1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to complete testing on the Crude/Vacuum Heater (EU05-CRUDEHTR-S1 & EU04-VACHTR-S-1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), sulfuric acid mist (H₂SO₄), and volatile organic compound (VOC) 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.

Table 1-1: Summary of Compliance Results

Source		Average	
Constituent	Sampling Method	Emission	Permit Limit ¹
Crude/Vacuum Heater Stac	<u>k</u>		
FPM (lb/MMBtu) H₂SO₄ (lb/MMBtu)	USEPA 5 CTM-013 (Mod)	0.0016 0.0011	N/A N/A
PM (lb/MMBtu) ² VOC (lb/MMBtu) NSFPM (lb/MMBtu)	USEPA 5 / CTM-013 (Mod) USEPA 25A USEPA 5B	0.00075 <0.00078 0.0013	0.0019 0.0055 N/A

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

 2 PM assumed equivalent to FPM less H $_2$ SO $_4$. The letter from MDEQ referenced in the

appendices further outlines the correction of PM emission for H_2SO_4 bias.

Table 1-2: Summary of RATA Results

<u>Source</u> Constituent	Reference Method	Relative Accuracy (%) ¹	Applicable Specification	Specification Limit ²
Crude/Vacuum Heater				
O ₂ (% dv)	ЗA	0.06	PS3	±1.0 % dv
NOx(ppm @ 0%O2)	7E	4.4	PS2	20% of RM
NOx (lb/MMBtu)	7E	4.5	PS2	20% of RM

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

standard (% Std.) The specific expression used depends on the specification limit cited.

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

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Test Program Details

Parameters

The test program included the following emissions measurements:

- filterable particulate matter (FPM)
- sulfuric acid mist (H₂SO₄), conducted concurrently with FPM measurements
- particulate matter (PM), assumed equivalent to FPM minus H₂SO₄
- nonsulfuric acid particulate matter (NSFPM)
- nitrogen oxides (NO_X)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
 - methane (CH₄)
 - \circ ethane (C₂H₆)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

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Schedule

Testing was performed on June 11 and 12, 2019. 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	Crude/Vacuum Heater	USEPA Method 5	FPM	06/11/19	09:25	10:41
3	Crude/Vacuum Heater	USEPA Method 5	FPM	06/11/19	14:05	15:18
4	Crude/Vacuum Heater	USEPA Method 5	FPM	06/11/19	16:12	17:25
1	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	06/11/19	09:25	10:41
2	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	06/11/19	11:55	13:10
3	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	06/11/19	14:05	15:18
4	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	06/11/19	16:13	17:25
1	Crude/Vacuum Heater	CTM-013 (mod)	H_2SO_4	06/11/19	09:25	10:25
2	Crude/Vacuum Heater	CTM-013 (mod)	H_2SO_4	06/11/19	11:55	12:55
3	Crude/Vacuum Heater	CTM-013 (mod)	H_2SO_4	06/11/19	14:05	15:05
4	Crude/Vacuum Heater	CTM-013 (mod)	H_2SO_4	06/11/19	16:12	17:12
1	Crude/Vacuum Heater	USEPA Method 25A / 18	VOC	06/12/19	08:15	09:38
2	Crude/Vacuum Heater	USEPA Method 25A / 18	VOC	06/12/19	09:52	11:11
3	Crude/Vacuum Heater	USEPA Method 25A / 18	VOC	06/12/19	11:25	12:45
1	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	08:15	08:36
2	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	08:48	09:09
3	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	09:17	09:38
4	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	09:52	10:13
5	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	10:22	10:43
6	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	10:50	11:11
7	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	11:25	11:46
8	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	11:55	12:16
9	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	12:24	12:45
10	Crude/Vacuum Heater	USEPA Method 3A / 7E	O_2 / NO_X	06/12/19	12:58	13:19
1	Crude/Vacuum Heater	USEPA Method 4	Moisture	06/12/19	08:15	09:15
2	Crude/Vacuum Heater	USEPA Method 4	Moisture	06/12/19	09:52	10:52
3	Crude/Vacuum Heater	USEPA Method 4	Moisture	06/12/19	11:30	12:30

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Discussion

Project Synopsis

FPM Testing

A total of four (4) 60-minute EPA Method 5 test runs were performed. FPM emission results were calculated in units of pounds per million Btu (lb/MMBtu). The final result was expressed as the average of the four (4) valid runs.

