

1. PROJECT OVERVIEW

TEST PROGRAM SUMMARY

DTE Electric Company (DTE) contracted Clean Air Engineering (CleanAir) to perform a relative accuracy test audit (RATA) on a sorbent trap mercury (Hg) monitoring system (STMS) used for mercury compliance monitoring on the Unit 3 Stack at the River Rouge Power Plant (RRPP). The River Rouge Power Plant is located in River Rouge, Michigan.

The purpose of the test program was to complete an annual relative accuracy test audit (RATA) on the STMS as required by 40 CFR 63, Subpart UUUUU, National Emission Standards for Hazardous Air Pollutants: Coal- and Oil-Fired Electric Utility Steam Generating Units. The STMS is a CleanAir MET-80 STMS sorbent trap monitoring system that meets or exceeds 40 CFR 60, Appendix B, Performance Specification 12B (PS 12B) requirements.

All testing was performed in accordance with the regulations set-forth by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environment, Great Lakes, and Energy (EGLE). The Reference Method (RM) used was USEPA Method 30B, detailed in 40 CFR 60, Appendix A.

All RATA testing was performed while the unit was operating at an appropriate operating level based on the unit condition on the day of each test. Unit operating conditions are included in Appendix H.

A summary of the test program results is presented below. Section 2 Results provide a more detailed account of the test conditions and data analysis. The appendices contain detailed sampling and analytical parameters that were used to calculate both the reference method and the STMS results in Table 1-1.

**Table 1-1:
 Summary of RATA Results**

<u>Source</u> Constituent	Reference Method	Applicable Specification	Relative Accuracy (%) ¹	Limit ²
<u>Unit 3 Stack (Probe 1)</u> Hg (µg/dscm)	EPA 30B	PS12B	2.7%	≤ 20% of RM _{avg}

¹ Relative Accuracy is expressed in terms of comparison to the reference method (% RM) in accordance with specifications outlined in 40 CFR 60, App B, PS12B and MDEQ APC Rule R336.2158, Table 111.

TEST PROGRAM DETAILS

MERCURY MONITORING SYSTEM INFORMATION

The mercury monitoring system is a CleanAir MET-80 sorbent trap monitoring system (STMS) that samples flue gas at the EPA monitoring level of Unit 3 Stack. A summary of STMS information including serial number is shown in Table 1-2.

**Table 1-2:
 Mercury Monitoring System Information**

Facility:	DTE Energy - River Rouge Power Plant
Pollutant:	Mercury (Hg) total vapor phase
Measurement Technology:	Hg Sorbent Trap Monitoring System
Manufacturer:	Clean Air Engineering
Model No.:	MET-80XR2
Source ID:	Unit 3 Stack
System Serial Number:	12651110

PARAMETERS

The test program included reference method measurements of total vapor-phase mercury (Hg) using EPA Method 30B sampling and analysis procedures.

A summary of test parameters and methods is shown in Table 1-3.

**Table 1-3:
 Parameters and Test Methods Summary**

Parameter	Test Method/Procedure
Mercury (Hg)	40 CFR 60, App A, M30B
Hg Relative Accuracy	MDEQ Air Pollution Control Rules, Part 11, R 336.2158 and Table 111 40 CFR 60, App B, PS 2 and PS 12B 40 CFR 63, Subpart UUUUU, App A, Section 4

SCHEDULE

Testing was performed on June 12, 2019. The on-site schedule followed during the test program is outlined in Table 1-4.

**Table 1-4:
 Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	07:58	08:28
2	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	08:42	09:12
3	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	09:27	09:57
4	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	10:12	10:42
5	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	10:59	11:29
6	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	11:46	12:16
7	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	12:32	13:02
8	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	13:17	13:47
9	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	14:04	14:34
10	Unit 3, Probe 1	USEPA Method 30B	Hg (Total Vapor Phase)	06/12/19	14:48	15:18

DISCUSSION

Program Design

CleanAir performed the RM 30B sampling during the RATA tests. The RM 30B sorbent traps were manufactured by the Ohio Lumex Company. These traps contained two sections and included an iodinated, activated charcoal sorbent. A minimum of three (3) traps, each spiked with 30 ng of mercury, were used to complete a spike recovery study in accordance with RM 30B requirements. The test run duration was 30 minutes in order to meet minimum sample mass (5 ng) and spike recovery study volume requirements.

