



Marathon Petroleum Company
1300 South Fort Street
Detroit, MI 48217

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REPORT ON RATA TESTING

Performed for:
MARATHON PETROLEUM COMPANY
DETROIT REFINERY

DHT NEW HEATER STACK (SV77-H1)

Client Reference No: CN00081321
CleanAir Project No: 12384-1
Revision 0: January 3, 2014

To the best of our knowledge, the data presented in this report are accurate, complete, error free, legible and representative of the actual emissions during the test program. Clean Air Engineering operates in conformance with the requirements of ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies.

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REVISION HISTORY

REPORT ON RATA TESTING

DRAFT REPORT REVISION HISTORY

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PROJECT OVERVIEW

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INTRODUCTION

Marathon Petroleum Company (MPC) contracted Clean Air Engineering (CleanAir) to perform a relative accuracy test audit (RATA) on a continuous emissions monitoring system (CEMS) installed at the Detroit Refinery and to demonstrate compliance with permit limits.

All testing was conducted in accordance with the regulations set-forth by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environmental Quality (DEQ). The permit limits are referenced in Michigan Department of Environmental Quality, Air Quality Division Permit to Install No. 63-08C, issued January 11, 2012.

Key Project Participants

Individuals responsible for coordinating and conducting the test program were:

Crystal Davis – MPC
Joe Reidy – MPC
Thomas Gasloli – DEQ
John Rooney– CleanAir

Test Program Parameters

The testing was performed at the DHT New Heater Stack (Emission Unit ID No. EG77-DHTHTR; Stack ID No. SV77-H1) on November 5, 2013 and included the following emissions measurements:

- nitrogen oxides (NO_x)
- oxygen (O₂)

PROJECT OVERVIEW

1-2

TEST PROGRAM SYNOPSIS**Test Schedule**

The on-site schedule followed during the test program is outlined in Table 1-1.

**Table 1-1:
Schedule of Activities**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	12:06	12:27
2	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	12:35	12:56
3	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	13:02	13:23
4	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	13:30	13:51
5	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	13:57	14:18
6	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	14:28	14:49
7	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	14:58	15:19
8	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	15:28	15:49
9	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	15:55	16:16
10	DHT New Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	11/05/13	16:22	16:43

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PROJECT OVERVIEW

1-3

Results Summary

Table 1-2 and Table 1-3 summarize the results of the test program. A more detailed presentation of the test conditions and results of analysis are shown on pages 2-1 through 2-3.

**Table 1-2:
Summary of RATA Results**

<u>Source</u> Constituent (Units)	Reference Method (USEPA)	Applicable Specification	Relative Accuracy (%)	Specification Limit ¹
<u>DHT New Heater Stack</u>				
O ₂ (% dv)	M-3A	PS3	0.13	±1.0% dv
NO _x (ppmdv)	M-7E	PS2	4.3%	20% of RM or

¹ Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

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**Table 1-3:
Summary of Emission Compliance Test Results**

<u>Source</u> Constituent (Units)	Sampling Method	Average Emission	Permit Limit ¹
<u>DHT New Heater Stack</u>			
NO _x (lb/MMBtu)	USEPA M-7E	0.03	0.05

¹ Permit limits obtained from MDEQ Permit To Install No. 63-08C.

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PROJECT OVERVIEW

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Discussion of Test Program***O₂ and NO_x Emissions / RATA Testing - USEPA Methods 3A and 7E;
Performance Specifications 2 and 3***

Minute-average data points for O₂, CO₂, and NO_x (dry basis) were collected over a period of 21 minutes for each RATA Reference Method (RM) run. The average result for each RM run was calculated and compared to the average result from the facility CEMs over an identical time interval in order to calculate relative accuracy (RA).

- For O₂, RA is expressed as the average absolute difference between the RM and facility CEMs runs. The final result was below the limit of $\pm 1.0\%$ dv set by PS3.
- For NO_x, RA is expressed as the percent difference between RM and facility CEMs runs. The final result was below the limit of 20% of the RM set by PS2.
- CO₂ data was collected only as supplemental information.

NO_x results from the RATA were converted from units of dry volume-based concentration (ppmdv) to mass-based emission rate units (lb/MMBtu) to demonstrate compliance with permit limits. The final result was expressed as the average of all ten (10) RATA runs. The final result was below the permit limit.

Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted to units of pounds per million Btu (lb/MMBtu) by calculating an oxygen-based fuel factor (F_d) for refinery gas per USEPA Method 19 specifications. The heat content and F_d factor were calculated from percent volume composition analytical data provided by MPC and tabulated heating values for the measured constituent.

End of Section 1 – Project Overview

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RESULTS

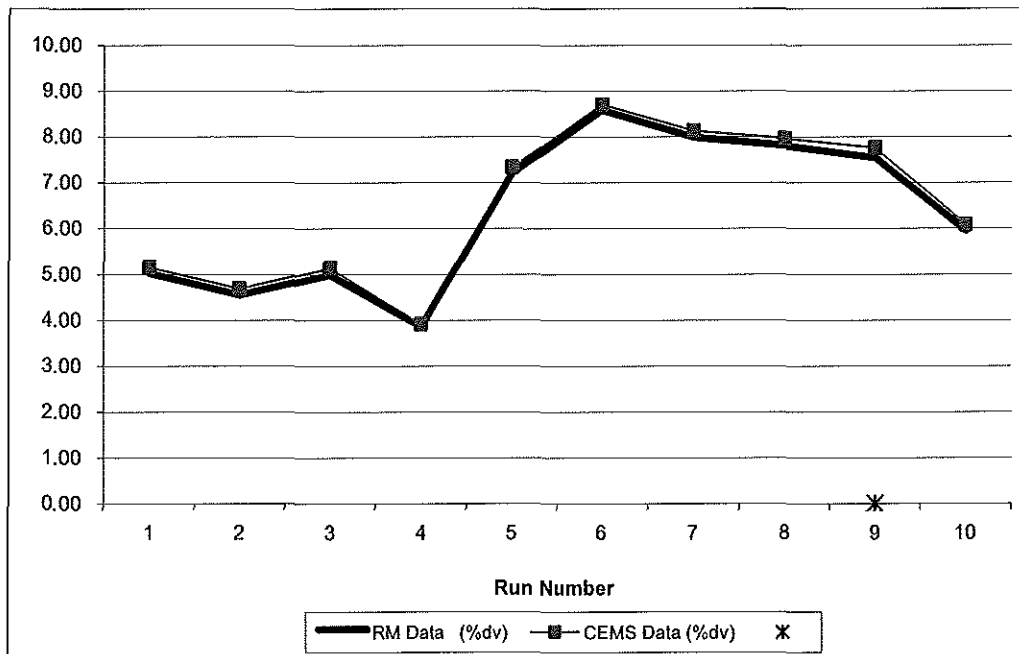
**Table 2-1:
DHT New Heater Stack – O₂ Relative Accuracy (USEPA M-3A / PS3)**

Run No.	Start Time	Date (2013)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)
1	12:06	Nov 5	5.03	5.15	-0.12
2	12:35	Nov 5	4.55	4.69	-0.14
3	13:02	Nov 5	4.98	5.13	-0.15
4	13:30	Nov 5	3.85	3.91	-0.06
5	13:57	Nov 5	7.21	7.33	-0.12
6	14:28	Nov 5	8.58	8.70	-0.13
7	14:58	Nov 5	7.98	8.13	-0.15
8	15:28	Nov 5	7.80	7.96	-0.16
9 *	15:55	Nov 5	7.54	7.76	-0.22
10	16:22	Nov 5	5.95	6.08	-0.12
Average			6.21	6.34	-0.13

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.027	
Confidence Coefficient (CC)	0.021	
t-Value for 9 Data Sets	2.306	
Avg. Abs. Diff. (%dv)	0.13	Limit 1.0

RM = Reference Method (CleanAir Data) 121613 162728
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
 RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



RESULTS

**Table 2-2:
DHT New Heater Stack – NO_x Relative Accuracy (USEPA M-7E / PS2)**

Run No.	Start Time	Date (2013)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	12:06	Nov 5	19.40	18.71	0.69	3.5%
2	12:35	Nov 5	19.06	18.36	0.70	3.7%
3	13:02	Nov 5	19.37	18.60	0.77	4.0%
4	13:30	Nov 5	17.31	16.72	0.59	3.4%
5	13:57	Nov 5	22.75	21.89	0.86	3.8%
6	14:28	Nov 5	24.03	23.14	0.89	3.7%
7	14:58	Nov 5	24.38	23.45	0.93	3.8%
8	15:28	Nov 5	24.48	23.50	0.98	4.0%
9	15:55	Nov 5	24.69	23.64	1.04	4.2%
10 *	16:22	Nov 5	23.44	22.43	1.01	4.3%
Average			21.72	20.89	0.83	3.8%