H₂SO₄ Testing – CTM-013

 H_2SO_4 emissions were determined referencing Conditional Test Method 013 (CTM-013). Four (4) 60-minute CTM-013 test runs were performed concurrently with all Method 5 runs. H_2SO_4 emission results were calculated in units of Ib/MMBtu. The H_2SO_4 final results were expressed as the average of four (4) valid runs.

PM Results

PM is assumed equivalent to the difference of FPM and H₂SO₄ emissions. This is recommended in a letter from the DEQ, dated December 18, 2017; "Marathon Petroleum, Crude/Vacuum Heater Stack, Request to Substitute Method 5B for Method 5, Permit: MI-ROP-A9831-2012c, SRN: A9831."

 H_2SO_4 emissions were determined concurrently with FPM emissions, converted to units of lb/MMBtu and subtracted from total FPM emissions from each respective run. The PM final results were expressed as the average of the three (3) highest runs.

VOC Testing – USEPA Methods 25A and 18

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 60-minute test runs. The Method 25A test runs were performed concurrently with three (3) 60-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 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 concurrent EPA Method 4 runs.

RATA Testing – USEPA Methods 3A, 7E, and 10

Minute-average data points for O_2 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 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

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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 CEMS and compared for relative accuracy.

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted into units of lb/MMBtu by applying an oxygen-based fuel factor (F_d) provided by MPC for each test run.

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.

End of Section

Marathon Petroleum Company LP Detroit Refinery - Crude/Vacuum Heater Report on Compliance & RATA Testing

2. RESULTS

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

Table 2-1: Crude/Vacuum Heater – FPM Emissions

Run No	•	1	2	3	4	Average
Date (2	019)	Jun 11	Jun 11	Jun 11	Jun 11	
Start Ti	me (approx.)	09:25	11:55	14:05	16:12	
Stop Ti	me (approx.)	10:41	13:10	15:18	17:25	
Proces	s Conditions					
P ₁	Production Rate (BPD)	150,493	150,238	150,394	149,783	150,227
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,508	8,508	8,517	8,521	8,513
Hi	Actual heat input (MMBtu/hr)	308	307	303	303	305
Gas Co	nditions					
O ₂	Oxygen (dry volume %)	6.8	6.7	6.7	6.7	6.7
CO_2	Carbon dioxide (dry volume %)	8.0	8.1	8.2	8.1	8.1
Τs	Sample temperature (°F)	299	301	301	302	301
B_w	Actual water vapor in gas (% by volume)	12.9	13.4	14.2	14.6	13.8
Gas Flo	w Rate					
Q_a	Volumetric flow rate, actual (acfm)	115,000	113,000	114,000	111,000	113,000
Q_s	Volumetric flow rate, standard (scfm)	78,700	77,000	77,800	76,000	77,400
Q_{std}	Volumetric flow rate, dry standard (dscfm)	68,500	66,700	66,700	64,900	66,700
Sampli	ng Data					
V _{mstd}	Volume metered, standard (dscf)	32.13	31.17	32.54	31.73	31.89
%I	lsokinetic sampling (%)	98.5	98.2	102.4	102.6	100.4
Labora	tory Data					
m _{filter}	Matter collected on filter(s) (g)	0.00126	0.00091	0.00110	0.00163	
ms	Matter collected in solvent rinse(s)(g)	0.00087	0.00093	0.00056	0.00032	
m'n	Total FPM (g)	0.00213	0.00184	0.00166	0.00195	
FPM Re	sults					
C_{sd}	Particulate Concentration (lb/dscf)	1.46E-07	1.30E-07	1.12E-07	1.36E-07	1.31E-07
E _{lb/hr}	Particulate Rate (lb/hr)	0.601	0.520	0.450	0.528	0.525
E_{Fd}	Particulate Rate - F _a -based (lb/MMBtu)	0.00184	0.00163	0.00141	0.00170	0.00165

Average includes 4 runs.