RRPP technicians performed sorbent trap exchanges for the Unit 3 Hg STMS during the test program. The STMS traps contained the same type of sorbent (iodinated, activated charcoal) as is used during normal operation, with the exception of the sorbent bed size being smaller (400 mg versus normally 1000 mg) to accommodate the short duration of the RATA runs. All PS 12B traps were spiked with 30 ng of mercury.

CleanAir performed sorbent trap analyses for both the EPA Method 30B and Performance Specification 12B (PS 12B) sorbent traps. Analysis was performed on-site using an Ohio Lumex model RA-915+ analyzer with RP-M324 detector, which utilizes thermal desorption with Zeeman atomic absorption spectrometry.

RATA Determination

All test runs included collection and analysis of traps in pairs. Only relative accuracy runs which met all QA/QC criteria for both traps were used. The average concentration of each pair of associated traps is reported in units of $\mu\text{g}/\text{dscm}$. The relative accuracy was calculated following the procedures specified in PS 12B, Section 8.3.

RATA Results Criteria

The criteria to evaluate the relative accuracy (RA) of the STMs is detailed in 40 CFR 63, Subpart UUUUU, Appendix A, Table A-2. The RA met the $\leq 20\%$ criteria for RA acceptance (see Table 1-2).

A total of 10 sample runs were performed. The relative accuracy was based on nine (9) valid sample runs following provisions allowed in 40 CFR 60, Appendix A, Performance Specification 12B, Section 8.3.

Modifications to Test Methodology

No modifications to the EPA Method 30B sampling or analysis procedures were required for the test program. Test methodology specifications are included in the Appendix.

End of Section

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices.

**Table 2-1:
 RRPP Unit 3 – Mercury RATA Results**

RATA Set Label			P1 Q2 2019 RATA			
Run #	Start Date/Time	Duration	Ref Value	CEM Value	Run Used	Load
1	06/12/2019 07:58	30	0.593	0.595	Y	209
2	06/12/2019 08:42	30	0.544	0.575	Y	209
3	06/12/2019 09:27	30	0.617	0.63	Y	209
4	06/12/2019 10:12	30	0.668	0.659	Y	209
5	06/12/2019 10:59	30	0.668	0.686	Y	209
6	06/12/2019 11:46	30	0.691	0.706	Y	209
7	06/12/2019 12:32	30	0.69	0.701	Y	209
8	06/12/2019 13:17	30	0.688	0.668	Y	209
9	06/12/2019 14:04	30	0.7	0.694	Y	209
10	06/12/2019 14:48	30	0.667	0.732	N	209
Test #			1			
Average Load			209			
Operational Level			M			
Mean Of CEM			0.657			
Mean Of Reference			0.651			
Mean Of Difference			-0.006			
Standard Deviation Of Difference			0.016			
Coefficient Of Confidence			0.012			
Relative Accuracy			2.74			
T-Value			2.306			
Bias Adjustment Factor			1			
Result			Passed			
RATA Frequency			4QTRS			
Testers						

