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REPORT ON COMPLIANCE &
RATA TESTING

Detroit Refinery
GOHT Heater Stack

Marathon Petroleum Company LP
1300 South Fort Street
Detroit, MI 48217
Client Reference No. 4101004604

CleanAir Project No. 13313
STAC Certificate No. 2007.002.0113.1217
Revision 0, Final Report
August 28, 2017

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1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing at the GOHT Heater (EU08-GOHTCHARHTR-S1) at the Detroit Refinery located in Detroit, Michigan. The test program included the following objectives:

- Perform particulate matter (PM), volatile organic compounds (VOCs) and sulfuric acid (H₂SO₄) testing to demonstrate compliance with the Michigan Department of Environmental Quality (DEQ) Permit No. MI-ROP-A9831-2012c.
- Perform a relative accuracy test audit (RATA) on the facility's continuous emissions monitoring system (CEMS) for oxygen (O₂) and nitrogen oxides (NO_x).

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis. Test program information, including the test parameters, on-site schedule and a project discussion, begins on page 2.

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

Source Constituent	Sampling Method	Average Emission	Permit Limit ¹
<u>GOHT Heater Stack</u>			
PM ₁₀ (lb/MMBtu)	USEPA 5 / 202	0.0028	0.0076
H ₂ SO ₄ (lb/MMBtu)	ASTM Draft CCM	0.0002	N/A
VOC (lb/MMBtu)	USEPA 18 / 25A	< 0.0007	0.0055

¹ Permit limits obtained from MDEQ Renewable Operation Permit No. MI-ROP-A9831-2012c.

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

Source Constituent (Units)	Reference Method	Relative Accuracy (%) ¹	Applicable Specification	Specification Limit ²
<u>GOHT Heater Stack</u>				
O ₂ (% dv)	USEPA 3A	0.17	PS3	±1.0% of RM
NO _x (lb/MMBtu)	USEPA 7E / 3A / 19	12.2	PS2	20% of RM

¹ Relative Accuracy is expressed in terms of comparison to the reference method (% RM).

² Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

Test Program Details

Parameters

The test program included the following emissions measurements:

- total particulate matter less than 10 microns in diameter (PM₁₀), assumed equivalent to the sum of the following constituents:
 - filterable particulate matter (FPM)
 - condensable particulate matter (CPM)
- nitrogen oxides (NO_x)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents
 - methane (CH₄)
 - ethane (C₂H₆)
- sulfuric acid mist (H₂SO₄)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed on July 25 and 26, 2017. The on-site schedule followed during the test program is outlined in Table 1-3.

**Table 1-3:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	GOHT Heater Stack	USEPA Method 5/202	FPM/CPM	07/25/17	08:45	10:58
2	GOHT Heater Stack	USEPA Method 5/202	FPM/CPM	07/25/17	11:32	13:43
3	GOHT Heater Stack	USEPA Method 5/202	FPM/CPM	07/25/17	14:31	16:47
1	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	09:21	09:42
2	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	09:59	10:20
3	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	10:32	10:53
4	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	11:10	11:31
5	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	11:47	12:08
6	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	12:19	12:40
7	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	13:13	13:34
8	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	13:47	14:08
9	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	14:20	14:41
10	GOHT Heater Stack	USEPA Method 3A/7E	O ₂ /CO ₂ /NO _x	07/25/17	15:08	15:29
1	GOHT Heater Stack	USEPA Method 25A/18	VOC	07/25/17	09:21	10:53
2	GOHT Heater Stack	USEPA Method 25A/18	VOC	07/25/17	11:10	12:40
3	GOHT Heater Stack	USEPA Method 25A/18	VOC	07/25/17	13:13	14:41
0	GOHT Heater Stack	Draft ASTM CCM	Sulfuric Acid	07/26/17	08:12	09:12
1	GOHT Heater Stack	Draft ASTM CCM	Sulfuric Acid	07/26/17	10:00	11:00
2	GOHT Heater Stack	Draft ASTM CCM	Sulfuric Acid	07/26/17	11:52	12:52
3	GOHT Heater Stack	Draft ASTM CCM	Sulfuric Acid	07/26/17	13:30	14:30

Discussion

Test Scope Synopsis

FPM & PM₁₀ Testing

A total of three (3) 120-minute EPA Method 5/202 test runs were performed. FPM/CPM emission results were calculated in units of pounds per million Btu (lb/MMBtu). The final result was expressed as the average of the three (3) valid runs.

