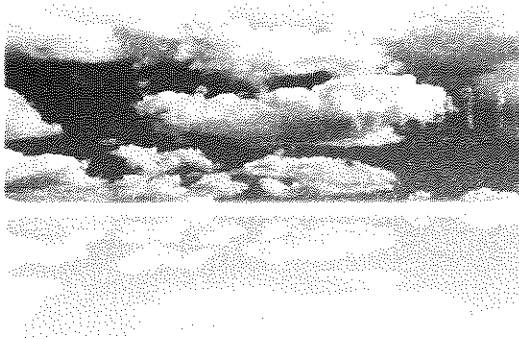
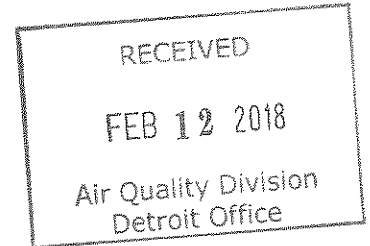




RECEIVED

FEB 13 2018

AIR QUALITY DIVISION



REPORT ON RATA &
COMPLIANCE TESTING

Detroit Refinery
Zurn Boiler Stack (SV22-BR7)

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

CleanAir Project No. 13441
STAC Certificate No. 2007.002.0113.1217
Revision 0, Final Report
January 31, 2018

AIR QUALITY DIVISION

1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted Clean Air Engineering (CleanAir) to successfully complete testing at the newly retrofitted BR10 Boiler (EU27-ZURNBOILER-S1) at the Detroit Refinery, located in Detroit, Michigan. The test program included the following objectives:

- Perform particulate matter (PM), sulfuric acid (H₂SO₄) and volatile organic compounds (VOCs) testing to demonstrate compliance with the MDEQ Permit No. MI-ROP-A9831-2012c;
- Perform a relative accuracy test audit (RATA) on the facility 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	Average Emission	Permit Limit ¹
<u>Zurn Boiler Stack</u>				
	PM (lb/MMBtu)	USEPA M-5	0.0005	0.0019
	PM ₁₀ (lb/MMBtu)	USEPA M-5 / 202	0.0021	0.0076
	H ₂ SO ₄ (lb/MMBtu)	Draft ASTM CCM	7.0E-05	N/A
	VOC (lb/MMBtu)	USEPA M-18 / 25A	<0.0006	0.0055

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

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

Source	Constituent	Reference Method	Relative Accuracy (%) ¹	Applicable Specification	Specification Limit ²
<u>Zurn Boiler Stack</u>					
	O ₂ (% dv)	EPA 3A	0.31	PS3	±1.0 % dv
	NO _x (lb/MMBtu)	EPA 7E, 3A, 19	15.7	PS2	20% of RM
	CO (lb/MMBtu)	EPA 10, 3A, 19	0.12	PS4	5% of Std. ³

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.

³ Standard = 0.10 lb/MMBtu, obtained from MDEQ Permit to Install No. MI-ROP-A9831-2012c.

Test Program Details

Parameters

The test program included the following emissions measurements:

- particulate matter (PM), assumed equivalent to filterable particulate matter (FPM) only
- 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)
- carbon monoxide (CO)
- 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