Relative Accuracy Test Audit Results

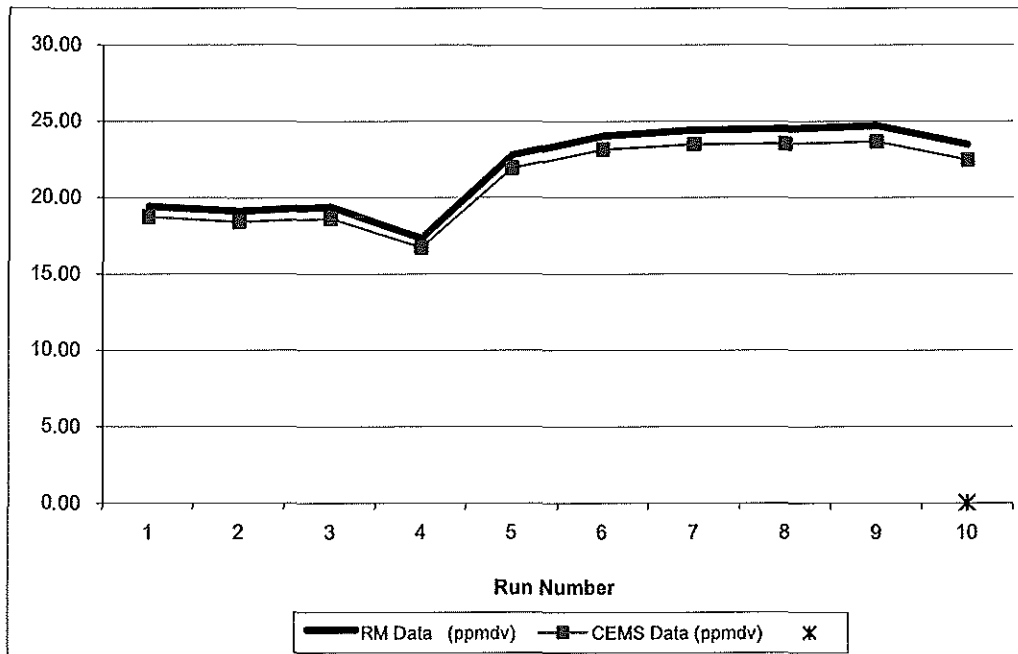
Standard Deviation of Differences	0.150	
Confidence Coefficient (CC)	0.116	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	4.3%	Limit 20.0%

RM = Reference Method (CleanAir Data)

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CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



RESULTS**Table 2-3:
DHT New Heater Stack – NO_x Emissions (USEPA M-7E)**

Run No.		1	2	3	4	5	6
Date (2013)		Nov 5	Nov 5	Nov 5	Nov 5	Nov 5	Nov 5
Start Time (approx.)		12:06	12:35	13:02	13:30	13:57	14:28
Stop Time (approx.)		12:27	12:56	13:23	13:51	14:18	14:49
Process Conditions							
P ₁	Fuel gas flow rate (Mscf/day)	900	889	846	1,126	1,364	1,390
F _d	Oxygen-based F-factor (dscf/MMBtu)	7,666	7,666	7,666	7,666	7,666	7,666
H _i	Actual heat input (MMBtu/hr)	26	26	24	32	39	40
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760	8,760
Gas Conditions							
O ₂	Oxygen (dry volume %)	5.0	4.5	5.0	3.8	7.2	8.6
CO ₂	Carbon dioxide (dry volume %)	7.1	7.6	7.6	8.1	6.3	5.2
Nitrogen Oxides Results							
C _{sd}	Concentration (ppmdv)	19.4	19.1	19.4	17.3	22.7	24.0
C _{sd}	Concentration (lb/dscf)	2.32E-06	2.28E-06	2.31E-06	2.07E-06	2.72E-06	2.87E-06
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0234	0.0223	0.0233	0.0194	0.0318	0.0373

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**Table 2-3 (Continued):
DHT New Heater Stack – NO_x Emissions (USEPA M-7E)**