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Table 2-2:

Crude/Vacuum	Heater –	H_2SO_4	Emissions
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Run No		1	2	3	4	Average
Date (2	019)	Jun 11	Jun 11	Jun 11	Jun 11	
Start Tir	ne (approx.)	09:25	11:55	14:05	16:12	
Stop Tir	ne (approx.)	10:25	12:55	15:05	17:12	
Proces	s Conditions					
P ₁	Charge rate (BPD)	150,588	150,252	150,445	149,770	149,770
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,508	8,508	8,516	8,521	8,521
H_i	Actual heat input (MMBtu/hr)	307	308	303	303	303
Gas Co	nditions					
O ₂	Oxygen (dry volume %)	6.9	6.8	7.1	7.2	7.0
CO_2	Carbon dioxide (dry volume %)	7.9	8.0	7.9	7.6	7.9
Ts	Sample temperature (°F)	305	307	306	306	306
B_w	Actual water vapor in gas (% by volume)	13.2	14.4	14.0	13.8	13.9
Samplii	ng Data					
V_{mstd}	Volume metered, standard (dscf)	27.57	27.66	27.69	27.73	27.66
Labora	tory Data (Ion Chromatography)					
m _n	Total H_2SO_4 collected (mg)	0.7772	1.8142	0.9191	0.9341	
Sulfurio	Acid Vapor (H₂SO₄) Results					
C_{sd}	H_2SO_4 Concentration (lb/dscf)	6.22E-08	1.45E-07	7.32E-08	7.43E-08	8.86E-08
C_{sd}	H_2SO_4 Concentration (ppmdv)	0.244	0.568	0.288	0.292	0.348
E_{Fd}	H ₂ SO ₄ Rate - Fd-based (Ib/MMBtu)	0.000789	0.00182	0.000944	0.000965	0.00113

Average includes 4 runs.

Marathon Petroleum Company LP Detroit Refinery - Crude/Vacuum Heater Report on Compliance & RATA Testing

Table 2-3:

Crude/Vacuum	Heater –	PM	Emissions
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Run No	•	1	2	3	4	Average
Date (2	019)	Jun 11	Jun 11	Jun 11	Jun 11	
Start Ti	me (approx.)	09:25	11:55	14:05	16:12	
Stop Ti	me (approx.)	10:41	13:10	15:18	17:25	
Proces	s Conditions					
P ₁	Production Rate (BPD)	150,493	150,238	150,394	149,783	150,227
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,508	8,508	8,517	8,521	8,513
H_i	Actual heat input (MMBtu/hr)	308	307	303	303	305
Gas Co	nditions					
O ₂	Oxygen (dry volume %)	6.8	6.7	6.7	6.7	6.7
CO_2	Carbon dioxide (dry volume %)	8.0	8.1	8.2	8.1	8.1
T_s	Sample temperature (°F)	299	301	301	302	301
B_w	Actual water vapor in gas (% by volume)	12.9	13.4	14.2	14.6	13.8
FPM Re	sults					
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.00184	0.00163	0.00141	0.00170	0.00165
Sulfurio	c Acid Vapor (H ₂ SO ₄) Results					
E_{Fd}	H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	0.000789	0.00182	0.000944	0.000965	0.00113
Particu	late Matter (PM) Results ^{1,2}					
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.00105	<0.000455	0.000466	0.000734	0.000751

¹ Final PM results = the average of three (3) highest valid runs (Runs 1, 3 &4). PM assumed equivalent to FPM less H₂SO₄.

² For Run 2, H₂SO₄ results exceeded FPM results. PM result displayed is assumed/calculated based on avg. stdev difference.

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Table 2-4:

Crude/Vacuum Heater – NSFPM Emissions

Run No	•	1	2	3	4	Average
Date (2	019)	Jun 11	Jun 11	Jun 11	Jun 11	
Start Tir	ne (approx.)	09:25	11:55	14:05	16:13	
Stop Tir	me (approx.)	10:41	13:10	15:18	17:25	
Proces	s Conditions					
P ₁	Charge Rate (BPD)	150,493	150,238	150,394	149,783	150,227
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,508	8,508	8,517	8,521	8,513
Hi	Actual heat input (MMBtu/hr)	308	307	303	303	305
Gas Co	nditions					
O ₂	Oxygen (dry volume %)	6.8	6.8	6.7	7.1	6.9
CO_2	Carbon dioxide (dry volume %)	8.0	8.0	8.2	7.8	8.0
Ts	Sample temperature (°F)	302	303	303	303	303
Bw	Actual water vapor in gas (% by volume)	12.9	14.4	14.6	14.5	14.1
Gas Flo	w Rate					
Q_a	Volumetric flow rate, actual (acfm)	113,000	115,000	113,000	115,000	114,000
Q_s	Volumetric flow rate, standard (scfm)	77,300	78,700	76,900	78,200	77,800
Q_{std}	Volumetric flow rate, dry standard (dscfm)	67,300	67,400	65,700	66,900	66,800
Samplii	ng Data					
V _{mstd}	Volume metered, standard (dscf)	30.91	31.22	31.52	32.08	31.43
%I	lsokinetic sampling (%)	96.4	97.2	100.8	100.7	98.8
Labora	tory Data					
m _{filter}	Matter collected on filter(s)(g)	0.00041	0.00121	0.00115	0.00130	
ms	Matter collected in solvent rinse(s)(g)	0.00071	0.00032	0.00040	0.00032	
m _n	Total NSFPM (g)	0.00112	0.00153	0.00155	0.00162	
NSFPM	Results					
C_{sd}	Particulate Concentration (lb/dscf)	7.99E-08	1.08E-07	1.08E-07	1.11E-07	1.02E-07
E _{lb/hr}	Particulate Rate (lb/hr)	0.323	0.437	0.427	0.447	0.409
E_{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00101	0.00136	0.00136	0.00144	0.00129

Average includes 4 runs.

Marathon Petroleum Company LP Detroit Refinery - Crude/Vacuum Heater Report on Compliance & RATA Testing

Table 2-5:

Crude/Vacuum	Heater –	voc	Emissions
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Run No.		1	2	3	Average
Date (201	19)	Jun 12	Jun 12	Jun 12	
Start Time	e (approx.)	08:15	09:52	11:25	
Stop Time	e (approx.)	09:38	11:11	12:45	
Process	Conditions				
P ₁	Production Rate (BPD)	150,427	150,227	150,394	150,349
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,521	8,509	8,517	8,516
Hi	Actual heat input (MMBtu/hr)	312	307	304	308
Gas Conc	litions				
O2	Oxygen (dry volum e %)	6.9	6.9	6.8	6.8
CO2	Carbon dioxide (dry volume %)	7.9	7.9	8.0	8.0
Bw	Actual water vapor in gas (% by volume) ¹	13.5	14.3	14.5	14.1
THC Resu	ults ²				
C_{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.545	<0.537	<0.538	<0.540
C_{sd}	Concentration (lb/dscf)	<6.24E-08	<6.14E-08	<6.16E-08	<6.18E-08
E_{Fd}	Emission Rate - F _d -based (Ib/MMBtu)	< 0.000791	< 0.000780	< 0.000776	< 0.000783
VOC Res	ults ³				
C_{sd}	Concentration (ppmdv as C_3H_8)	< 0.545	< 0.537	< 0.538	< 0.540
C_{sd}	Concentration (Ib/dscf)	<6.24E-08	<6.14E-08	<6.16E-08	<6.18E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000791	< 0.000780	< 0.000776	< 0.000783

Average includes 3 runs.

 1 Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent EPA M4 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 less than VOC limit.

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Table 2-6:

Crude/Vacuum Heater -	• O ₂ (%dv) Relative	Accuracy
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Run	Start	Date			CEMS Data	Difference	Difference
No.	Time	(2019)	RM Data	(%dv)	(%dv)	(%dv)	Percent
1 *	08:15	Jun 12		6.83	6.90	-0.07	-1.0%
2	08:48	Jun 12		6.83	6.89	-0.06	-0.9%
3	09:17	Jun 12		6.90	6.96	-0.06	-0.9%
4	09:52	Jun 12		6.89	6.95	-0.06	-0.9%
5	10:22	Jun 12		6.88	6.93	-0.05	-0.7%
6	10:50	Jun 12		6.87	6.93	-0.06	-0.9%
7	11:25	Jun 12		6.85	6.91	-0.06	-0.9%
8	11:55	Jun 12		6.75	6.81	-0.06	-0.9%
9	12:24	Jun 12		6.71	6.77	-0.06	-0.9%
10	12:58	Jun 12		6.72	6.78	-0.06	-0.9%
	Average			6.82	6.88	-0.06	-0.9%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.00333		
Confidence Coefficient (CC)	0.00256		
t-Value for 9 Data Sets	2.306		
		Limit	
Avg. Abs. Diff. (%dv)	0.06	1.0	

RM = Reference Method (CleanAir Data)

