value, the Hg_T result from Run 8 is excluded from calculation of the RA of the Apex system.

4.1.2 OH Blank and Spike Results

Analyses were conducted on ten total samples collected at the Schahfer site from the blank reagents used in the OH method in the July 10–13 period. Only two of those samples showed detectable mercury, with concentrations of 0.003 and 0.006 microgram per liter (µg/L), respectively. This blank reagent concentration is negligible in comparison 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 4 µg/L in potassium chloride (KCl) solution, hydrogen peroxide (H₂O₂) solution, and potassium permanganate (KMnO₄) 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 July 10-13 sampling period, the total amounts of mercury recovered from the three blank trains range from 0.193 to 0.250 µg, equivalent to approximately 10 percent 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 0.1 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 88 to 117%, and averaged 100%. 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 performance evaluation (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 Audit

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 their serial numbers 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. Note that most of the PE audit procedures were carried out in the initial period of OH sampling conducted four weeks before the OH measurements against which the Apex results were compared.

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 4-2 shows that all the PE audit results were within the target tolerances set in the test/QA plan.⁽¹⁾

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 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 14.58 L/min ^b	14.56 L/min 14.35 L/min	3.2% 1.6%	5 %	
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 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 Apex system with respect to the OH reference method results was assessed as a percentage, using Equation 1:

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

where d refers to the difference between the OH reference mercury concentration and the Apex 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_{n-1}^{α} is the t value for the $100(1 - \alpha)$ 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 criterion and were included in the RA calculation for the Apex system. A RA of less than 20% is considered acceptable.⁽²⁾ Alternatively, when the mean reference mercury level is less than 5.0 $\mu\text{g}/\text{dscm}$ (as in this test), agreement of the overall average Apex value within 1.0 $\mu\text{g}/\text{dscm}$ of the mean OH value is also considered acceptable.⁽²⁾

5.2 Data Completeness

Data completeness was calculated as the percentage of the total possible data return that was achieved by the Apex system 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 the Apex system produced valid data. In addition, any down time when the Apex system 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 Apex system are presented below for each of the performance parameters.

6.1 Relative Accuracy

The RA of the Apex system 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 Apex sorbent samples. In addition, RA was calculated after applying the acceptance criteria and spike recovery correction required under Appendix K⁽²⁾ to the Apex 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 Apex system. Table 6-1 lists the date, run number, and trap number of each Apex sorbent sample; the Hg_T concentration in stack gas determined by analysis of the first sorbent stage of each trap; and the corresponding average concentration of each pair of traps. Also shown are the spike recovery percentage found by analysis of the third stage of each trap, which was spiked with nominally 60 ng of mercury; the Hg_T concentration that results from applying the spike recovery correction to each trap as indicated in Appendix K;⁽²⁾ the corresponding average spike-corrected concentration of each pair of traps; and the percent relative difference of the spike-corrected paired trap results. It should be noted that several of the sorbent traps were broken during sampling. For four such traps, the first sorbent stage could not be recovered, resulting in no measurement of stack gas mercury. However, for three of those traps, the third sorbent stage was recovered, allowing determination of spike recovery. Also, because of the breakage of traps, only a single trap was available for use in the 12th sampling run.

Table 6-1 shows that the Hg_T results from paired sorbent traps were generally closely similar. Table 6-1 also shows the spike recovery percentage for each trap, and indicates that this percentage was always within the acceptable range of 75 to 125%. The analysis of the sorbent traps had a minimum reporting limit of 10 ng of mercury per section of sorbent, and this value of < 10 ng was reported for the second sorbent section (i.e., the backup sampling section) in every trap. The maximum mass of mercury collected on any of the first sorbent sections was about 80 ng, so this reporting limit amounted to at least 12 percent of the mercury found on the first section. As a result, it was not possible to determine whether mercury breakthrough from the first to the second section was within the 5% limit stated in Appendix K.⁽²⁾