PM₁₀ is assumed equivalent to the sum of FPM less than 10 micrometers (μm) in diameter (FPM₁₀) and CPM. The Method 5/202 sample train yields a front-half, FPM result and a back-half, CPM result. The total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of total PM₁₀ since Method 5 collects all FPM present in the flue gas (regardless of particle size).

O₂ & NO_x RATA Testing

Minute-average data points for O₂ and NO_x (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A and 7E. Relative accuracy was determined based on nine (9) of ten (10) total runs conducted per procedures outlined in PS2, Section 8.4.4.

Sampling occurred at the three (3) points as specified in Section 8.1.3.2 of PS2 during each run. The average result for each run was converted to identical units of measurement as the facility CEMs and compared for relative accuracy.

VOC Testing

VOC emissions were determined using EPA Method 25A to quantify THC emissions and EPA Method 18 to quantify methane (CH₄) and ethane (C₂H₆) emissions. VOC emissions are assumed equivalent to THC emissions minus CH₄ and C₂H₆.

Nine (9) 21-minute Method 25A test runs were performed concurrently with three (3) 63-minute Method 18 bag collections (Method 25A Runs 1-3 were concurrent with Method 18 Run 1, etc.). The final result for each VOC run was expressed as the average of three (3) consecutive 21-minute runs. Other CEMS methods referencing Method 7E were performed simultaneously using the same sampling system. Data was collected from all of the required Method 7E points rather than from the centroid of the duct as specified by Method 25A.

THC, CH₄ and C₂H₆ emission results were calculated in units of lb/MMBtu as propane. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from averaging overlapping Method 5/202 runs.

For all VOC runs, the measured concentrations of THC were below the detection limit defined as 'less than 1%' of the calibration span of THC instrument. For all runs, CH₄ and C₂H₆ were below analytical detection limits. Assuming worst-case scenario, VOC emissions are reported as 'less than' the defined detection limit corrected to dry conditions.

H₂SO₄ Testing

H₂SO₄ emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM).

Three (3) 60-minute Draft ASTM CCM test runs were performed. H₂SO₄ emission results were calculated in units of lb/MMBtu. The final results were expressed as the average of three (3) valid runs.

Prior to the first official test run, a 60-minute sample conditioning run (Run 0) was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H₂SO₄-collecting portion of the sample train). The conditioning run was recovered in the same manner as the official test runs, but the condenser rinse and SAM filter were not analyzed.

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of pound per million BTU (lb/MMBtu) by calculating an oxygen-based fuel factor (F_d) for refinery gas per EPA Method 19 specifications. The F_d factor was calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents. One fuel sample was taken during the test program on July 25.

Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions compliance test runs and no less than 50% of the maximum normal operating capacity during RATA test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test reports.