070819 165309

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



Marathon Petroleum Company LP Detroit Refinery - Crude/Vacuum Heater Report on Compliance & RATA Testing

Table 2-7:

Crude/Vacuum Heater – NO_X (ppmdv @ 0%O₂) Relative Accuracy

Run No.	Start Time	Date (2019)	RM Data (ppm@0%O2)	CEMS Data (ppm@0%O2)	Difference (ppm@0%O2)	Difference Percent
1	08:15	Jun 12	35.26	36.71	-1.45	-4.1%
2	08:48	Jun 12	35.31	36.78	-1.47	-4.2%
3	09:17	Jun 12	35.83	37.30	-1.47	-4.1%
4	09:52	Jun 12	36.08	37.58	-1.50	-4.2%
5 *	10:22	Jun 12	35.53	37.44	-1.91	-5.4%
6	10:50	Jun 12	35.53	37.13	-1.60	-4.5%
7	11:25	Jun 12	35.48	36.94	-1.46	-4.1%
8	11:55	Jun 12	35.25	36.51	-1.26	-3.6%
9	12:24	Jun 12	34.60	36.23	-1.63	-4.7%
10	12:58	Jun 12	34.80	36.25	-1.45	-4.2%
	Average	•	35.35	36.83	-1.48	-4.2%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.1049		
Confidence Coefficient (CC)	0.0806		
t-Value for 9 Data Sets	2.306		
		Limit	
Relative Accuracy (as % of RM)	4.4%	20.0%	

RM = Reference Method (CleanAir Data)

070819165315

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



Marathon Petroleum Company LP Detroit Refinery - Crude/Vacuum Heater Report on Compliance & RATA Testing

Table 2-8:

Crude/Vacuum Heater – NO _X (lb/MMBtu) Relative Accurac	ÿ
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Run No.	Start Time	Date (2019)	RM Data (Ib/MMBtu)	CEMS Data (Ib/MMBtu)	Difference (Ib/MMBtu)	Difference Percent
1	08:15	Jun 12	0.0359	0.0373	-0.0014	-3.9%
2	08:48	Jun 12	0.0359	0.0374	-0.0015	-4.2%
3	09:17	Jun 12	0.0365	0.0379	-0.0014	-3.8%
4	09:52	Jun 12	0.0367	0.0382	-0.0015	-4.1%
5 *	10:22	Jun 12	0.0362	0.0381	-0.0019	-5.2%
6	10:50	Jun 12	0.0361	0.0378	-0.0017	-4.7%
7	11:25	Jun 12	0.0361	0.0376	-0.0015	-4.2%
8	11:55	Jun 12	0.0359	0.0371	-0.0012	-3.3%
9	12:24	Jun 12	0.0352	0.0369	-0.0017	-4.8%
10	12:58	Jun 12	0.0354	0.0369	-0.0015	-4.2%
	Average		0.0360	0.0375	-0.0015	-4.1%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.000154		
Confidence Coefficient (CC)	0.000118		
t-Value for 9 Data Sets	2.306		
		Limit	
Relative Accuracy (as % of RM)	4.5%	20.0%	

RM = Reference Method (CleanAir Data)

070819 165321

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



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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 Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to other units in the refinery for further processing. The Crude Unit consists of process vessels (including heat exchangers and fractionation columns), the Alcorn Heater (EU05-CRUDEHTR-S1), tanks, containers, compressors, pumps, piping, drains, and various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Vacuum Unit (EU04-VACUUM) separates the reduced crude from the Crude Unit through the use of a vacuum column. The reduced crude is separated into light vacuum gas oil, medium vacuum gas oil, heavy vacuum gas oil, and a bottoms product called flux. The various fractions are sent to other units in the refinery for further processing. The vacuum unit consists of process vessels (including heat exchangers and vacuum column), two process heaters, tanks, containers, two cooling towers, flare, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

Both the Crude Heater (EU05-CRUDEHTR-S1) and the Vacuum Heater (EU04-VACHTR-S1) are fired by refinery fuel gas. Emissions are vented to the atmosphere via a common stack known as the Crude/Vacuum Heater Stack (SV04-H1-05-H1), where testing was performed.

Test Location

The sample point locations were determined by EPA Method 1 and PS 2. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 15 and 16 represent the layout of the test location.