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	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	12:28	12:49
2	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	13:05	13:26
3	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	13:42	14:03
4	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	14:17	14:38
5	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	14:53	15:14
6	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	15:26	15:47
7	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	16:00	16:21
8	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	16:35	16:56
9	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	17:08	17:29
10	Zurn Boiler Stack	USEPA Method 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	12/12/17	17:41	18:02
0	Zurn Boiler Stack	Draft ASTM CCM	Sulfuric Acid	12/12/17	15:16	16:37
1	Zurn Boiler Stack	Draft ASTM CCM	Sulfuric Acid	12/12/17	16:54	17:54
2	Zurn Boiler Stack	Draft ASTM CCM	Sulfuric Acid	12/12/17	18:15	19:15
3	Zurn Boiler Stack	Draft ASTM CCM	Sulfuric Acid	12/13/17	08:30	09:30
1	Zurn Boiler Stack	USEPA Method 5/202	FPM/CPM	12/13/17	11:30	13:45
2	Zurn Boiler Stack	USEPA Method 5/202	FPM/CPM	12/13/17	14:42	17:30
3	Zurn Boiler Stack	USEPA Method 5/202	FPM/CPM	12/13/17	18:10	20:37
1	Zurn Boiler Stack	USEPA Method 25A/18	VOC	12/13/17	16:37	17:37
2	Zurn Boiler Stack	USEPA Method 25A/18	VOC	12/13/17	17:54	18:54
3	Zurn Boiler Stack	USEPA Method 25A/18	VOC	12/13/17	19:00	20:00

Discussion

Project Synopsis

PM & 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 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).

The inorganic fraction of the CPM portion of the sample train of Run 1 yielded elevated results comparatively to Runs 2 and 3. Despite investigation, there is no overt explanation for this occurrence.

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. Relative accuracy was determined based on nine (9) of ten (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 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.

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.

THC, CH₄ and C₂H₆ emission results were calculated in units of lb/MMBtu as propane. Oxygen concentrations from nearly concurrent Method 5/202 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 5/202 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. For all runs, C₂H₆ concentrations were below analytical detection limits. For runs resulting in non-detects, the final result is treated as 'less than' the entire value of the detection limit. Assuming worst-case scenario, if the resultant VOC emissions are less than the defined THC detection limit, then they are reported as 'less than' the defined THC 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.

An integrated gas sample was not collected with Runs 0, 1 and 2. Ambient conditions were too cold for the gas sample container (a vinyl bag) to have enough elasticity for sufficient collection. O₂ and CO₂ concentrations from nearly concurrent Method 3A test runs were utilized for relevant calculations.

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 natural 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.

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 report.

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:
Zurn Boiler Stack – PM & PM₁₀ Emissions**

Run No.		1	2	3	Average
Date (2017)		Dec 13	Dec 13	Dec 13	
Start Time (approx.)		11:30	14:42	18:10	
Stop Time (approx.)		13:45	17:30	20:37	
Process Conditions					
P ₁	Steam production (mlb/hr)	151.6	151.3	149.6	150.8
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,384	8,384	8,384	
Gas Conditions					
O ₂	Oxygen (dry volume %)	3.8	3.5	3.5	3.6
CO ₂	Carbon dioxide (dry volume %)	9.7	9.8	10.3	9.9
T _s	Sample temperature (°F)	308	310	308	309
B _w	Actual water vapor in gas (% by volume)	15.9	15.5	15.7	15.7
Gas Flow Rate					
Q _a	Volumetric flow rate, actual (acfm)	64,200	66,600	66,500	65,800
Q _s	Volumetric flow rate, standard (scfm)	42,700	44,200	44,200	43,700
Q _{std}	Volumetric flow rate, dry standard (dscfm)	35,900	37,300	37,300	36,800
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	73.18	75.09	75.74	74.67
%I	Isokinetic sampling (%)	100.8	99.5	100.5	100.3
Laboratory Data					
m _{FPM}	Total FPM (g)	0.00134	0.00176	0.00142	
m _{CPM}	Total CPM (g)	0.01185	0.00213	0.00264	
m _{Part}	Total particulate matter (as PM ₁₀) (g)	0.01319	0.00389	0.00406	
FPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	4.05E-08	5.17E-08	4.14E-08	4.45E-08
E _{lbr}	Particulate Rate (lb/hr)	0.0871	0.1158	0.0925	0.0985
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.000415	0.000521	0.000417	0.000451
CPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	3.57E-07	6.26E-08	7.69E-08	1.65E-07
E _{lbr}	Particulate Rate (lb/hr)	0.769	0.140	0.172	0.360
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00366	0.00063	0.00077	0.00169
Total Particulate Matter (as PM₁₀) Results					
C _{sd}	Particulate Concentration (lb/dscf)	3.98E-07	1.14E-07	1.18E-07	2.10E-07
E _{lbr}	Particulate Rate (lb/hr)	0.856	0.256	0.264	0.459
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00407	0.00115	0.00119	0.00214

