

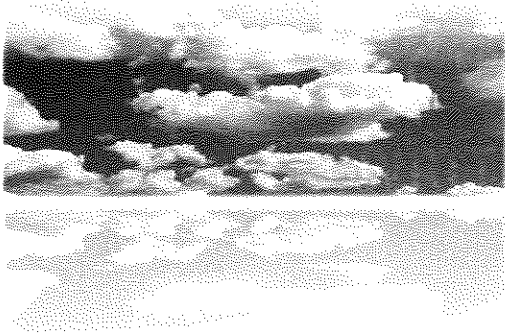


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AIR QUALITY DIVISION



REPORT ON COMPLIANCE &
RATA TESTING

Detroit Refinery

CCR Charge Heater Stack (SV14-H6)

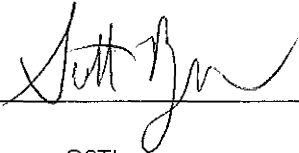
Marathon Petroleum Company LP
1300 South Fort Street
Detroit, MI 48217
Client Reference No. 4101379616

CleanAir Project No. 13599-1
A2LA ISO 17025 Certificate No. 4342.01
A2LA / STAC Certificate No. 4342.02
Revision 0, Final Report
July 27, 2018

COMMITMENT TO QUALITY

To the best of our knowledge, the data presented in this report are accurate, complete, error free 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.

Report Writer:



July 27, 2018

Scott Brown, QSTI
Senior Project Manager / Quality Director
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(800) 627-0033 ext. 4544

Date

I hereby certify that the information contained within the final test report has been reviewed and, to the best of my ability, verified as accurate.

Independent Report and Appendix Reviewer:



July 27, 2018

Ken Sullivan
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Date

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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 CCR Charge Heater (EU14-CCRPLCHARHTR) at the Detroit Refinery, located in Detroit, Michigan. The test program included the following objectives:

- Perform volatile organic compounds (VOCs) 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), nitrogen oxides (NO_x) and carbon monoxide (CO).

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 Results - Compliance**

Source Constituent	Sampling Method (USEPA)	Average Emission	Permit Limit ¹
<u>CCR Charge Heater</u>			
VOC (lb/MMBtu)	25A/18	<0.0007	0.0055

¹ Permit limit obtained from MDEQ Renewable Operating Permit No. MI-ROP-A9831-2012c.

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

Source Constituent	Reference Method (USEPA)	Relative Accuracy (%) ¹	Applicable Specification	Specification Limit ²
<u>CCR Charge Heater</u>				
O ₂ (% dv)	3A	0.3	PS3	±1.0% dv
NO _x (lb/MMBtu)	7E / 3A	0.5	PS2	20% of RM
CO (lb/MMBtu)	10	0.0	PS4A ³	10% of RM

¹ Relative Accuracy is expressed in terms of comparison to the reference method (% RM) or applicable emission standard (% Std.).

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

³ For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4A RA limit is either < 10% of RM, < 5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

Test Program Details

Parameters

The test program included the following measurements:

- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents
 - methane (CH₄)
 - ethane (C₂H₆)
- nitrogen oxides (NO_x)
- carbon monoxide (CO)
- flue gas composition (e.g., O₂, CO₂, H₂O)

Schedule

Testing was performed on June 26, 2018. 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	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	08:56	09:17
2	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	09:32	09:53
3	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	10:07	10:28
4	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	10:43	11:04
5	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	11:16	11:37
6	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	11:49	12:10
7	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	12:25	12:46
8	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	12:58	13:19
9	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	13:31	13:52
10	CCR Charge Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _x /CO	06/26/18	14:05	14:26
1	CCR Charge Heater Stack	USEPA 25A, 18	VOC	06/26/18	08:56	10:28
2	CCR Charge Heater Stack	USEPA 25A, 18	VOC	06/26/18	10:43	12:10
3	CCR Charge Heater Stack	USEPA 25A, 18	VOC	06/26/18	12:25	13:52
1	CCR Charge Heater Stack	USEPA 4	H ₂ O	06/26/18	09:32	10:07
2	CCR Charge Heater Stack	USEPA 4	H ₂ O	06/26/18	10:43	11:18
3	CCR Charge Heater Stack	USEPA 4	H ₂ O	06/26/18	11:49	12:24
4	CCR Charge Heater Stack	USEPA 4	H ₂ O	06/26/18	12:58	13:33

Discussion

Project Synopsis

O₂, NO_x and CO RATA Testing

Minute-average data points for O₂, NO_x and CO (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A, 7E and 10. Unless statistically inconsequential (CO), relative accuracy was determined based on at least nine (9) of 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

Sampling occurred at the three (3) points as specified in Section 8.1.3.2 of PS 2 during each run. The average result for each run was converted to identical units of measurement as the facility's CEMS and compared for relative accuracy.

