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**AIR QUALITY DIV.**



REPORT ON RATA &  
COMPLIANCE TESTING

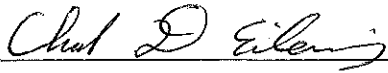
Detroit Refinery  
Zurn Boiler Stack (SV22-BR7)

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

CleanAir Project No. 13240-2  
STAC Certificate No. 2007.002.0113.1217  
Revision 0, Final Report  
May 24, 2017

## COMMITMENT TO QUALITY

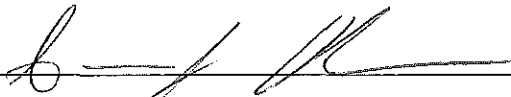
To the best of our knowledge, the data presented in this report are accurate, complete, error free and representative of the actual emissions during the test program. Clean Air Engineering operates in conformance with the requirements of ASTM D7036-04 Standard Practice for Competence of Air Emission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



May 24, 2017

Chad Eilering  
Field Test Leader  
ceilering@cleanair.com  
(800)-627-0033 ext. 4536

Date

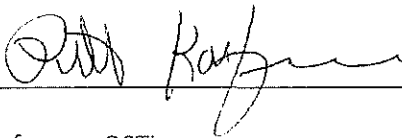


May 24, 2017

Andy Obuchowski  
Midwest Engineering Group Leader  
aobuchowski@cleanair.com  
(800) 627-0033 ext. 4537

Date

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



May 24, 2017

Peter Kaufmann, QSTI  
Project Manager  
pkaufmann@cleanair.com  
(847) 778-8172

Date

**RECEIVED****1. PROJECT OVERVIEW**

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**AIR QUALITY DIV.****Test Program Summary**

Marathon Petroleum Company LP (MPC) contracted Clean Air Engineering (CleanAir) to successfully complete testing on the Zurn Boiler Stack at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), H<sub>2</sub>SO<sub>4</sub>, and volatile organic compound (VOC) testing to demonstrate compliance with the MDEQ Permit No. MI-ROP-A9831-201c;
- Perform a relative accuracy test audit (RATA) on the facility continuous emissions monitoring system (CEMS) for oxygen (O<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>).

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**

<u>Source</u> Constituent	<u>Sampling</u> Method	<u>Average</u> Emission	<u>Permit Limit</u> <sup>1</sup>
<i>Zurn Boiler Stack</i>			
PM (lb/MMBtu)	USEPA 5	0.0012	0.0019
H <sub>2</sub> SO <sub>4</sub> (ppm dv)	Draft ASTM CCM	0.015	N/A
H <sub>2</sub> SO <sub>4</sub> (lb/MMBtu)	Draft ASTM CCM	4.7E-05	N/A
VOC (lb/MMBtu)	USEPA 25A/18	<0.00072	0.0055

<sup>1</sup> Permit limits obtained from MDEQ Permit No: MI-ROP-A9831-201c.

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

<u>Source</u> Constituent	<u>Reference</u> Method	<u>Relative</u> Accuracy (%) <sup>1</sup>	<u>Applicable</u> Specification	<u>Specification</u> Limit <sup>2</sup>
<i>Zurn Boiler Stack</i>				
O <sub>2</sub> (% dv)	EPA 3A	0.27	PS3	±1.0 % dv
NO <sub>x</sub> (lb/MMBtu)	EPA 7E, 3A, 19	3.8	PS2	20% of RM

<sup>1</sup> 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.