**Table 2-2:
 Summary of RM 30B QA/QC Results – Unit 3 STMS (Probe 1)**

QA/QC and Performance								
Run No.	Start Date/Time (EST)	Valid? ¹	%Breakthrough ²		Paired Trap Agreement ⁴	%Spike Recovery ³		
			Trap A	Trap B		Trap A	Trap B	
1	06/12/2019 07:58	PASS	0.0%	0.0%	0.013 (µg/dscm)	n/a	n/a	
2	06/12/2019 08:42	PASS	0.0%	0.0%	0.011 (µg/dscm)	n/a	n/a	
3	06/12/2019 09:27	PASS	0.0%	0.0%	0.037 (µg/dscm)	n/a	n/a	
4	06/12/2019 10:12	PASS	0.0%	0.0%	0.018 (µg/dscm)	98.0%	*	n/a
5	06/12/2019 10:59	PASS	0.0%	0.0%	0.024 (µg/dscm)	97.2%	*	n/a
6	06/12/2019 11:46	PASS	0.0%	0.0%	0.004 (µg/dscm)	99.5%	*	n/a
7	06/12/2019 12:32	PASS	0.0%	0.0%	0.020 (µg/dscm)	n/a		n/a
8	06/12/2019 13:17	PASS	0.0%	0.0%	0.018 (µg/dscm)	n/a		n/a
9	06/12/2019 14:04	PASS	0.0%	0.0%	0.025 (µg/dscm)	n/a		n/a
10	06/12/2019 14:48	PASS	0.0%	0.0%	0.029 (µg/dscm)	n/a		n/a
						98.2%		
						PASS		

¹ "PASS" indicates the sample run is valid and all required QA/QC specifications were met, including QA/QC criteria not shown in this table.

² Maximum sorbent breakthrough criteria: ≤ 10% of section 1 Hg mass for Hg concentrations > 1 µg/dscm; ≤ 20% of section 1 Hg mass for Hg concentrations ≤ 1 µg/dscm and > 0.5 µg/dscm; ≤ 50% of section 1 Hg mass for Hg concentrations ≤ 0.5 µg/dscm and > 0.1 µg/dscm; no breakthrough criteria for Hg concentrations below 0.1 µg/dscm.

³ Spike Recovery criteria: Average of 3 or more runs, 85% - 115%

⁴ Paired trap agreement maximum %RD criteria: ≤ 10% RD for Hg concentrations > 1 µg/dscm; ≤ 20% RD or ≤ 0.2 µg/dscm absolute difference for Hg concentrations ≤ 1 µg/dscm.

**Table 2-3:
 Summary of RM 30B QA/QC Results – Unit 3 STMS (Probe 1) - Continued**

		QA/QC and Performance								
Run No.	Start Date/Time (EST)	Valid? ¹	Spike Recovery Study - Volume % Diff ⁵		Spike Recovery Study - Volume (dscm)		Pre-Test Leak Check		Post-Test Leak Check	
			Trap A	Trap B	Trap A	Trap B	Trap A	Trap B	Trap A	Trap B
1	06/12/2019 07:58	PASS	0.0%	-0.2%	0.034229	0.034266	PASS		PASS	
2	06/12/2019 08:42	PASS	0.0%	-0.1%	0.034224	0.034263	PASS		PASS	
3	06/12/2019 09:27	PASS	0.0%	-0.1%	0.034222	0.034265	PASS		PASS	
4	06/12/2019 10:12	PASS	n/a	-0.1%	0.034216	0.034261	PASS		PASS	
5	06/12/2019 10:59	PASS	n/a	-0.1%	0.034217	0.034264	PASS		PASS	
6	06/12/2019 11:46	PASS	n/a	-0.1%	0.03421	0.034258	PASS		PASS	
7	06/12/2019 12:32	PASS	0.0%	-0.1%	0.034206	0.034253	PASS		PASS	
8	06/12/2019 13:17	PASS	0.0%	-0.1%	0.03421	0.03426	PASS		PASS	
9	06/12/2019 14:04	PASS	0.0%	-0.1%	0.034208	0.034254	PASS		PASS	
10	06/12/2019 14:48	PASS	0.0%	-0.1%	0.0342	0.034252	PASS		PASS	
Average					0.03421					

⁵ Individual trap sample volumes must within +/- 20% of the average sample volume measured during the spike recovery study.

3. DESCRIPTION OF INSTALLATION

PROCESS DESCRIPTION

The DTE Energy (DTE) owns and operates the River Rouge Power Plant located in River Rouge, Michigan. The station operates one (1) coal-fired unit, identified as Unit 3. The RATA testing outlined in this report was performed on Unit 3 only.