VOC Testing

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 63-minute test runs. The Method 25A test runs were performed concurrently with three (3) 63-minute Method 18 bag collections. The final result for each VOC run was expressed as the average of three (3) runs.

For all Method 25A runs, the measured concentrations of THC were below the detection limit defined as 'less than 1%' of the calibration span of the THC instrument. Assuming worst-case scenario, the resultant VOC emissions are reported as 'less than' the defined THC detection limit and Method 18 analyses are deemed extraneous. The Method 18 bag collections have been archived.

VOC emission results were calculated in units of pounds per million Btu (lb/MMBtu) as propane. O₂ concentrations from concurrent Method 3A runs were utilized to convert VOC results to lb/MMBtu. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from nearly concurrent Method 4 runs.

Moisture Testing

Four (4) 35-minute Method 4 test runs were performed using EPA Method 4. The moisture content was utilized to convert THC concentrations from a wet basis to a dry basis.

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of lb/MMBtu by calculating an oxygen-based fuel factor (Fd) for refinery gas per EPA Method 19 specifications. The heat content and Fd factor were calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents.

Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions compliance test runs and RATA test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test report.

2. RESULTS

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

**Table 2-1:
CCR Charge Heater Stack – VOC Emissions**

Run No.		1	2	3	Average
Date (2018)		Jun 26	Jun 26	Jun 26	
Start Time (approx.)		08:56	10:43	12:25	
Stop Time (approx.)		10:28	12:10	13:52	
Process Conditions					
P ₁	Charge rate (bpd)	22,000	21,993	22,010	22,001
P ₂	Heat Input (MMBtu/hr)	126	125	125	126
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,247	8,247	8,247	
Gas Conditions					
O ₂	Oxygen (dry volume %)	4.9	4.9	4.8	4.9
CO ₂	Carbon dioxide (dry volume %)	9.5	9.5	9.5	9.5
B _w	Actual water vapor in gas (% by volume) ¹	14.4	15.2	15.4	15.0
THC Results^{2,3}					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.538	<0.544	<0.545	<0.542
C _{sd}	Concentration (lb/dscf)	<6.16E-08	<6.22E-08	<6.24E-08	<6.21E-08
E _{Fd}	Emission Rate - F _r -based (lb/MMBtu)	<0.000665	<0.000670	<0.000669	<0.000668

¹ Moisture data used for ppmv v to ppmdv correction obtained from nearly-concurrent M-4 runs.

² For THC, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

³ VOC is reported as THC since all THC results were non-detect.

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

Run No.	Start Time	Date (2018)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	08:56	Jun 26	4.91	5.25	-0.34	-6.9%
2	09:32	Jun 26	4.98	5.32	-0.34	-6.8%
3 *	10:07	Jun 26	4.93	5.28	-0.35	-7.1%
4	10:43	Jun 26	4.91	5.24	-0.33	-6.7%
5	11:16	Jun 26	4.84	5.17	-0.33	-6.8%
6	11:49	Jun 26	4.92	5.27	-0.35	-7.0%
7	12:25	Jun 26	4.75	5.08	-0.33	-7.0%
8	12:58	Jun 26	4.90	5.19	-0.29	-5.9%
9	13:31	Jun 26	4.83	5.16	-0.33	-6.8%
10	14:05	Jun 26	4.83	5.17	-0.34	-7.0%
Average			4.88	5.21	-0.33	-6.8%