<sup>2</sup> Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

## Test Program Details

### Parameters

The test program included the following emissions measurements:

- particulate matter (PM), assumed equivalent to filterable particulate matter (FPM) only
- nitrogen oxide (NO<sub>x</sub>)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
  - methane (CH<sub>4</sub>)
  - ethane (C<sub>2</sub>H<sub>6</sub>)
- sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>)
- flue gas composition (e.g., O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O)
- 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 5	FPM	04/05/17	09:55	12:00
2	Zurn Boiler Stack	USEPA Method 5	FPM	04/05/17	12:39	14:43
3	Zurn Boiler Stack	USEPA Method 5	FPM	04/05/17	15:26	N/A*
4	Zurn Boiler Stack	USEPA Method 5	FPM	04/06/17	08:46	10:51
0	Zurn Boiler Stack	CTM-013 (mod) / Draft ASTM CCM	H <sub>2</sub> SO <sub>4</sub>	04/06/17	11:50	12:50
1	Zurn Boiler Stack	CTM-013 (mod) / Draft ASTM CCM	H <sub>2</sub> SO <sub>4</sub>	04/06/17	13:47	14:47
2	Zurn Boiler Stack	CTM-013 (mod) / Draft ASTM CCM	H <sub>2</sub> SO <sub>4</sub>	04/06/17	15:20	16:20
3	Zurn Boiler Stack	CTM-013 (mod) / Draft ASTM CCM	H <sub>2</sub> SO <sub>4</sub>	04/06/17	16:48	17:48
1	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	09:23	09:44
2	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	09:53	10:14
3	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	10:23	10:44
4	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	10:56	11:17
5	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	11:26	11:47
6	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	11:58	12:19
7	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	12:28	12:49
8	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	13:00	13:21
9	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	13:29	13:50
10	Zurn Boiler Stack	USEPA Methods 3A, 7E	O <sub>2</sub> / NO <sub>x</sub>	04/06/17	14:06	14:27
1	Zurn Boiler Stack	USEPA Methods 3A, 25A	O <sub>2</sub> / THC	04/06/17	16:56	17:56
2	Zurn Boiler Stack	USEPA Methods 3A, 25A	O <sub>2</sub> / THC	04/07/17	08:33	09:33
3	Zurn Boiler Stack	USEPA Methods 3A, 25A	O <sub>2</sub> / THC	04/07/17	09:40	10:40
1	Zurn Boiler Stack	USEPA Method 4	Moisture	04/07/17	08:33	09:33
2	Zurn Boiler Stack	USEPA Method 4	Moisture	04/07/17	09:40	10:40

\* Due to inclement weather this run was incomplete

## Discussion

### *Project Synopsis*

#### FPM Testing – USEPA Method 5

The PM emission rate is assumed equivalent to FPM emission rate. Four (4) 120-minute Method 5 test runs were performed on April 5 and 6, 2017. The result was expressed as the average of three valid runs.

During Run 3, the PM test was paused approximately 85 minutes into the run due to inclement weather. Because forecasts determined the inclement weather would continue late into the night, the decision was made on-site to abort Run 3 and to conduct Run 4 the following day. Run 3 was not recovered.

#### H<sub>2</sub>SO<sub>4</sub> Testing – Draft ASTM Controlled Condensation Method

Four (4) 60-minute test runs, one conditioning test (Run 0) followed by three official tests (Runs 1-3) were performed on April 6. The result was expressed as the average of three valid runs excluding Run 0.

#### VOC Testing – USEPA Methods 25A and 18

Three (3) 60-minute Method 25A test runs for total hydrocarbons (THCs) were performed concurrently with three (3) 60-minute Method 18 bag collections for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The results for each parameter were expressed as the average of three valid runs.

The VOC emission rate is normally equivalent to THC emission rate, minus CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emission rate. For all runs, the calculated emission rate of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> detected through analysis of each Method 18 sample bag exceeded the amount of THCs measured by the online THC analyzer. This is likely due to variations in the calibration standards, measurement and analytical technique. Therefore, VOC emissions are reported as a value “less than” 1% of the calibration span of the THC instrument.

Moisture contents, utilized to convert wet volumetric basis concentrations to dry basis, were determined for each run from the following sources:

- For Run 1, procedures incorporated in nearly concurrent ASTM Draft CCM Run 3;
- For Run 2, procedures in concurrent EPA Method 4 Run 1;
- For Run 3, procedures in concurrent EPA Method 4 Run 2.