Unit 3, commissioned in 1958, is a dry-bottom wall-fired boiler connected to a 300-megawatt turbine. The sorbent trap probe is installed at the monitoring platform of the Unit 3 stack. Sample gas is transported through an extended heated sample line to an environmentally controlled shelter on the roof of the facility where the auto sampler cabinet is located. The reference method sampling was performed using an available EPA sampling port located on the same stack elevation as the STMS monitoring location.

STMS DESCRIPTION

The STMS consists of a Clean Air Engineering MET-80 dual-probe sorbent trap monitoring system (Model: MET-80XR2). The system has the provision for monitoring using two independent sample probes (i.e. Probe 1 and Probe 2). Current operation includes the certification and compliance monitoring using one probe only (i.e. Probe 1).

Aside from the sorbent traps, the MET-80 system consists of five major hardware components; sorbent trap probe with an integrated heated sample line (HSL) attached to a stack junction box (SJB), a single extended heated sample line containing teflon pathways for transport of sample gas, an automated gas sampler, and a logic control system.

Two independent sorbent traps are located in-situ in the flue gas with separate gas paths and volume measurement that result in a time-integrated mercury measurement. Mercury is captured on the sorbent traps and the sample gas passes through an extended heated sample line and through a gas conditioner where the moisture is removed. After the gas conditioning module, the sample gas paths pass through a scrubber material for collection or residual moisture and acid gases. The sample gas then enters the gas sampling module where the sample volume of each path A and B is measured using thermal mass flow meter technology.

The gas sampling module contains two mass flow meters per pathway (High and Low range). The dual range meters allow for a wide sample flow rate range (nominally 50 cc/min to 2000 cc/min). Sample gas flows through only one mass flow meter per side (A or B) depending on the target flow that is selected by the user and required for proportional sampling.

EPA Performance Specification 12B requires that a sample gas be withdrawn proportionally to changes in the flue gas flow rate. The MET-80 system uses a programmable automation controller (PAC) and a plant-supplied stack flow signal provided through Modbus to adjust the sampling rate set-point. The controller continuously adjusts the control valves in the GSM to maintain the sample flow rate.