Run No.		7	8	9	10	Average
Date (2013)		Nov 5	Nov 5	Nov 5	Nov 5	
Start Time (approx.)		14:58	15:28	15:55	16:22	
Stop Time (approx.)		15:19	15:49	16:16	16:43	
Process Conditions						
P ₁	Fuel gas flow rate (Mscf/day)	1,516	1,581	1,571	1,512	1,269
F _d	Oxygen-based F-factor (dscf/MMBtu)	7,666	7,666	7,666	7,666	7,666
H _i	Actual heat input (MMBtu/hr)	44	45	45	43	36
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760
Gas Conditions						
O ₂	Oxygen (dry volume %)	8.0	7.8	7.5	6.0	6.3
CO ₂	Carbon dioxide (dry volume %)	5.3	5.1	5.4	6.2	6.4
Nitrogen Oxides Results						
C _{sd}	Concentration (ppmdv)	24.4	24.5	24.7	23.4	21.9
C _{sd}	Concentration (lb/dscf)	2.91E-06	2.92E-06	2.95E-06	2.80E-06	2.61E-06
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0361	0.0358	0.0353	0.0300	0.0295

Average includes 10 runs.

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End of Section 2 – Results

MARATHON PETROLEUM COMPANY
DETROIT REFINERY

Client Reference No: CN00081321
CleanAir Project No: 12384-1

3-1

DESCRIPTION OF INSTALLATION

PROCESS DESCRIPTION

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. As part of the Detroit Heavy Oil Upgrade Project (DHOUP), new equipment is being installed to process heavy crude oil from Canada. As a condition of proceeding with the DHOUP, MPC must demonstrate that select process units are in compliance with permitted emission limits.

The Distillate Hydrotreater Unit (EG77-DHHTREAT) reacts sour distillate (and occasionally gas oil) streams with hydrogen over a catalyst bed to removed sulfur. The DHT unit consists of process vessels (reactors, distillation tower absorbing towers, stripper tower), heater (EG77-DHTHTR), cooling tower, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The DHT New Heater is fired by refinery fuel gas. Emissions are vented to the atmosphere via the DHT New Heater Stack (SV77-H1).

The testing reported in this document was performed at the DHT New Heater Stack.

DESCRIPTION OF SAMPLING LOCATIONS

Sampling point locations were determined according to Performance Specification 2.

Table 3-1 outlines the sampling point configurations. The figure shown on the following page illustrates the sampling points and orientation of sampling ports.

Table 3-1:
Sampling Points

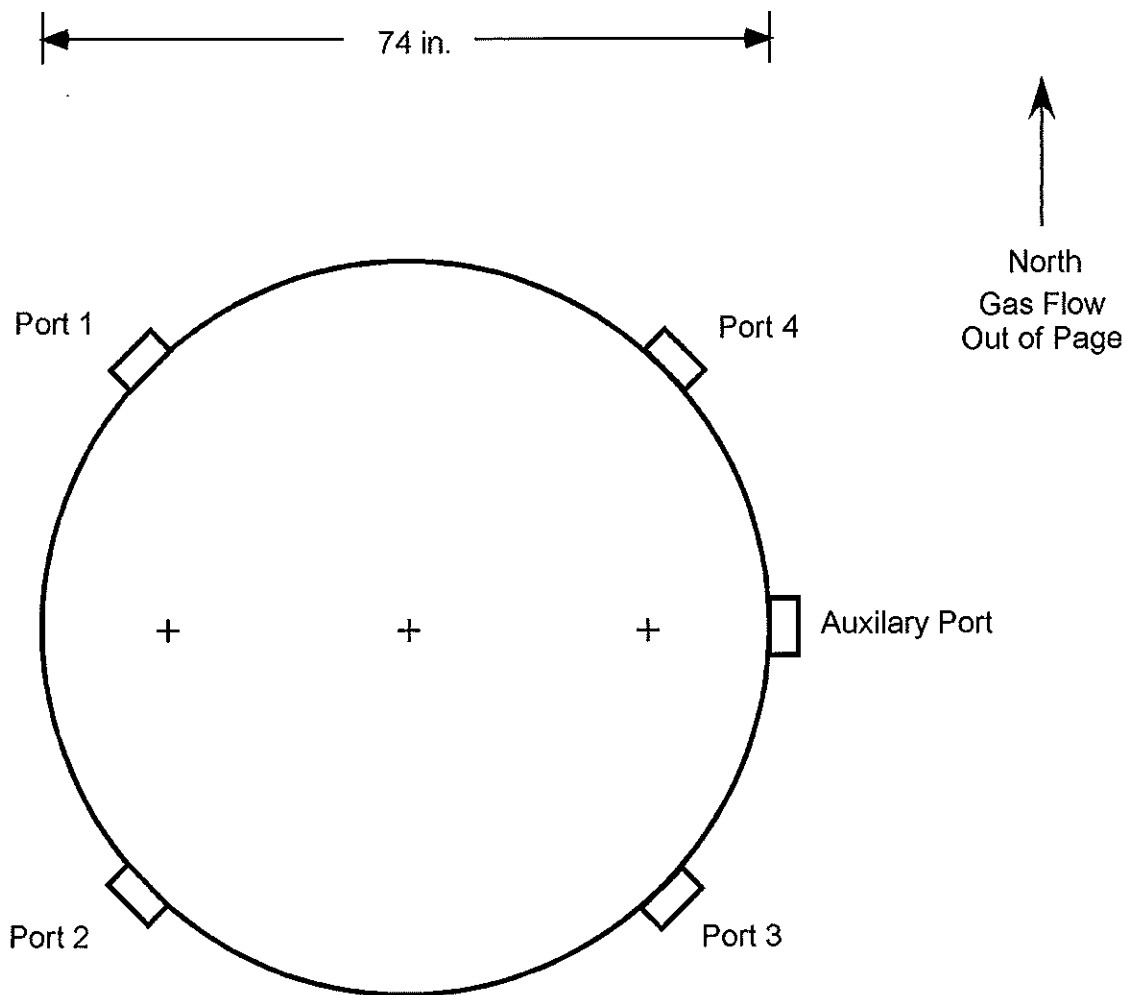
Source Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
DHT New Heater Stack O ₂ /NO _x (RATAs)	M-3A+PS3 / 7E+PS2	1-10	1	3	7	21	3-1