End of Section

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

**Table 2-1:
 GOHT Heater Stack – PM₁₀ Emissions**

Run No.		1	2	3	Average
Date (2017)		Jul 25	Jul 25	Jul 25	
Start Time (approx.)		08:45	11:32	14:31	
Stop Time (approx.)		10:58	13:43	16:47	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	2,507	2,416	2,397	2,440
P ₂	Charge rate (bpd)	44,256	44,328	44,082	44,222
F _d	Oxygen-based F-factor (dscf/MMBtu)	7,768	7,768	7,768	7,768
H _i	Actual heat input (MMBtu/hr)	78.3	75.5	74.9	76.2
Gas Conditions					
O ₂	Oxygen (dry volume %)	6.8	7.3	7.4	7.2
CO ₂	Carbon dioxide (dry volume %)	6.8	6.9	6.7	6.8
T _s	Sample temperature (°F)	326	327	326	326
B _w	Actual water vapor in gas (% by volume)	15.9	15.4	15.4	15.6
Gas Flow Rate					
Q _a	Volumetric flow rate, actual (acfm)	29,200	29,100	28,500	28,900
Q _s	Volumetric flow rate, standard (scfm)	19,700	19,600	19,200	19,500
Q _{std}	Volumetric flow rate, dry standard (dscfm)	16,600	16,600	16,300	16,500
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	70.16	69.97	68.53	69.56
%I	Isokinetic sampling (%)	98.5	98.1	97.9	98.2
Laboratory Data					
m _{FPM}	Total FPM (g)	0.00295	0.00272	0.00237	
m _{CPM}	Total CPM (g)	0.00394	0.00701	0.00361	
m _{Part}	Total particulate matter (as PM ₁₀) (g)	0.00689	0.00973	0.00598	
FPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	9.27E-08	8.57E-08	7.63E-08	8.49E-08
E _{lbhr}	Particulate Rate (lb/hr)	0.0921	0.0853	0.0745	0.0840
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00107	0.00102	0.00092	0.00100
CPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	1.24E-07	2.21E-07	1.16E-07	1.54E-07
E _{lbhr}	Particulate Rate (lb/hr)	0.123	0.220	0.114	0.152
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00143	0.00264	0.00140	0.00182
Total Particulate Matter (as PM₁₀) Results					
C _{sd}	Particulate Concentration (lb/dscf)	2.16E-07	3.07E-07	1.93E-07	2.39E-07
E _{lbhr}	Particulate Rate (lb/hr)	0.215	0.305	0.188	0.236
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00249	0.00366	0.00232	0.00282

**Table 2-2:
 GOHT Heater Stack – O₂ (% dv) RATA**

Run No.	Start Time	Date (2017)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	09:21	Jul 25	6.80	7.01	-0.21	-3.1%
2	09:59	Jul 25	6.97	7.10	-0.13	-1.9%
3	10:32	Jul 25	7.06	7.24	-0.18	-2.5%
4	11:10	Jul 25	7.23	7.36	-0.13	-1.8%
5	11:47	Jul 25	7.31	7.44	-0.13	-1.8%
6	12:19	Jul 25	7.29	7.42	-0.13	-1.8%
7	13:13	Jul 25	7.31	7.48	-0.17	-2.3%
8	13:47	Jul 25	7.26	7.44	-0.18	-2.5%
9	14:20	Jul 25	7.07	7.35	-0.28	-4.0%
10 *	15:08	Jul 25	7.30	7.67	-0.37	-5.1%
Average			7.14	7.32	-0.17	-2.5%

Relative Accuracy Test Audit Results

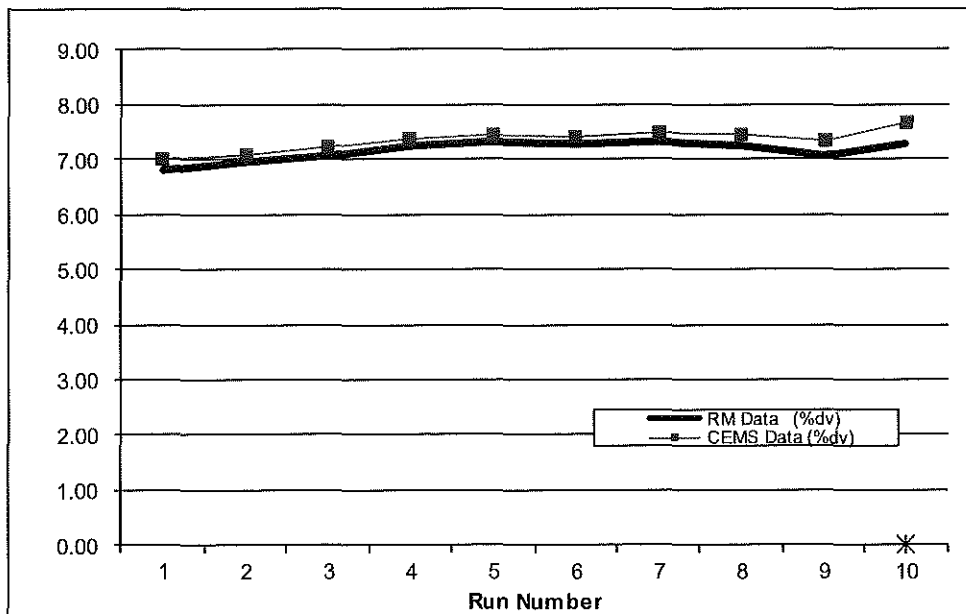
Standard Deviation of Differences	0.0504
Confidence Coefficient (CC)	0.0387
t-Value for 9 Data Sets	2.306
	Limit
Avg. Abs. Diff. (%dv)	0.17 1.0

RM = Reference Method (CleanAir Data)

082117 091645

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

RATA calculations are based on 9 of 12 runs. * indicates the excluded runs.