Table 6-1. Apex System Hg_T Results

Date/Run/Trap	Hg _T (µg/dscm)	Pair Avg Hg _T (µg/dscm)	% Spike Recovery	Spike- Corrected Hg _T (µg/dscm) ^a	Pair Avg Spike- Corrected Hg _T (µg/dscm)	%RD ^b
7/10/06 R1 T1	1.146	1.130	105	1.092	1.076	1.5
7/10/06 R1 T2	1.113		105	1.060		
7/10/06 R2 T1	1.059	1.059	95	1.115	1.115	d
7/10/06 R2 T2	c		90	c		
7/10/06 R3 T1	1.083	1.083	103	1.048	1.084	3.3
7/10/06 R3 T2	1.082		97	1.119		
7/11/06 R4 T1	1.127	1.127	113	0.994	0.994	d
7/11/06 R4 T2	c		113	c		
7/11/06 R5 T1	c	1.269	e	c	1.120	d
7/11/06 R5 T2	1.269		113	1.120		
7/11/06 R6 T1	1.312	1.316	123	1.064	1.141	6.8
7/11/06 R6 T2	1.320		108	1.219		
7/12/06 R7 T1	0.956	1.047	88	1.082	1.174	7.8
7/12/06 R7 T2	1.138		90	1.265		
7/12/06 R8 T1	1.172	1.099	110	1.065	1.073	0.7
7/12/06 R8 T2	1.027		95	1.081		
7/12/06 R9 T1	1.114	1.075	100	1.114	1.075	3.6
7/12/06 R9 T2	1.036		100	1.036		
7/13/06 R10 T1	c	1.254	95	c	1.213	d
7/13/06 R10 T2	1.254		103	1.213		
7/13/06 R11 T1	1.305	1.283	105	1.243	1.285	3.3
7/13/06 R11 T2	1.260		95	1.327		
7/13/06 R12 T1	1.233	1.233	105	1.174	1.174	d
7/13/06 R12 T2	f					

a: Spike-corrected result = (Hg_T/% Spike Recovery) x 100.

b: %RD (percent relative deviation) = 100 x absolute value of (T1-T2)/(T1+T2).

c: Trap broken, first sorbent stage not recovered.

d: Only one valid result, %RD not calculated.

e: Trap broken, third (spiked) sorbent stage not recovered.

f: Only one trap available for this run.

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 Apex sorbent sampler (see Table 6-1, third column), for OH runs 1 through 12. Table 6-2 also notes which five Apex results are from a single trap, as opposed to the average of paired traps. The RA of the Apex sorbent sampler based on 11 runs (OH Run 8 is excluded, as noted in Section 4.1.1) using the uncorrected data is 26.6%. Also for these 11 runs, the overall average Hg_T value from the OH reference method is 1.008 µg/dscm, whereas the uncorrected Apex average is 1.171 µg/dscm, a difference of 0.162 µg/dscm.

Table 6-2. Data Used for Comparison of OH and Apex Hg_T Results

Date	OH Run No.	OH Hg _T (µg/dscm)	Apex Hg _T (µg/dscm)
7/10/06	1	0.935	1.130
7/10/06	2	0.860	1.059 ^b
7/10/06	3	0.969	1.083
7/11/06	4	0.952	1.127 ^b
7/11/06	5	0.787	1.269 ^b
7/11/06	6	1.056	1.316
7/12/06	7	1.083	1.047
7/12/06	8	1.081 ^a	1.099
7/12/06	9	1.215	1.075
7/13/06	10	1.074	1.254 ^b
7/13/06	11	1.107	1.283
7/13/06	12	1.053	1.233 ^b

a: This run excluded from RA calculation because %RD outside limits.

b: This result from a single trap; all others from paired traps.

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 Apex system (see Table 6-1, sixth column), for OH runs 1 through 12. Table 6-3 also notes which five Apex results are from a single trap, as opposed to the average of paired traps. The RA of the Apex system based on 11 runs (OH Run 8 is excluded, as noted in Section 4.1.1) using the spike-corrected data is 20.3%. Also for these 11 runs, the overall average Hg_T value from the OH reference method is 1.008 µg/dscm, whereas the spike-corrected Apex average is 1.132 µg/dscm, a difference of 0.124 µg/dscm.

The paired trap precision requirement of <10% RD stated in Appendix K⁽²⁾ was met in the seven Apex runs in which paired traps were recovered (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 Apex sampler was operated during all 12 of the OH runs conducted July 10–13, 2006. However, as noted in Section 6.1 and described below in Section 6.3, the recovery of sorbent traps for analysis was incomplete. Both of the paired sorbent traps were recovered and analyzed for seven of the 12 OH runs, and one trap was recovered and analyzed in four other runs. In the remaining run, only one sorbent trap was used because the Apex representative had exhausted his supply of traps and did not have a second trap to install in the sampling probe. Treating those runs with only one trap recovered as one-half of a complete sampling run, the overall data completeness for the Apex sampler is calculated to be 79.2%.