Relative Accuracy Test Audit Results

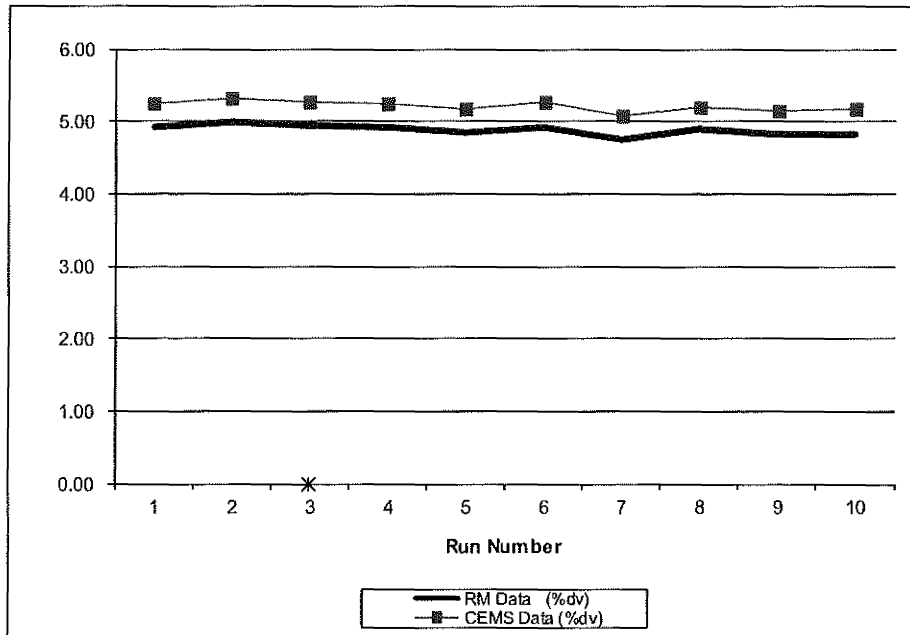
Standard Deviation of Differences	0.017
Confidence Coefficient (CC)	0.013
t-Value for 9 Data Sets	2.306
Avg. Abs. Diff. (%dv)	0.33
	Limit 1.0

RM = Reference Method (CleanAir Data)

071818 072121

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

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



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

Run No.	Start Time	Date (2018)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	08:56	Jun 26	0.0299	0.0303	-0.0004	-1.3%
2	09:32	Jun 26	0.0300	0.0298	0.0002	0.7%
3	10:07	Jun 26	0.0301	0.0303	-0.0002	-0.5%
4	10:43	Jun 26	0.0301	0.0301	0.0000	0.0%
5 *	11:16	Jun 26	0.0291	0.0289	0.0002	0.7%
6	11:49	Jun 26	0.0300	0.0299	0.0001	0.3%
7	12:25	Jun 26	0.0297	0.0296	0.0001	0.3%
8	12:58	Jun 26	0.0307	0.0305	0.0002	0.7%
9	13:31	Jun 26	0.0304	0.0305	-0.0001	-0.3%
10	14:05	Jun 26	0.0303	0.0302	0.0001	0.3%
Average			0.0301	0.0301	0.0000	0.0%

Relative Accuracy Test Audit Results

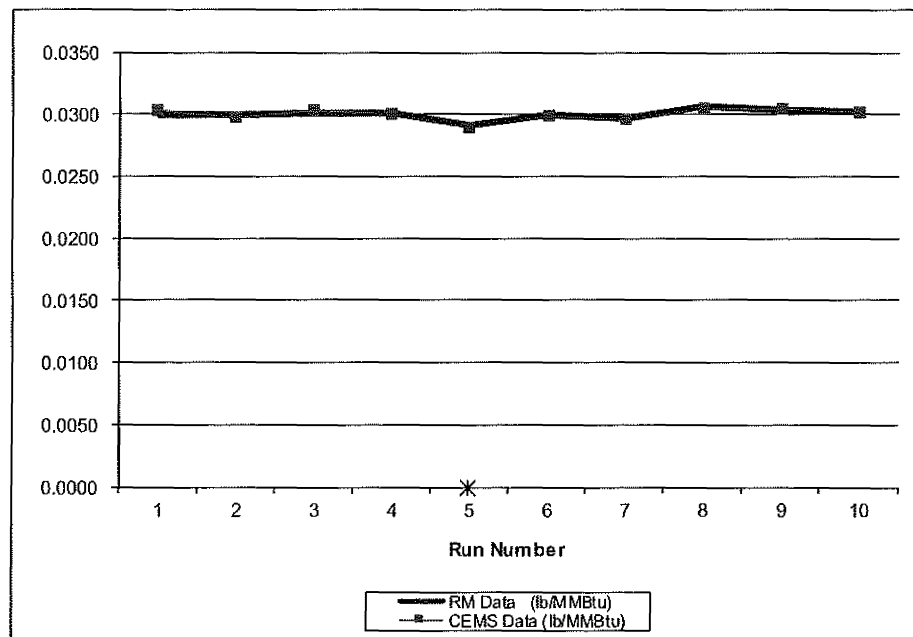
Standard Deviation of Differences	0.000195	
Confidence Coefficient (CC)	0.000150	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	0.5%	20.0%
Relative Accuracy (as % of Appl. Std.)	0.3%	10.0%

RM = Reference Method (CleanAir Data)