#### CEMS RATA

Minute-average data points for O<sub>2</sub>, carbon dioxide (CO<sub>2</sub>) and NO<sub>x</sub> (dry basis) were collected over a period of 21 minutes for each RATA Reference Method (RM) run. The average result for each RM run was calculated and compared to the average result from the facility CEMS over an identical time interval in order to calculate relative accuracy (RA).

The nine (9) best fit runs were used to calculate the RA.

#### Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppm<sub>v</sub>) were converted to units of pounds per million Btu (lb/MMBtu) using the oxygen-based fuel factor (F<sub>d</sub>) for natural gas in EPA Method 19, Table 19-2.

## 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 Emissions (USEPA Method 5)**

Run No.		1	2	4	Average
Date (2017)		Apr 5	Apr 5	Apr 6	
Start Time (approx.)		09:55	12:39	08:46	
Stop Time (approx.)		12:00	14:43	10:51	
<b>Process Conditions</b>					
P <sub>1</sub>	Natural gas flow rate (Mscf/day)	137	136	135	136
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.5	6.6	6.2	6.4
CO <sub>2</sub>	Carbon dioxide (dry volume %)	8.4	8.4	8.7	8.5
T <sub>s</sub>	Sample temperature (°F)	312	313	312	312
B <sub>w</sub>	Actual water vapor in gas (% by volume)	14.0	14.4	14.5	14.3
<b>Gas Flow Rate</b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	32,000	31,300	33,100	32,200
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	21,400	20,800	21,600	21,300
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	18,400	17,800	18,500	18,200
Q <sub>a</sub>	Volumetric flow rate, actual (acf/hr)	1,920,000	1,880,000	1,990,000	1,930,000
Q <sub>s</sub>	Volumetric flow rate, standard (scf/hr)	1,280,000	1,250,000	1,300,000	1,280,000
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscf/hr)	1,100,000	1,070,000	1,110,000	1,090,000
<b>Sampling Data</b>					
V <sub>std</sub>	Volume metered, standard (dscf)	50.54	49.57	54.59	51.57
%I	Isokinetic sampling (%)	100.7	101.8	108.1	103.5
<b>Laboratory Data</b>					
m <sub>filter</sub>	Matter collected on filter(s) (g)	0.00074	0.00103	0.00095	
m <sub>s</sub>	Matter collected in solvent rinse(s) (g)	0.00138	0.00167	0.00106	
m <sub>n</sub>	Total FPM (g)	0.00212	0.00270	0.00201	
<b>FPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	9.25E-08	1.20E-07	8.12E-08	9.79E-08
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.10	0.13	0.090	0.11
E <sub>T/yr</sub>	Particulate Rate (Ton/yr)	0.45	0.56	0.39	0.47
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.0012	0.0015	0.0010	0.0012

Run 3 was halted due to inclement weather, sample not recovered.

**Table 2-2:  
Zurn Boiler Stack – Sulfuric Acid Mist Emissions (Draft ASTM CCM)**

Run No.		1	2	3	Average
Date (2017)		Apr 6	Apr 6	Apr 6	
Start Time (approx.)		13:47	15:20	16:48	
Stop Time (approx.)		14:47	16:20	17:48	
<b>Process Conditions</b>					
P <sub>1</sub>	Natural gas flow rate (Mscf/day)	138	139	139	<b>139</b>
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	<b>8,710</b>
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.4	6.3	6.1	<b>6.3</b>
CO <sub>2</sub>	Carbon dioxide (dry volume %)	8.6	8.6	8.9	<b>8.7</b>
T <sub>s</sub>	Sample temperature (°F)	307	314	309	<b>310</b>
B <sub>w</sub>	Actual water vapor in gas (% by volume)	14.2	14.2	14.2	<b>14.2</b>
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	28.73	28.83	28.26	<b>28.61</b>
<b>Laboratory Data (Ion Chromatography)</b>					
m <sub>n</sub>	Total H <sub>2</sub> SO <sub>4</sub> collected (mg)	0.0927	0.0285	0.0259	
<b>Sulfuric Acid Vapor (H<sub>2</sub>SO<sub>4</sub>) Results</b>					
C <sub>sd</sub>	H <sub>2</sub> SO <sub>4</sub> Concentration (lb/dscf)	7.1E-09	2.2E-09	2.0E-09	<b>3.8E-09</b>
C <sub>sd</sub>	H <sub>2</sub> SO <sub>4</sub> Concentration (ppmdv)	0.028	0.0086	0.0079	<b>0.015</b>
E <sub>Fd</sub>	H <sub>2</sub> SO <sub>4</sub> Rate - Fd-based (lb/MMBtu)	8.9E-05	2.7E-05	2.5E-05	<b>4.7E-05</b>