**Table 2-3:
 GOHT Heater Stack – NO_x (lb/MMBtu) RATA**

Run No.	Start Time	Date (2017)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	09:21	Jul 25	0.0386	0.0352	0.0034	8.8%
2	09:59	Jul 25	0.0398	0.0350	0.0048	12.1%
3	10:32	Jul 25	0.0402	0.0354	0.0048	11.9%
4	11:10	Jul 25	0.0413	0.0367	0.0046	11.1%
5	11:47	Jul 25	0.0417	0.0369	0.0048	11.5%
6	12:19	Jul 25	0.0413	0.0364	0.0049	11.9%
7 *	13:13	Jul 25	0.0422	0.0371	0.0051	12.1%
8	13:47	Jul 25	0.0409	0.0362	0.0047	11.5%
9	14:20	Jul 25	0.0395	0.0350	0.0045	11.4%
10	15:08	Jul 25	0.0416	0.0369	0.0047	11.3%
Average			0.0405	0.0360	0.0046	11.2%

Relative Accuracy Test Audit Results

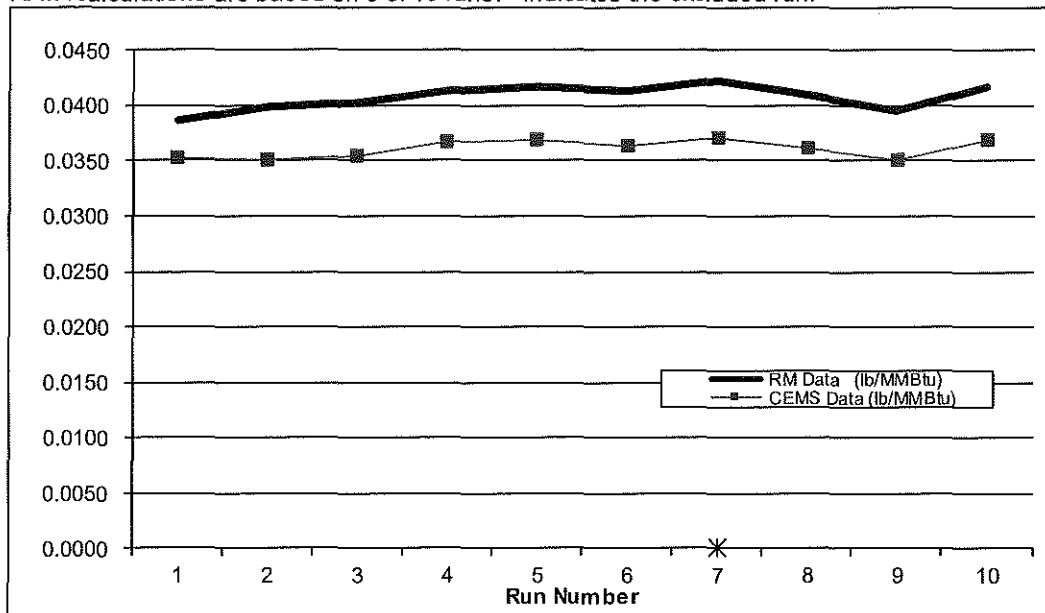
Standard Deviation of Differences	0.000458	
Confidence Coefficient (CC)	0.000352	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	12.2%	20.0%
Relative Accuracy (as % of Appl. Std.)	9.9%	10.0%
Appl. Std. = 0.05 lb/MMBtu		

RM = Reference Method (CleanAir Data)