**Table 2-2:
Zurn Boiler Stack – H₂SO₄ Emissions**

Run No.	1	2	3	Average
Date (2017)	Dec 12	Dec 12	Dec 13	
Start Time (approx.)	16:54	18:15	08:30	
Stop Time (approx.)	17:54	19:15	09:30	
Process Conditions				
P ₂ Steam production (mlb/hr)	149.9	150.7	114.2	138.3
F _d Oxygen-based F-factor (dscf/MMBtu)	8,384	8,384	8,384	
Gas Conditions				
O ₂ Oxygen (dry volume %) ¹	3.5	3.5	3.9	3.6
CO ₂ Carbon dioxide (dry volume %) ¹	10.1	10.1	9.7	10.0
T _s Sample temperature (°F)	311	312	294	306
B _w Actual water vapor in gas (% by volume)	16.1	16.3	16.4	16.3
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	25.27	27.36	25.99	26.21
Laboratory Data (Ion Chromatography)				
m _n Total H ₂ SO ₄ collected (mg)	0.1057	0.0912	0.0481	
Sulfuric Acid Vapor (H₂SO₄) Results				
C _{sd} H ₂ SO ₄ Concentration (lb/dscf)	9.22E-09	7.35E-09	4.08E-09	6.88E-09
C _{sd} H ₂ SO ₄ Concentration (ppm _{dv})	0.036	0.029	0.016	0.027
E _{Fd} H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	0.000093	0.000074	0.000042	0.000070

¹ From nearly concurrent Method 3A test runs.

**Table 2-3:
Zurn Boiler Stack – VOC Emissions**

Run No.		1	2	3	Average
Date (2017)		Dec 13	Dec 13	Dec 13	
Start Time (approx.)		16:37	17:54	19:00	
Stop Time (approx.)		17:37	18:54	20:00	
Process Conditions					
P ₁	Steam production (mlb/hr)	152.4	152.0	148.1	150.8
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,384	8,384	8,384	
Gas Conditions					
O ₂	Oxygen (dry volume %) ¹	3.5	3.5	3.5	3.5
CO ₂	Carbon dioxide (dry volume %)	9.8	10.3	10.3	10.1
B _w	Actual water vapor in gas (% by volume) ¹	15.5	15.7	15.7	15.6
THC Results²					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.539	<0.540	<0.540	<0.539
C _{sd}	Concentration (lb/dscf)	<6.17E-08	<6.18E-08	<6.18E-08	<6.17E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000621	< 0.000622	< 0.000622	< 0.000622
Methane Results³					
C _{sd}	Concentration (ppmdv)	1.04	1.00	0.97	1.00
C _{sd}	Concentration (lb/dscf)	4.33E-08	4.16E-08	4.04E-08	4.18E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	4.36E-04	4.19E-04	4.07E-04	4.21E-04
Ethane Results³					
C _{sd}	Concentration (ppmdv)	<0.79	<0.79	<0.79	<0.79
C _{sd}	Concentration (lb/dscf)	<6.17E-08	<6.17E-08	<6.17E-08	<6.17E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	<6.21E-04	<6.21E-04	<6.21E-04	<6.21E-04
VOC Results⁴					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	< 0.539	< 0.540	< 0.540	< 0.539
C _{sd}	Concentration (lb/dscf)	<6.17E-08	<6.18E-08	<6.18E-08	<6.17E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000621	< 0.000622	< 0.000622	< 0.000622

¹ O₂ data and Moisture data used for lb/MMBtu calculations and ppmv to ppmdv correction obtained from nearly-concurrent M-5/202 runs.