072318 100114

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

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



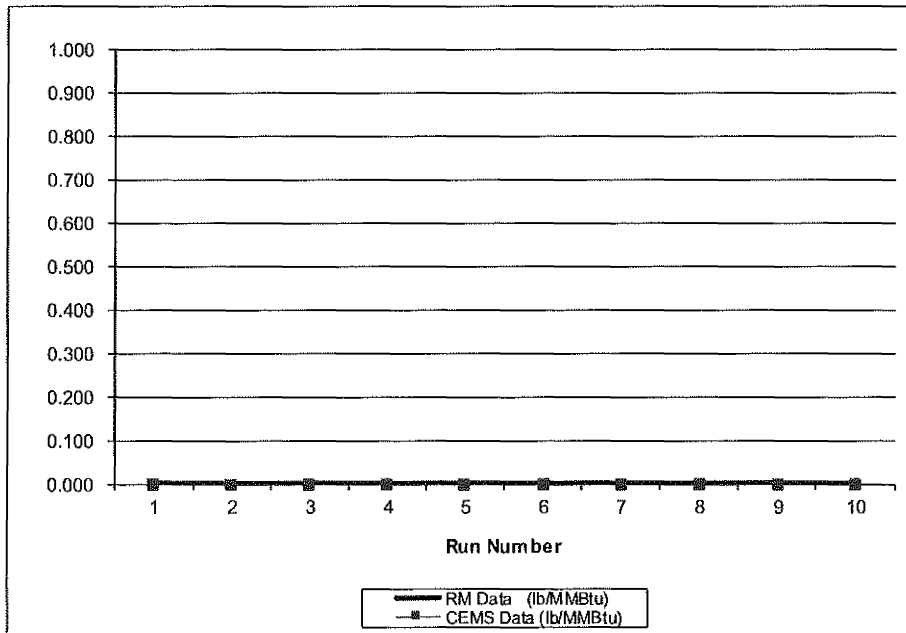
**Table 2-4:
 CCR Charge Heater Stack – CO (lb/MMBtu) RATA**

Run No.	Start Time	Date (2018)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	08:56	Jun 26	0.000	0.000	0.000	0.0%
2	09:32	Jun 26	0.000	0.000	0.000	0.0%
3	10:07	Jun 26	0.000	0.000	0.000	0.0%
4	10:43	Jun 26	0.000	0.000	0.000	0.0%
5	11:16	Jun 26	0.000	0.000	0.000	0.0%
6	11:49	Jun 26	0.000	0.000	0.000	0.0%
7	12:25	Jun 26	0.000	0.000	0.000	0.0%
8	12:58	Jun 26	0.000	0.000	0.000	0.0%
9	13:31	Jun 26	0.000	0.000	0.000	0.0%
10	14:05	Jun 26	0.000	0.000	0.000	0.0%
Average			0.000	0.000	0.000	0.0%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.00	
Confidence Coefficient (CC)	0.00	
t-Value for 10 Data Sets	2.262	
		Limit
Relative Accuracy (as % of RM)	0.0%	10.0%
Relative Accuracy (as % of Appl. Std.)	0.0%	5.0%
Appl. Std. = 0.013 lb/MMBtu		
Avg. Abs. Diff. (lb/MMBtu)	0.000	5.0

RM = Reference Method (CleanAir Data) 072318 100848
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
 RATA calculations are based on all 10 runs.



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 Continuous Catalytic Regeneration Platformer Unit (EG14-CCRPLATFORMER) is a catalytic reformer that rearranges the structure of low octane naphtha feed into higher octane reformates. Hydrogen is produced as a product of the reaction and is used in other refinery processes. The CCR Charge Heater (EG14-CCRPLCHARHTR) preheats the feed to the reactor.

The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the CCR Charge Heater Stack (SV14-H6) where testing was performed.