082117 091645

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

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



**Table 2-4:
GOHT Heater Stack – VOCs Emissions**

Run No.		1	2	3	Average
Date (2017)		Jul 25	Jul 25	Jul 25	
Start Time (approx.)		09:21	11:10	13:13	
Stop Time (approx.)		10:53	12:40	14:41	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	2,490	2,465	2,379	2,445
P ₂	Charge rate (bpd)	44,262	44,213	44,275	44,250
F _d	Oxygen-based F-factor (dscf/MMBtu)	7,768	7,768	7,768	7,768
H _i	Actual heat input (MMBtu/hr)	77.8	77.0	74.3	76.4
Gas Conditions					
O ₂	Oxygen (dry volume %)	6.9	7.3	7.2	7.1
CO ₂	Carbon dioxide (dry volume %)	7.3	7.2	7.3	7.3
B _w	Actual water vapor in gas (% by volume) ¹	15.9	15.4	15.4	15.6
THC Results					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.541	<0.538	<0.538	<0.54
C _{sd}	Concentration (lb/dscf)	<6.19E-08	<6.16E-08	<6.16E-08	<6.17E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000720	< 0.000734	< 0.000730	< 0.000728
Methane Results					
C _{sd}	Concentration (ppmdv)	<0.50	<0.50	<0.50	<0.50
C _{sd}	Concentration (lb/dscf)	<2.1E-08	<2.1E-08	<2.1E-08	<2.1E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.00024	< 0.00025	< 0.00025	< 0.00025
Ethane Results					
C _{sd}	Concentration (ppmdv)	<0.37	<0.37	<0.37	<0.37
C _{sd}	Concentration (lb/dscf)	<2.9E-08	<2.9E-08	<2.9E-08	<2.9E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.00034	< 0.00034	< 0.00034	< 0.00034
VOC Results					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.538	<0.538	<0.538	<0.54
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000716	< 0.000734	< 0.000730	< 0.000727

¹ Moisture data used for ppmw v to ppmdv correction obtained from an average of overlapping M5/202 runs.

**Table 2-5:
GOHT Heater Stack – H₂SO₄ Emissions**

Run No.		1	2	3	Average
Date (2017)		Jul 26	Jul 26	Jul 26	
Start Time (approx.)		10:00	11:52	13:30	
Stop Time (approx.)		11:00	12:52	14:30	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	2,411	2,455	2,399	2,422
P ₂	Charge rate (bpd)	44,049	44,167	44,092	44,102
F _d	Oxygen-based F-factor (ds cf/MMBtu)	7,768	7,768	7,768	7,768
H _i	Actual heat input (MMBtu/hr)	76.5	78.2	76.3	77.0
Gas Conditions					
O ₂	Oxygen (dry volume %)	7.6	7.9	8.0	7.8
CO ₂	Carbon dioxide (dry volume %)	6.6	6.2	6.1	6.3
T _s	Sample temperature (°F)	334	335	334	334
B _w	Actual water vapor in gas (% by volume)	15.9	16.7	17.0	16.5
Sampling Data					
V _{metd}	Volume metered, standard (ds cf)	27.27	27.05	27.12	27.14
Laboratory Data (Ion Chromatography)					
m _n	Total H ₂ SO ₄ collected (mg)	0.1672	0.1761	0.1948	
Sulfuric Acid Vapor (H₂SO₄) Results					
C _{sd}	H ₂ SO ₄ Concentration (lb/dscf)	1.35E-08	1.44E-08	1.58E-08	1.46E-08
C _{sd}	H ₂ SO ₄ Concentration (ppmdv)	0.0532	0.0564	0.0623	0.0573
E _{Fd}	H ₂ SO ₄ Rate - Fd-based (lb/MMBtu)	0.000165	0.000179	0.000199	0.000181

End of Section

3. DESCRIPTION OF INSTALLATION

Process Description

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Gas Oil Hydrotreater Unit (EU08-GOHT) reacts sour gasoil streams with hydrogen over a catalyst bed to remove sulfur. The GOHT unit consists of process vessels (reactors, distillation tower, absorbing towers, stripper tower), a charge heater (EU08-GOHTCHARHTR), cooling tower, flare, compressors, pumps, piping, drains and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The GOHT Heater (EU08-GOHTCHARHTR-S1) is fired by refinery fuel gas. Emissions are vented to the atmosphere via the GOHT Heater Stack (SV08-H1) where testing was performed.