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

³ For methane and ethane, '<' indicates a measured response below the analytical detection limit determined by the laboratory.

⁴ For VOCs, '<' indicates at least one non-detectable fraction was used in the calculations.

**Table 2-4:
 Zurn Boiler Stack – O₂ (%dv) Relative Accuracy**

Run No.	Start Time	Date (2017)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	12:28	Dec 12	3.46	3.79	-0.33	-9.5%
2	13:05	Dec 12	3.50	3.66	-0.16	-4.6%
3 *	13:42	Dec 12	3.57	4.44	-0.87	-24.4%
4	14:17	Dec 12	3.54	3.84	-0.30	-8.5%
5	14:53	Dec 12	3.47	3.88	-0.41	-11.8%
6	15:26	Dec 12	3.45	3.64	-0.19	-5.5%
7	16:00	Dec 12	3.43	3.69	-0.26	-7.6%
8	16:35	Dec 12	3.54	4.25	-0.71	-20.1%
9	17:08	Dec 12	3.47	3.69	-0.22	-6.3%
10	17:41	Dec 12	3.47	3.70	-0.23	-6.6%
Average			3.48	3.79	-0.31	-9.0%

Relative Accuracy Test Audit Results

Standard Deviation of Differences 0.1675
 Confidence Coefficient (CC) 0.1287
 t-Value for 9 Data Sets 2.306

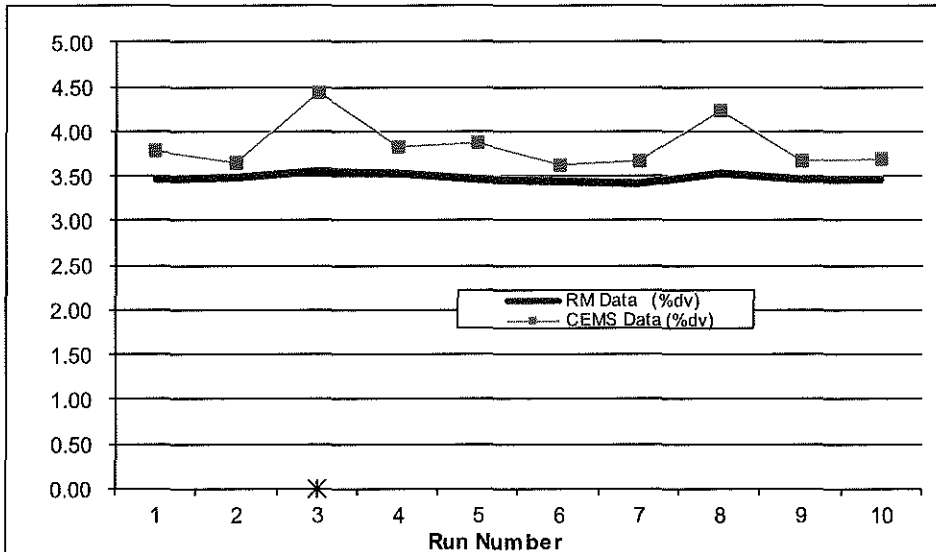
Avg. Abs. Diff. (%dv) **0.31** **Limit 1.0**

RM = Reference Method (CleanAir Data)

011218 152826

CEMS = Continuous Emissions Monitoring System (MPC Data)