TEST LOCATION

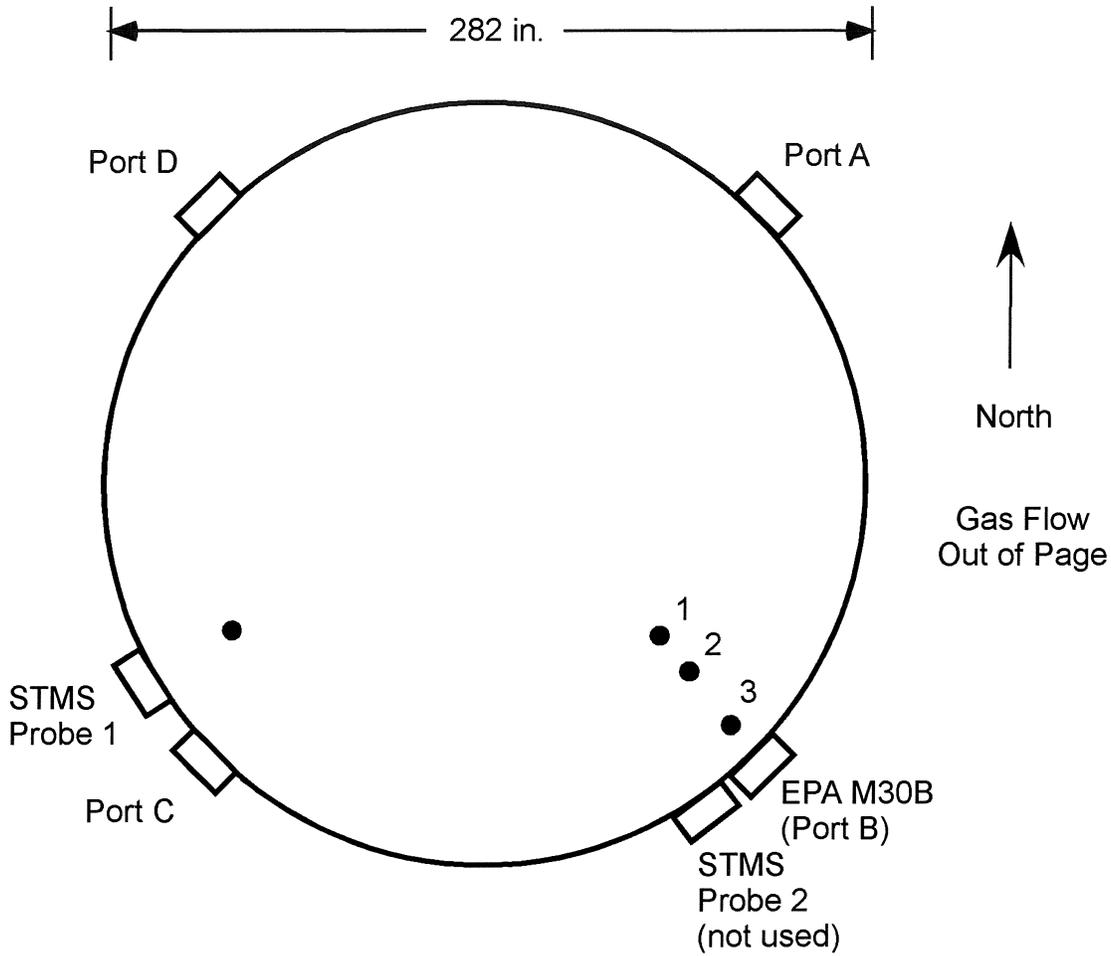
Based on facility Hg process monitor data just prior to the RATA and EPA M30B RA Runs 1 and 2, the mercury concentration was below 3 µg/dscm at the time of the RATA, therefore the sampling location was exempt from stratification testing (EPA M30B, Section 8.1.3.4). Reference method sampling was performed at three sample points located at 0.4, 1.2 and 2.0 meters from the stack wall in accordance with EPA M30B, Section 8.1.3.2.2.

Table 3-1 outlines the sampling point configurations. Figure 3-1 illustrates the sampling points and orientation of sampling ports for the test program.

**Table 3-1:
 Sampling Information**

<i>Source</i> Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes
<i>Unit 3 Stack, Probe 1</i> Vapor Phase Hg	EPA M30B	1-10	1	3	10	30

**Figure 3-1:
 Unit 3 Stack Sample Point Layout (EPA Method 30A, Section 8.1.3.4 and 8.1.3.2.2)**



Sampling Point	Port to Point Distance (inches)
1	78.7
2	47.2
3	15.7

4. METHODOLOGY

PROCEDURES AND REGULATIONS

The test program sampling measurements followed procedures and regulations outlined by the USEPA and Michigan Department of Environment, Great Lakes and Energy (EGLE). These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix. In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

TITLE 40 CFR PART 60, APPENDIX A

Method 30B "Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps"

TITLE 40 CFR PART 60, APPENDIX B PERFORMANCE SPECIFICATIONS

PS2 "Specifications and Test Procedures for SO₂ and NO_x Continuous Emission Monitoring Systems in Stationary Sources"

PS12A "Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Monitoring Systems in Stationary Sources"

PS12B "Specifications and Test Procedures for Monitoring Total Vapor Phase Mercury Continuous Monitoring Systems in Stationary Sources Using a Sorbent Trap Monitoring System"

TITLE 40 CFR PART 63, APPENDIX A

Section 4 "Certification and Recertification Requirements"

METHODOLOGY DISCUSSION

INTRODUCTION

Mercury measurements were made using sorbent trap technology and EPA Reference Method 30B (EPA 30B) procedures. The following sections highlight the procedures to be used.