Test Location

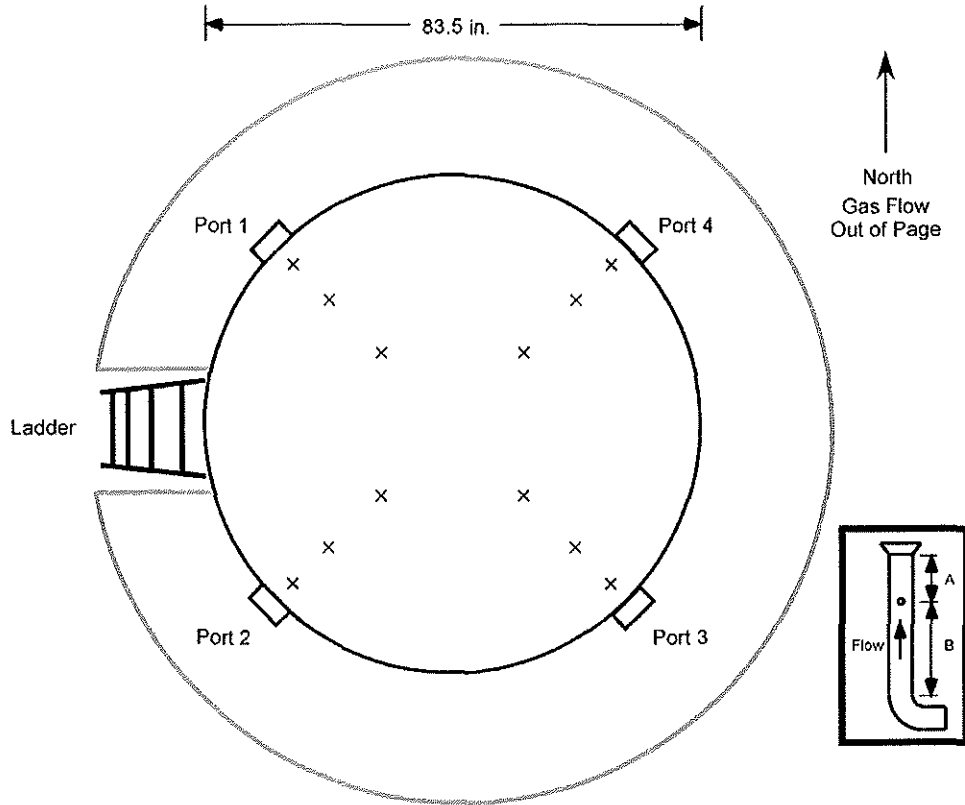
The sample point locations were determined by EPA Methods 1 and 7E specifications. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 11 and 12 represent the layout of the test location.

**Table 3-1:
Sampling Point Information**

Source		Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
Constituent								
<u>GOHT Heater Stack</u>								
FPM/CPM		5 / 202	1-3	4	3	10	120	3-1
H ₂ SO ₄		Draft ASTM CCM	1-3	1	1	60	60	N/A ¹
O ₂ /CO ₂ /NO _x		3A/7E	1-10	1	3	7	21	3-2
O ₂ /CO ₂ /CH ₄ /C ₂ H ₆ /THC		3A/18/25A	1-3	1	3	21	63	3-2

¹ Draft ASTM CCM sampling occurred at a single point near the center of the duct.