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



**Table 2-5:
 Zurn Boiler Stack – NO_x (lb/MMBtu) Relative Accuracy**

Run No.	Start Time	Date (2017)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	12:28	Dec 12	0.0397	0.0364	0.0033	8.3%
2	13:05	Dec 12	0.0442	0.0366	0.0076	17.2%
3	13:42	Dec 12	0.0419	0.0372	0.0047	11.2%
4	14:17	Dec 12	0.0439	0.0372	0.0067	15.3%
5	14:53	Dec 12	0.0388	0.0367	0.0021	5.4%
6	15:26	Dec 12	0.0420	0.0363	0.0057	13.6%
7	16:00	Dec 12	0.0408	0.0364	0.0044	10.8%
8	16:35	Dec 12	0.0420	0.0371	0.0049	11.7%
9 *	17:08	Dec 12	0.0443	0.0363	0.0080	18.1%
10	17:41	Dec 12	0.0436	0.0365	0.0071	16.3%
Average			0.0419	0.0367	0.0052	12.3%

Relative Accuracy Test Audit Results

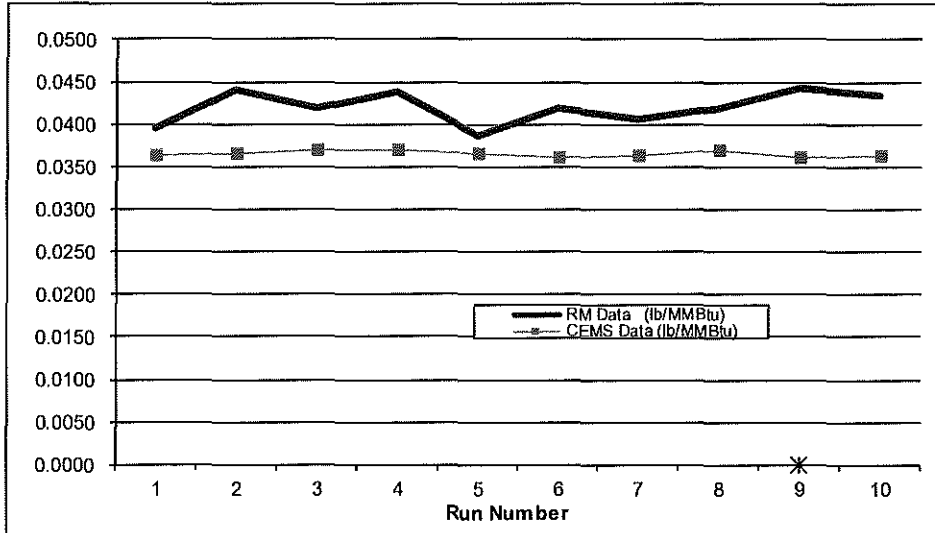
Standard Deviation of Differences	0.00180	
Confidence Coefficient (CC)	0.00139	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	15.7%	20.0%
Relative Accuracy (as % of Appl. Std.)	8.2%	10.0%
Appl. Std. = 0.08 lb/MMBtu		

RM = Reference Method (CleanAir Data)

012'18 152826

CEMS = Continuous Emissions Monitoring System (MPC Data)

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



**Table 2-6:
 Zurn Boiler Stack – CO (lb/MMBtu) Relative Accuracy**

Run No.	Start Time	Date (2017)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1 *	12:28	Dec 12	0.00086	0.00122	-0.00036	-41.9%
2	13:05	Dec 12	0.00096	0.00123	-0.00027	-28.1%
3	13:42	Dec 12	0.00131	0.00124	0.00007	5.3%
4	14:17	Dec 12	0.00113	0.00123	-0.00010	-8.8%
5	14:53	Dec 12	0.00120	0.00123	-0.00003	-2.5%
6	15:26	Dec 12	0.00135	0.00124	0.00011	8.1%
7	16:00	Dec 12	0.00133	0.00127	0.00006	4.5%
8	16:35	Dec 12	0.00120	0.00123	-0.00003	-2.5%
9	17:08	Dec 12	0.00126	0.00130	-0.00004	-3.2%
10	17:41	Dec 12	0.00123	0.00132	-0.00009	-7.3%
Average			0.00122	0.00125	-0.00004	-2.9%