Table 6-3. Data Used for Comparison of OH and Spike-Corrected Apex Hg_T Results

Date	OH Run No.	OH Hg _T (µg/dscm)	Spike-Corrected Apex Hg _T (µg/dscm)
7/10/06	1	0.935	1.076
7/10/06	2	0.860	1.115 ^b
7/10/06	3	0.969	1.084
7/11/06	4	0.952	0.994 ^b
7/11/06	5	0.787	1.120 ^b
7/11/06	6	1.056	1.141
7/12/06	7	1.083	1.174
7/12/06	8	1.081 ^a	1.073
7/12/06	9	1.215	1.075
7/13/06	10	1.074	1.213 ^b
7/13/06	11	1.107	1.285
7/13/06	12	1.053	1.174 ^b

a: This run excluded from RA calculation because %RD outside limits.

b: This result from a single trap; all others from paired traps.

6.3 Operational Factors

Apex Instruments had originally intended that the system verified in this test would use a new product, a dual-train digital meter box. However, shortly before the field period, Apex personnel concluded that the dual digital unit was not quite ready for field evaluation. As a result, the system tested used two Apex Model XC-60 manual meter boxes, along with a SGC 4000 Hg Stirling cooler to remove moisture from the sample gas, and a 9-foot long dual sampling probe.

The greatest limitation of the Apex system was the poor quality of the sorbent traps used. The traps were very fragile, and the glass tubing used for the traps was of inconsistent diameter. With some traps the glass tubing was slightly small in diameter, so that it was difficult to tighten the Teflon[®] ferrule enough to achieve an adequate seal; with other traps the tubing was slightly too large, so that the ferrule and corresponding nut could not even slide on over the tube. This inconsistency made installation and retrieval of the traps difficult, and coupled with the relatively thin wall of the glass tubing led to frequent breakage of the traps. The Apex representative had brought 30 sorbent traps to the Schahfer site, more than enough to conduct 12 runs with dual traps. However, in only seven of those 12 runs were both traps recovered for analysis, and in four others only one trap could be recovered. For the final OH sampling interval, only a single usable sorbent trap was available for the Apex system. It should be noted that this limitation due to the traps is not related to the Apex sampling technology itself, i.e., improvements in the quality of the sorbent traps should translate directly into improved performance of the entire system.

An additional limitation of the Apex system was the relatively heavy sampling probe used with the system. This probe was very difficult for one operator to handle, and in fact the Apex operator suffered a burn from contacting the hot probe while attempting to withdraw the probe after an early sampling run. For safety, assistance was provided to the Apex operator in inserting and removing the probe for subsequent sampling runs. Development of a simpler, lighter sampling probe would be a valuable improvement to the Apex system.

Chapter 7 Performance Summary

The RA of the Apex system for determining Hg_T based on 11 OH runs was 26.6%, when the comparison was based on Apex results uncorrected for mercury spike recovery. For those 11 runs, the overall average Hg_T value from the OH reference method was $1.008 \mu\text{g/dscm}$, whereas that from the Apex system was $1.171 \mu\text{g/dscm}$, a difference of $0.162 \mu\text{g/dscm}$. When comparing Apex results corrected for mercury spike recovery, the RA for 11 runs was 20.3%, and the OH and Apex average values were $1.008 \mu\text{g/dscm}$ and $1.132 \mu\text{g/dscm}$, respectively, a difference of $0.124 \mu\text{g/dscm}$.

The Apex sampler was operated during all 12 OH runs conducted over four days with no delays or sampling interruptions. However, the recovery of sorbent traps for analysis was incomplete due to breakage of traps. Both paired sorbent traps were recovered for seven of the 12 OH runs, one trap was recovered for four runs, and in the remaining run only one usable sorbent trap was available. Treating those five runs with only one trap recovered as one-half of a complete sampling run, the overall data completeness for the Apex sampler is calculated to be 79.2%.

The greatest limitation of the Apex system was the poor quality of the sorbent traps used. The traps were fragile, and the glass tubing used for the traps was of inconsistent diameter. This made installation and retrieval of the traps difficult and led to frequent breakage of the traps. It should be noted that this limitation due to the traps is not related to the Apex sampling technology itself, i.e., improvements in the quality of the sorbent traps should translate directly into improved performance of the entire system. An additional limitation of the Apex system was the relatively heavy sampling probe used with the system, which was very difficult for one operator to handle alone.

The approximate cost of the Apex system as tested (i.e., a manually operated dual system) is \$10,000 to \$15,000, depending on options. The cost of each sorbent trap sample was \$205, including pre-spiking of the trap and analysis for mercury after sampling.

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, 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.