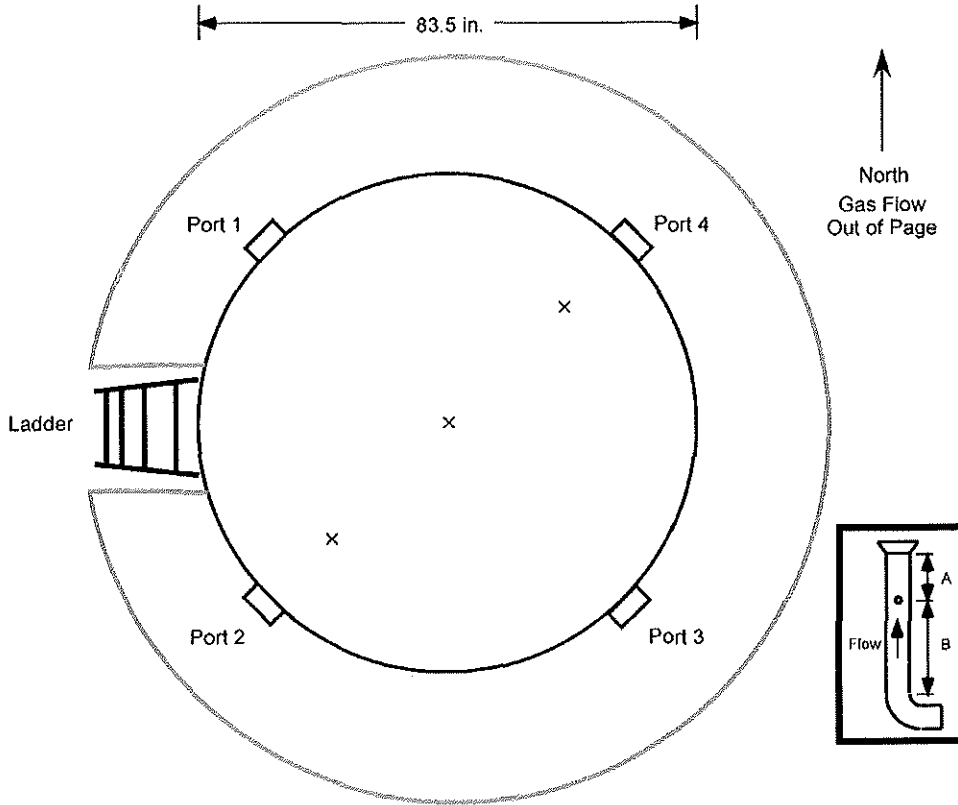
**Figure 3-1:
 PM₁₀ Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	29.6	24.7
2	14.6	12.2
3	4.4	3.7

Duct diameters upstream from flow disturbance (A): 5.8 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 7.2 Limit: 2.0

**Figure 3-2:
 O₂, NO_x & THC Sample Point Layout (EPA Method 7E)**



Sampling Point	Port to Point Distance (meters)	Port to Point Distance (inches)
1	83.3	69.6
2	50.0	41.8
3	16.7	13.9

Duct diameters upstream from flow disturbance (A): 5.8 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 7.2 Limit: 2.0

End of Section

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the USEPA and the DEQ. 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.

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 1	"Sample and Velocity Traverses for Stationary Sources"
Method 2	"Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"
Method 3	"Gas Analysis for the Determination of Dry Molecular Weight"
Method 3A	"Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 3B	"Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air"
Method 4	"Determination of Moisture Content in Stack Gases"
Method 5	"Determination of Particulate Matter Emissions from Stationary Sources"
Method 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer)"
Method 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"
Method 18	"Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"

Title 40 CFR Part 60, Appendix B Performance Specifications

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"

Title 40 CFR Part 51, Appendix M

Method 202	"Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources"
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CTM-013 (Mod.)/Draft ASTM Controlled Condensation Method (Draft ASTM CCM)

“Determination of Sulfur Oxides Including Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Vapor and Mist from Stationary Sources Using a Controlled Condensation Sampling Apparatus”

Methodology Discussion

PM₁₀ Testing – USEPA Method 5/202

The front-half (Method 5 portion) of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 248°F ± 25°F and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

The back-half (Method 202 portion) of the sampling train is designed to mimic ambient conditions and collect only the particles that would truly form CPM in the atmosphere by minimizing the sulfur dioxide (SO₂) and nitrogen oxide (NO_x) interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water and SO₂ and NO_x were absorbed and partially oxidized before they could be purged out with nitrogen (N₂).

Flue gas exiting the front-half heated filter passed through a coiled condenser and dry impinger system jacketed by water continually circulated at ambient temperature. Moisture was removed from the flue gas without bubbling through the condensed water. Flue gas then passed through a tetrafluoroethane (TFE) membrane filter at ambient temperature. The temperature of the flue gas at the exit of the filter was directly measured with an in-line thermocouple and maintained in the temperature range of 65°F to 85°F.