Relative Accuracy Test Audit Results

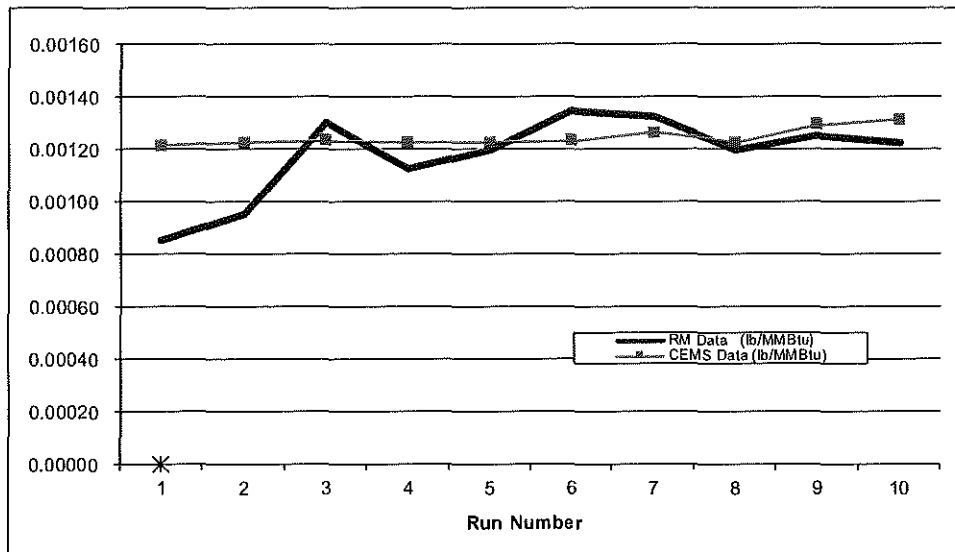
Standard Deviation of Differences	0.000114	
Confidence Coefficient (CC)	0.000087	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	10.1%	10.0%
Relative Accuracy (as % of Appl. Std.)	0.12%	5.0%
Appl. Std. = 0.1 lb/MMBtu		

RM = Reference Method (CleanAir Data)

011518 140900

CEMS = Continuous Emissions Monitoring System (MPC Data)

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



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 BR10 Boiler (EU27-ZURNBOILER-S1) was recently retrofitted with a new package boiler utilizing low NO_x burners and flue gas recirculation as required in the Tier 3 Gasoline Project Permit (PTI 118-15). This boiler generates steam required by other refinery process components. The unit is fired by natural gas. Emissions are vented to the atmosphere via the Zurn Boiler Stack (SV22-BR7), which is the same stack used for the original boiler.