**Table 2-3:  
Zurn Boiler Stack – VOC Emissions (USEPA Methods 25A & 18)**

Run No.	1	2	3	Average
Date (2017)	Apr 6	Apr 7	Apr 7	
Start Time (approx.)	16:56	08:33	09:40	
Stop Time (approx.)	17:56	09:33	10:40	
<b>Process Conditions</b>				
P <sub>1</sub> Steam production (mlb/hr)	61.0	56.8	55.9	<b>57.9</b>
P <sub>2</sub> Natural gas flow rate (mscf/day)	139	138	139	<b>139</b>
F <sub>d</sub> Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	<b>8,710</b>
<b>Gas Conditions</b>				
O <sub>2</sub> Oxygen (dry volume %)	5.8	5.9	5.7	<b>5.8</b>
CO <sub>2</sub> Carbon dioxide (dry volume %)	8.9	8.8	8.9	<b>8.9</b>
B <sub>w</sub> Actual water vapor in gas (% by volume) <sup>1</sup>	14.2	14.2	14.9	<b>14.4</b>
<b>THC Results</b>				
C <sub>sd</sub> Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	<0.52	<0.52	<0.53	<b>&lt;0.52</b>
C <sub>sd</sub> Concentration (lb/dscf)	<5.99E-08	<5.99E-08	<6.04E-08	<b>&lt;6.01E-08</b>
E <sub>Fd</sub> Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	< 0.00072	< 0.00073	< 0.00072	<b>&lt; 0.00072</b>
<b>Methane Results</b>				
C <sub>sd</sub> Concentration (ppmdv)	6.7	<0.26	0.78	<b>&lt;2.59</b>
C <sub>sd</sub> Concentration (lb/dscf)	2.80E-07	<1.08E-08	3.25E-08	<b>&lt;1.08E-07</b>
E <sub>Fd</sub> Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00337	< 0.00013	0.00039	<b>&lt; 0.00130</b>
<b>Ethane Results</b>				
C <sub>sd</sub> Concentration (ppmdv)	<0.22	<0.22	<0.22	<b>&lt;0.22</b>
C <sub>sd</sub> Concentration (lb/dscf)	<1.72E-08	<1.72E-08	<1.72E-08	<b>&lt;1.72E-08</b>
E <sub>Fd</sub> Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	< 0.00021	< 0.00021	< 0.00021	<b>&lt; 0.00021</b>
<b>VOC Results</b>				
C <sub>sd</sub> Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	<0.52	<0.52	<0.53	<b>&lt; 0.52</b>
E <sub>Fd</sub> Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	< 0.00072	< 0.00073	< 0.00072	<b>&lt; 0.00072</b>



**Table 2-4:  
 Zurn Boiler Stack – O<sub>2</sub> (%dv) Relative Accuracy (USEPA Method 3A)**

Run No.	Start Time	Date (2017)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1 *	09:23	Apr 6	6.17	5.88	0.29	4.7%
2	09:53	Apr 6	6.11	5.83	0.28	4.6%
3	10:23	Apr 6	5.94	5.70	0.24	4.0%
4	10:56	Apr 6	6.08	5.80	0.28	4.6%
5	11:26	Apr 6	6.19	5.91	0.28	4.5%
6	11:58	Apr 6	6.07	5.80	0.27	4.4%
7	12:28	Apr 6	6.21	5.94	0.27	4.3%
8	13:00	Apr 6	6.31	6.03	0.28	4.4%
9	13:29	Apr 6	6.26	5.99	0.27	4.3%
10	14:06	Apr 6	6.21	5.92	0.29	4.7%
<b>Average</b>			<b>6.15</b>	<b>5.88</b>	<b>0.27</b>	<b>4.4%</b>