Complete procedures and requirements of EPA 30B are found at <http://www.epa.gov/ttn/emc/promgate/Meth30B.pdf>.

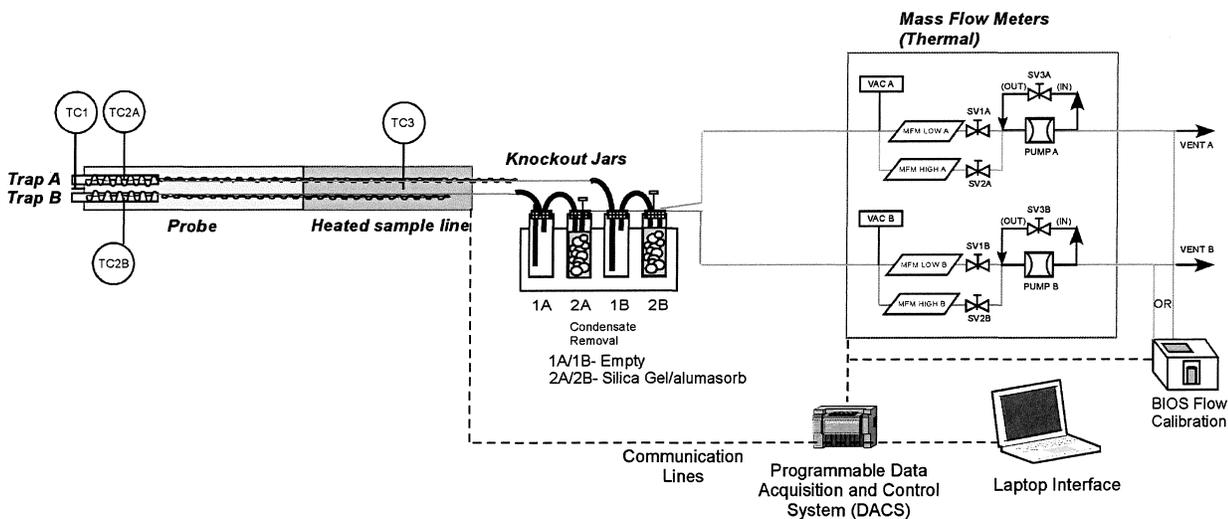
EPA Method 30B sampling procedures use two (or three) section sorbent traps containing an iodated activated charcoal sorbent. Sorbent traps were manufactured and supplied by Ohio Lumex Company located in Solon, Ohio. Known volumes of flue gas were extracted and passed through the sorbent traps for capture of total vapor phase mercury (oxidized and elemental). Sampling was performed using simultaneous, collocated, paired automated sampling systems as per EPA 30B specifications.

The following sections provide additional details for the sampling equipment, sampling procedures and QA/QC tests performed.

REFERENCE METHOD SAMPLING SYSTEM

Figure 4-1 contains a diagram of the sampling system used for EPA RM 30B sampling.

**Figure 4-1:
 EPA Method 30B Sampling System**



System Overview

The sorbent trap sampling system conforms to EPA Method 30B specifications. The system included two independent sample paths (identified as A and B). Sample gas enters a single stainless steel or hastelloy sample probe containing the two sorbent traps collocated in-situ to the flue gas. After passing through the traps, sample gas passes through a heated umbilical line, moisture removal components including an ice-bath condenser train and drierite scrubber, and an air-tight sample pump and a mass flow meter.

All system sensors, control and function are managed by an automated data acquisition and control system that uses a programmable automated controller. One-minute data averages were recorded for each sample run to a text file located on flash memory on the controller.

The sampling is a batch process. Using the dry gas sample volume measured by the sampling system and the results of the sorbent trap laboratory analyses, the average Hg concentration in the stack gas was determined on a dry basis.

Sorbent Traps

EPA 30B, Section 6.1.1, includes the specification for mercury sampling using sorbent traps that contain at least two sections and are capable of capturing gaseous total vapor phase mercury. The sorbent traps used to collect total vapor phase mercury typically contain activated charcoal that has been impregnated with a halogen such as iodine. Each sorbent trap section including applicable sorbent material is identified in Table 4-1. Each section is separated by quartz wool.