Test Locations

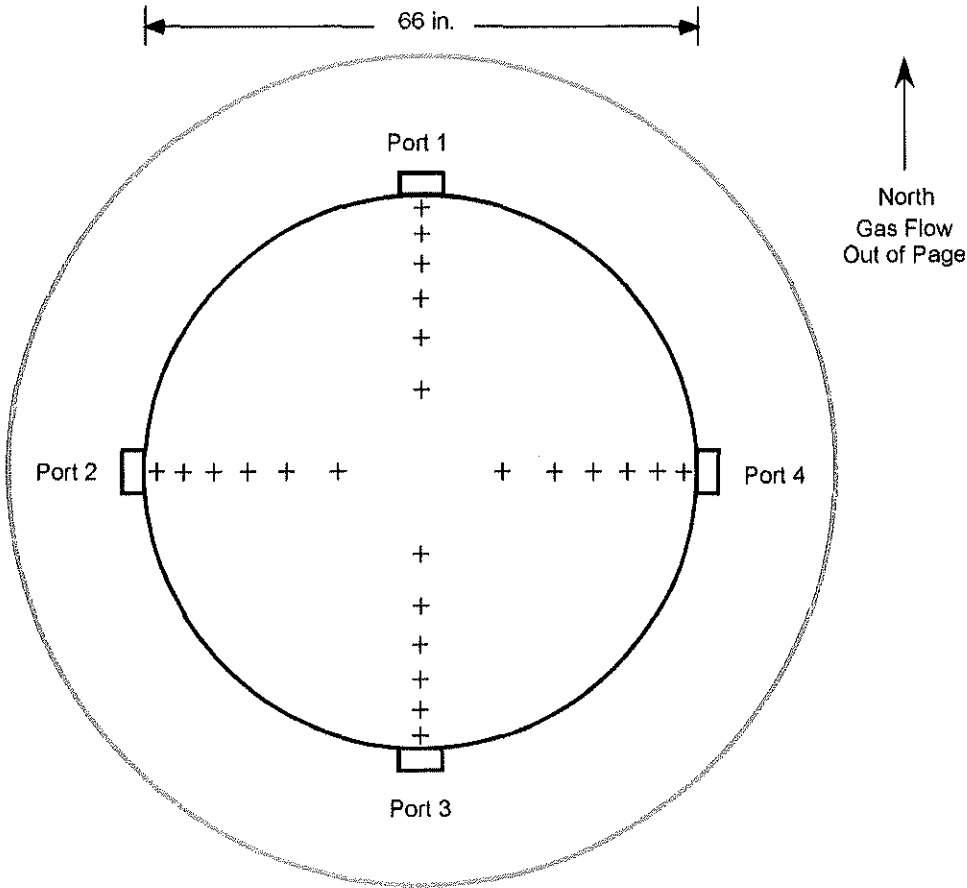
The sample point locations were determined by EPA Methods 1 and 7E specifications. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 13 and 14 represent the layout of the test location.