Table 3-1: Sampling Point Information

<u>Source</u> Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
Crude/Vacuum Heater St	ack						
PM	5	1-4	4	6	2.5	60	3-1
NSFPM	5B	1-4	4	6	2.5	60	3-1
H_2SO_4	CTM-013 (Mod)	1-4	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 / THC	3A / 25A	1-3	1	7	21	63	3-2
H ₂ O	4 (Mod)	1-3	1	1	60	60	N/A ¹

¹ CTM-013 (Mod) and Method 4 (Mod) sampling were conducted from a single point near the center of the duct.

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Figure 3-1: FPM and NSFPM Sample Point Layout



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	39.2
2	25.0	27.5
3	17.7	19.5
4	11.8	13.0
5	6.7	7.4
6	2.1	2.3

Duct diameters upstream from flow disturbance (A): 5.3	Limit: 0.5
Duct diameters downstream from flow disturbance (B): 2.4	Limit: 2.0

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Figure 3-2:





Sampling Point	Port to Point Distance (meters)	Port to Point Distance (inches)	
1	2.0	78.7	
2	1.2	47.2	
3	0.4	15.7	
Duct diamet	ers upstream fror	n flow disturbance (A): 5.3	Limit: 0.5

Development and a second second for a set of the second (D) O A	
Duct diameters downstream from flow disturbance (B): 2.4 Limit: 2	2.0

End of Section

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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 Michigan 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 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 5B	"Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources"
Method 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
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 CF PS 2	R Part 60, Appendix B Performance Specifications "Specifications and Test Procedures for SO2 and NOx Continuous Emission Monitoring Systems in Stationary Sources"
DC 3	"Specifications and Test Procedures for Ω_2 and Ω_2 Continuous Emission Monitoring Systems in

PS 3 "Specifications and Test Procedures for O₂ and CO₂ Continuous Emission Monitoring Systems in Stationary Sources"

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CTM-013 (Modified)

"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

FPM – USEPA Method 5

FPM emissions were determined using EPA Method 5.

The front-half of the sampling train consisted of a glass nozzle, glass liner, and filter holder heated to $248^{\circ}F \pm 25^{\circ}F$ and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

After exiting the front-half filter, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars were 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.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters dessicated for 24 hours at ambient temperature. The front-half rinses were evaporated at ambient temperature and pressure. The masses from each fraction were then summed for a total FPM mass.

H₂SO₄ – CTM-013 (Modified)

H₂SO₄ emissions were determined referencing modified CTM-013.

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

The sample then passed through a glass coil condenser for collection of sulfuric acid vapor and/or mist. A glass frit/filter was located at the condenser outlet for the collection of residual sulfuric acid mist (SAM) not collected by the condenser. The condenser temperature is regulated by a water jacket and the SAM filter is regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at 140°F \pm 9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point which eliminates the possibility of oxidation of dissolved SO₂ into the H₂SO₄-collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then 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 is maintained below 68°F. The sample gas then flowed into a dry gas meter where the collected sample gas volume is determined by means of a calibrated, dry gas 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 was stabilized in the H₂O matrix until analysis. Following the initial sample recovery, a second DI H₂O rinse was completed.

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Samples, back-up rinses, and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for ion chromatography analysis.

*O*₂, *CO*₂, and *NO*_X – USEPA Methods 3A and 7E; Performance Specifications 2 and 3

Reference method (RM) O_2 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. Carbon dioxide (CO_2) 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 ppmdv).

Calibration error checks were performed by introducing zero nitrogen (N_2) , 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 Appendix D of this report.

Minute-average data points for O_2 and NO_x (dry basis) were collected over a period of 21 minutes for each RATA run. Sampling occurred at the three (3) points specified in Section 8.1.3.2 of PS 2 during each run. A single port was used for each run.

Per EPA Methods 3A and 7E, the average results for each run was drift-corrected. The average result for each run was converted to identical units of measurement as the facility CEMS and compared for relative accuracy.

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 (C_3H_8) on an actual (wet) basis. FIA calibration was performed by introducing zero air, high, mid- and low range C_3H_8 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 EPA Method 18 sampling system consisted of a gas conditioner (for moisture removal), TFE sample lines, a 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 CH_4 and C_2H_6 are insoluble in water. Each bag was filled over a period of 60 minutes for each test run. The Tedlar bags were not analyzed because all Method 25A runs resulted in non-detect concentrations.