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DESCRIPTION OF INSTALLATION

3-2



<u>Sampling Point</u>	<u>Port to Point Distance (in.)</u>
1	61.7
2	37.0
3	12.3

Duct diameters upstream from flow disturbance (A):	7.0	Limit: 0.5
Duct diameters downstream from flow disturbance (B):	25.0	Limit: 2.0

Figure 3-1: USEPA Method 3A/7E Sampling Points – RATA and Emissions Testing

End of Section 3 – Description of Installation

METHODOLOGY

4-1

Clean Air Engineering followed procedures as detailed in USEPA Methods 3A, 7E, 19, and Performance Specifications 2 and 3. The following table summarizes the methods and their respective sources.

**Table 4-1:
Summary of Sampling Procedures**

<u>Title 40 CFR Part 60 Appendix A</u>	
Method 3A	"Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 7E	"Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates"
<u>Title 40 CFR Part 60 Appendix B (Performance Specifications (PS))</u>	
PS2	"Specifications and Test Procedures for SO ₂ and NO _x Continuous Emission Monitoring Systems in Stationary Sources"
PS3	"Specifications and Test Procedures for O ₂ and CO ₂ Continuous Emission Monitoring Systems in Stationary Sources"

These methods appear in detail in Title 40 of the Code of Federal Regulations (CFR) and are located on the internet at <http://ecfr.gpoaccess.gov>.

Diagrams of the sampling apparatus and major specifications of the sampling, recovery and analytical procedures are summarized for each method in Appendix A.

CleanAir followed specific quality assurance and quality control (QA/QC) procedures as outlined in the individual methods and as prescribed in CleanAir's internal Quality Manual. Results of all QA/QC activities performed by CleanAir are summarized in Appendix D.

METHODOLOGY

4-2

O₂, CO₂, and NO_x, Emissions / RATA Testing - USEPA Methods 3A and 7E; Performance Specifications 2 and 3

Reference method O₂ and CO₂ emissions were determined using a paramagnetic/NDIR CEMs analyzer per EPA Method 3A and Performance Specification 3. Reference method NO_x emissions were determined using a chemiluminescent CEMs analyzer per EPA Method 7E and Performance Specification 2.

The sampling system consisted of a heated probe, heated filter, and heated sample line. Flue gas was extracted at a constant rate at the points specified performance specification and delivered at 250°F to a gas conditioner which removed moisture. The flue gas was then delivered via a flow panel to an analyzer bank. Each analyzer measured concentration on a dry basis (units of %dv or ppm_{dv}).

Calibration error checks were performed by introducing zero nitrogen (N₂), high-range and mid-range calibration gases to the inlet of each analyzer during calibration error checks. Bias checks were performed before and after each sampling run by introducing calibration gas to the inlet of the sampling system's heated filter. Per M-3A and 7E, the average results for each run were drift-corrected. Documentation of interference checks and NO₂ converter efficiency checks are included in Appendix D.

End of Section 4 – Methodology