After exiting the ambient filter, the flue gas passed through two (2) additional impingers surrounded by ice in a “cold” section of the impinger bucket. The moisture collected in these impingers were not analyzed for CPM and was only collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent. The back-half of the sample train (heated filter outlet, condenser, dry impingers and TFE membrane filter) was recovered per Method 202 requirements. The impinger train was purged with nitrogen (N₂) at a rate of 14 liters per minute (lpm) for one (1) hour following each test run and prior to recovery.

A field train blank was assembled, purged and recovered as if it were an actual test sample; analysis of the field train blank was used to blank-correct the test run results. Reagent blanks were also collected to quantify background contamination. All samples and blanks were returned to CleanAir Analytical Services for gravimetric analysis. Method 202 samples were maintained at a temperature < 85°F during transport to the laboratory.

O₂, CO₂ & NO_x Testing – USEPA Methods 3A and 7E

Reference method oxygen (O₂) and carbon dioxide (CO₂) emissions were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. Reference method NO_x emissions were determined using a chemiluminescent analyzer per EPA Method 7E.

Sample gas was extracted at a constant rate, conditioned to remove moisture and delivered to an analyzer bank which measured concentration on a dry basis (units of %dv or ppm_{dv}).

Calibration error checks were performed by introducing zero 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 Method 3A and 7E, the average results for each run were drift-corrected.

VOCs Testing – USEPA Methods 25A & 18

The Method 25A sampling system consists of a heated probe, heated filter and heated sample line. Flue gas was delivered at 250°F to a flame ionization analyzer (FIA), which continuously measures minute-average THC concentration expressed in terms of propane (C₃H₈) on an actual (wet) basis. FIA calibration was performed by introducing zero air, high, mid- and low range C₃H₈ calibration gases to the inlet of the sampling system's heated filter. Bias checks were performed before and after each sampling run in a similar manner.

The Method 18 sampling system consists of a gas conditioner (for moisture removal), TFE sample lines, TFE-coated diaphragm pump and a mass flow meter ("Direct Pump Sampling Procedure"). This system pulled a slipstream of the flue gas from the Method 25A sample delivery system and delivered it into a FlexFoil bag at a constant rate. The moisture condensate was not collected for analysis as CH₄ and C₂H₆ are insoluble in water.

Analysis for CH₄ and C₂H₆ was performed off-site by CleanAir Analytical Services using gas chromatography (GC). Since moisture was removed from the sample prior to collection, the GC analyzer measured concentration on a dry basis. At least five (5) sample injections were analyzed for each run.

Analyzer calibration was performed by generating a calibration curve from triplicate injections of three (3) distinct CH₄ and C₂H₆ concentrations introduced directly into the GC. Upon completion of calibration, a recovery study was performed by spiking one of the bag samples with a known concentration of CH₄ and C₂H₆, storing the bags for the same period of time prior to analysis as the field samples, and analyzing the bags to determine percent recovery.

H₂SO₄ Testing – Draft ASTM CCM

A gas sample was extracted from the source at a constant flow rate from the source using a quartz-lined probe maintained at a temperature of 650°F ± 25°F (depending on the required probe length) and a quartz fiber filter maintained at the same temperature as the probe to remove particulate matter.

The sample then passed through a glass coil condenser for collection of sulfuric acid vapor and/or mist. A second quartz fiber filter (referred to as the sulfuric acid mist (SAM) filter) was located at the condenser outlet for the collection of residual SAM not collected by the condenser. The condenser temperature was regulated by a water jacket and the SAM filter was regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at 140°F ± 9°F.

After exiting the SAM filter, the sample gas continued through a series of four (4) glass knock-out jars; two (2) containing water, one (1) empty and one (1) containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set was maintained below 68°F. The sample gas then flowed into a dry gas meter, where the collected sample gas volume was determined by means of a calibrated, dry gas meter or an orifice-based flow meter.

The H₂SO₄-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H₂O as the recovery/extraction solvent; any H₂SO₄ disassociates into sulfate ion (SO₄²⁻) and is stabilized in the H₂O matrix until analysis.

Samples and blanks were returned to CleanAir Analytical Services for ion chromatography (IC) analysis.

End of Section