Test Location

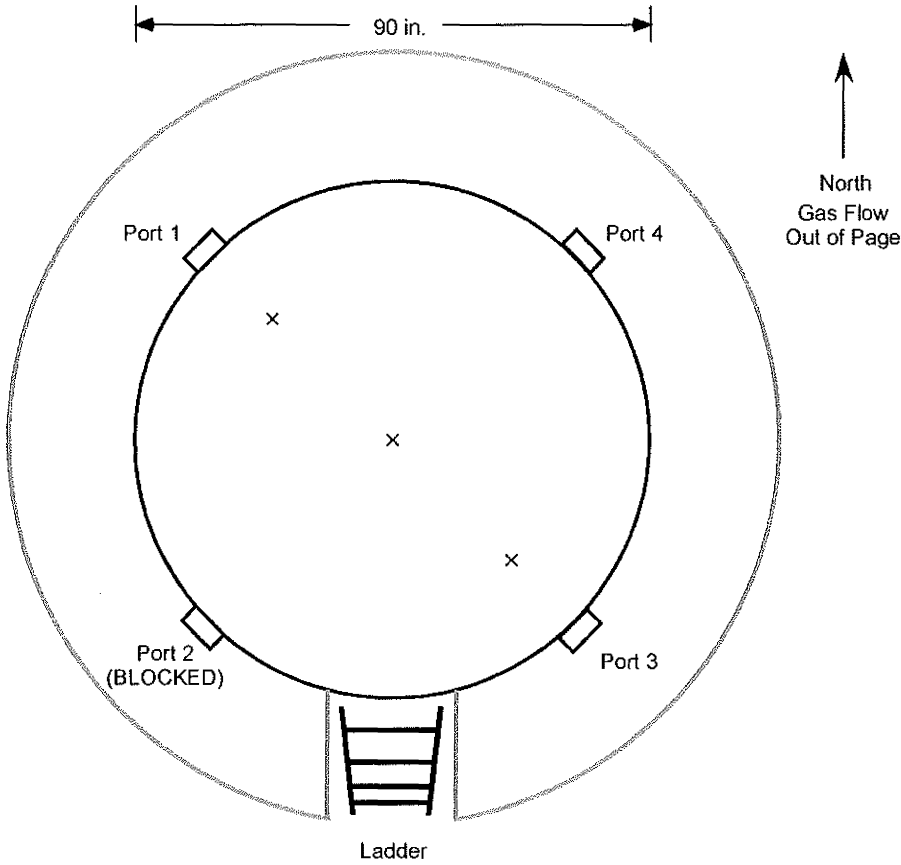
The sample point locations were determined by EPA Methods 1 and 7E specifications. Table 3-1 presents the sampling information for the test location described in this report. The figure shown on page 9 presents the layout of the test location.

**Table 3-1:
Sampling Information**

Source		Run	Points per	Minutes	Total		
Constituent	Method (USEPA)	No.	Port	per Point	Minutes	Figure	
CCR Charge Heater							
O ₂ / CO ₂ / CH ₄ / C ₂ H ₆ / THC	3A / 18 / 25A	1-3	1	3	21	63	3-1
O ₂ / CO ₂ / NO _x / CO	3A / 7E / 10	1-10	1	3	7	21	3-1
H ₂ O	4	1-4	1	1	35	35	N/A ¹

¹ Moisture sampling occurred at a single point near the center of the duct.

**Figure 3-1:
 O₂, CO, NO_x and THC Sample Point Layout (Performance Specification 2)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	75.0
2	50.0	45.0
3	16.7	15.0

Duct diameters upstream from flow disturbance (A): > 0.9 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 3.6 Limit: 2.0

End of Section

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (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. 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 3A "Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
- Method 4 "Determination of Moisture Content in Stack Gases"
- Method 7E "Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
- Method 10 "Determination of Carbon Monoxide 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"
- Method 25A "Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"

Title 40 CFR Part 60, Appendix B Performance Specifications

- PS 2 "Specifications and Test Procedures for SO₂ and NO_x Continuous Emission Monitoring Systems in Stationary Sources"
- PS 3 "Specifications and Test Procedures for O₂ and CO₂ Continuous Emission Monitoring Systems in Stationary Sources"
- PS 4A "Specifications and Test Procedures for Carbon Monoxide Continuous Emission Monitoring Systems in Stationary Sources"

Methodology Discussion

O₂, CO₂, NO_x and CO Testing – USEPA Methods 3A, 7E and 10; Performance Specifications 2, 3 and 4A

Reference method (RM) O₂ concentrations were determined using a paramagnetic analyzer per EPA Method 3A. RM NO_x emissions were determined using a chemiluminescent analyzer per EPA Method 7E. RM CO emissions were determined using an infrared analyzer per EPA Method 10. Carbon dioxide (CO₂) concentrations were determined using an NDIR analyzer per EPA Method 3A for supplemental purposes.

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 nitrogen (N₂), high 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. Documentation of interference checks and NO₂ converter efficiency checks are included in this report. Per EPA Methods 3A, 7E and 10, the average results for each run were drift-corrected.

VOC Testing – USEPA Methods 18 and 25A

VOC emissions were determined using EPA Method 25A to quantify THC emissions which were assumed equivalent to VOC emissions.

The Method 25A sampling system consisted 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 measured 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 consisted 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 Tedlar bag at a constant rate. The moisture condensate was not collected for analysis as CH₄ and C₂H₆ are insoluble in water. Each bag was filled over a period of 63 minutes for each test run. Tedlar bags were not analyzed because THC was non-detect.

Moisture Testing – USEPA Method 4 (Modified)

Flue gas was extracted at a single point and constant rate through an unheated, stainless steel tubing sampling probe. After exiting the unheated sampling probe, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars was 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.