Table 4-1:
EPA Method 30B Sorbent Trap Construction

Section	Material	Description
1	Iodinated Activated Carbon (1)	Primary capture of total vapor phase mercury ($Hg^0 + Hg^{+2}$). Contains mercury spike for applicable QA/QC sample runs.
2	Iodinated Activated Carbon (2)	Secondary capture of elemental mercury (Hg^0). Results used to determine Section 1 breakthrough.

Sample Probe and Flexible Sample Line

EPA 30B, Section 6.1.2, includes the specification for the sampling probe assembly. The sorbent trap probe consists of a 316 stainless steel or hastelloy sheath covering a pair of thermally controlled trap retaining devices and a separately controlled heated sample line containing dual PTFE tubes. The design accommodates the 30B requirement for collocated sorbent traps. This system is also designed for easy and rapid exchange of the traps between sampling periods.

Moisture Removal – Gas Conditioning Module

Moisture collection was performed using a condenser train system. The system employs a set of four (4) knockout jars chilled in an ice bath.

Gas Sampling Module – Mass Flow Meters

After conditioning, the gas sample volume was measured in the gas sampling module. The module contains two independent gas paths, with each path containing a sampling pump (PTFE-coated diaphragm), two thermal mass flow meters and flow control solenoid valves.

Each flow meter has an independent solenoid valve for control of sample flow rate during sampling. Sampling is performed at a constant sampling rate during the test period (+/- 10%). A third solenoid control valve is used to adjust the system vacuum during leak checks.

Programmable Automated Control System/User Interface

System operation is managed by a programmable automated controller (PAC). The flow control system keeps sampling at the set target flow rate (+/-10%). The set-point is based on collecting an appropriate amount of mercury on the sorbent traps. The controller continuously adjusts the control valves in the gas sampling system to maintain the sample flow rate at the set-point.

The controller also records data in one-minute averages to an electronic data file that is saved to the PAC memory.

SAMPLING PROCEDURES

RM 30B operational details are shown in Table 4-2.

**Table 4-2:
 Summary of EPA 30B Operational Parameters**

Method	40 CFR Part 60, Appendix A, Method 30B
Analyte Measured by Reference Method	Total vapor-phase mercury ($Hg^0 + Hg^{+2}$)
Number of Valid RM Runs	9 minimum
Length of RM Runs	30 minutes
Reference Method Traverse Points	Three (3) points located at 0.4, 1.2 and 2.0 meters from the stack wall
Reference Method Time per Point	10 minutes
Reference Method Sampling Rate	1150 cc/min
Number of RM Samples per Run	Two (paired, co-located samples), identified as samples A and B
Sorbent Trap Manufacturer	Ohio Lumex
Number of Sections in Sorbent Trap	2
Sorbent Material	Iodinated, activated charcoal, petroleum based
Sorbent Quantity	500 mg per section (approximate)
Sorbent Trap Tube Material	Glass
Spiked Section in Sorbent Trap	First section of traps
Spike Level	30 ng
Probe and Sample Line Material	PTFE
Probe Temperature Control	PID
Sample Line Temperature Control	PID
Gas Dryer Device	Condenser train knockout jars in ice bath
Temperature of Gas Dryer Device	~68°F
Analytical Method	Thermal Desorption / Zeeman atomic absorption spectrometry using high frequency modulation of light polarization
Analytical Instrument	Ohio Lumex RA-915+ with RP-M324 detector
Minimum Analytical Detection Limit	0.50 ng (nominal)
Calibration Range	5 – 300 ng
Method Validation Range (Based on Bias Tests)	5 – 4000 ng

CALIBRATION AND QA/QC REQUIREMENTS

QA/QC specifications for EPA Method 30B are summarized in Table 9-1 of the method. Results of system calibration and QA/QC performance are included in Appendix D.