**Table 3-1:
Sampling Information**

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

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

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

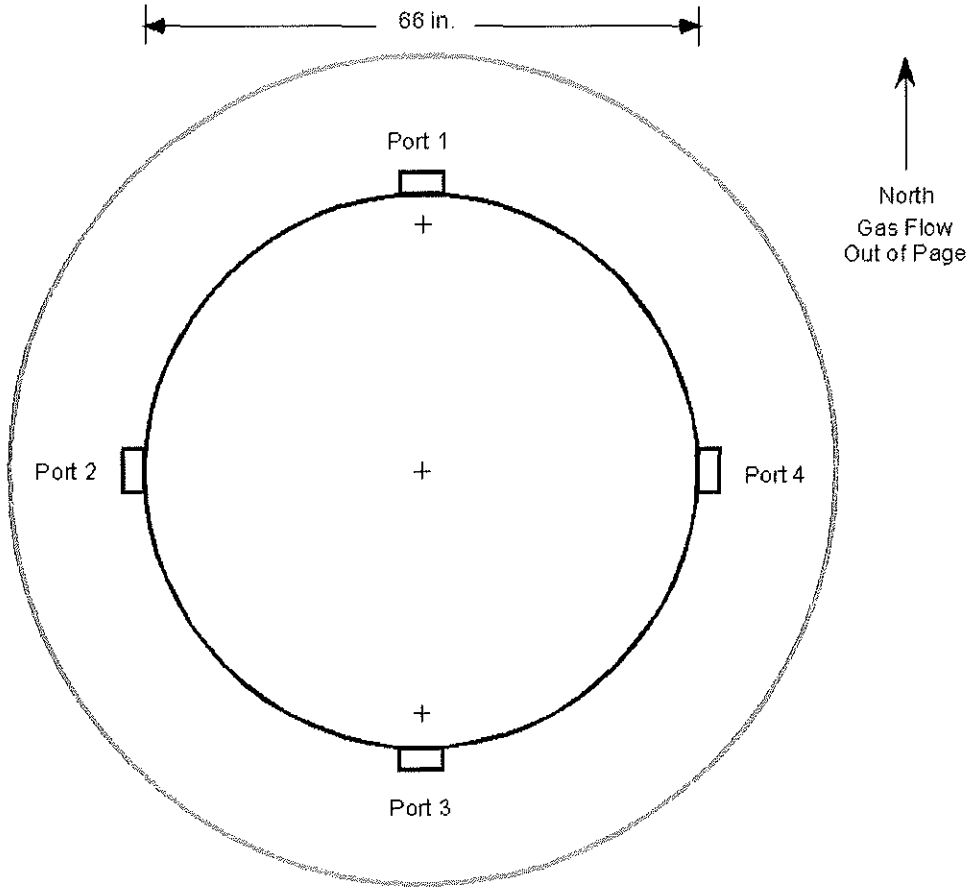


Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	23.5
2	25.0	16.5
3	17.7	11.7
4	11.8	7.8
5	6.7	4.4
6	2.1	1.4

Duct diameters upstream from flow disturbance (A): 10.0
 Duct diameters downstream from flow disturbance (B): 3.4

Limit: 0.5
 Limit: 2.0

**Figure 3-2:
 O₂, CO₂, NO_x & CO Sample Point Layout (EPA Performance Specification 2)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	55.0
2	50.0	33.0
3	16.7	11.0

Duct diameters upstream from flow disturbance (A): 10.0
 Duct diameters downstream from flow disturbance (B): 3.4

Limit: 0.5
 Limit: 2.0

End of Section

RECEIVED
 FEB 13 2010

4. METHODOLOGY

AIR QUALITY DIVISION

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the USEPA and the Michigan Department of Environmental Quality (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 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 Procedure)"
- Method 10 "Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
- Method 18 "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"
- 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 CO 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"

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

PM and PM₁₀ Testing – USEPA Method 5/202

Particulate matter (PM) emissions were determined using EPA Method 5. PM is equivalent to filterable particulate matter (FPM). PM₁₀ emissions were determined using EPA Method 5/202. PM₁₀ is equivalent to the sum of FPM less than 10 micrometers (μm) in diameter (FPM₁₀) and CPM.

The front-half (Method 5 portion) of the sampling train consists of a glass nozzle, glass liner and filter holder heated to $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$ 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 (SO_2) and nitrogen oxide (NO_x) interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water, and SO_2 and NO_x were absorbed and partially oxidized before they could be purged out with nitrogen (N_2).

Flue gas exiting the front-half heated filter passes through a coiled condenser and dry impinger system jacketed by water continually circulated at ambient temperature. Moisture is removed from the flue gas without bubbling through the condensed water. Flue gas then passes through a tetrafluoromethane (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 passes through two (2) additional impingers surrounded by ice in a “cold” section of the impinger bucket. The moisture collected in these impingers will not be analyzed for CPM and is only collected to determine the flue gas moisture and to thoroughly dry the gas. The sample gas then flows into a calibrated dry gas meter where the collected sample gas volume is 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 N_2 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 collected to quantify background contamination. All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Method 202 samples were maintained at a temperature $< 85^{\circ}\text{F}$ during transport to the laboratory.

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

Reference method O₂ concentrations were determined using a paramagnetic analyzer per EPA Method 3A. Reference method NO_x emissions were determined using a chemiluminescent analyzer per EPA Method 7E. Reference method 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 measures concentration on a dry basis (units of %dv or ppm_{dv}).

Calibration error checks were performed by introducing zero 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 the report.

Minute-average data points for O₂, NO_x and CO (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, 7E and 10, the average result 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 and EPA Method 18 to quantify methane (CH₄) and ethane (C₂H₆) emissions. VOC emissions are equivalent to THC emissions, minus CH₄ and C₂H₆.

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 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 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

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

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 (depending on the required probe length) 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 second quartz fiber filter (referred to as the sulfuric acid mist (SAM) filter) is located at the condenser outlet for the collection of residual 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 ± 9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the 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 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 was stabilized in the H₂O matrix until analysis.

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