**Relative Accuracy Test Audit Results**

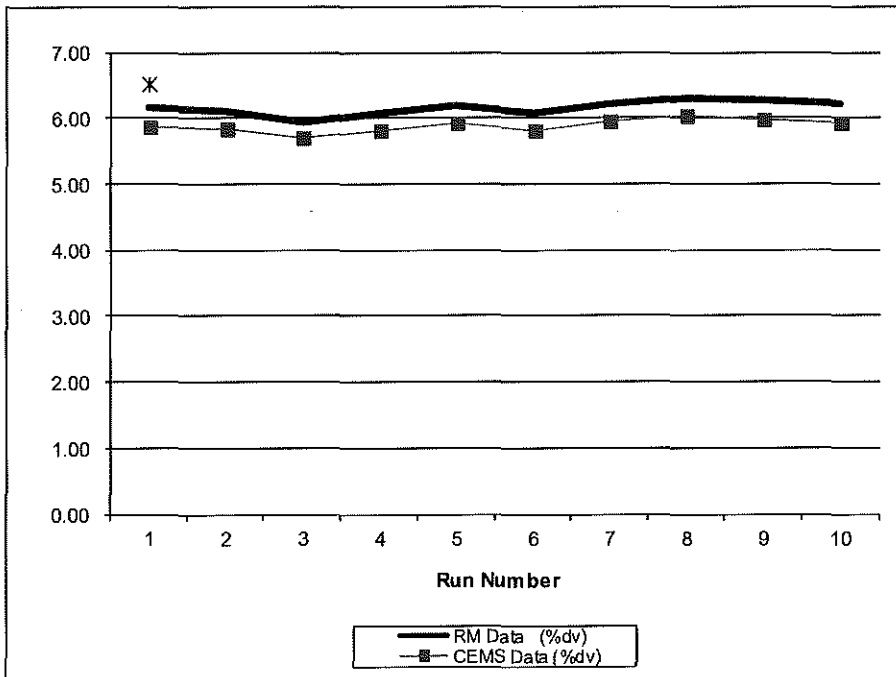
Standard Deviation of Differences	0.01414
Confidence Coefficient (CC)	0.01087
t-Value for 9 Data Sets	2.306
<b>Avg. Abs. Diff. (%dv)</b>	<b>0.27</b>
<b>Limit</b>	<b>1.0</b>

RM = Reference Method (CleanAir Data)

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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<sub>x</sub> (lb/MMBtu) Relative Accuracy (USEPA Method 7E)**

Run No.	Start Time	Date (2017)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	09:23	Apr 6	0.13	0.13	0.00	-2.7%
2	09:53	Apr 6	0.13	0.13	0.00	-2.9%
3	10:23	Apr 6	0.13	0.13	0.00	-3.1%
4	10:56	Apr 6	0.14	0.13	0.01	3.7%
5	11:26	Apr 6	0.14	0.14	0.00	3.0%
6 *	11:58	Apr 6	0.13	0.14	-0.01	-4.5%
7	12:28	Apr 6	0.13	0.14	-0.01	-4.1%
8	13:00	Apr 6	0.13	0.13	0.00	-3.6%
9	13:29	Apr 6	0.13	0.13	0.00	-3.2%
10	14:06	Apr 6	0.13	0.13	0.00	-2.0%
<b>Average</b>			<b>0.13</b>	<b>0.13</b>	<b>0.00</b>	<b>0.0%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences      0.003928  
 Confidence Coefficient (CC)              0.003019  
 t-Value for 9 Data Sets                  2.306

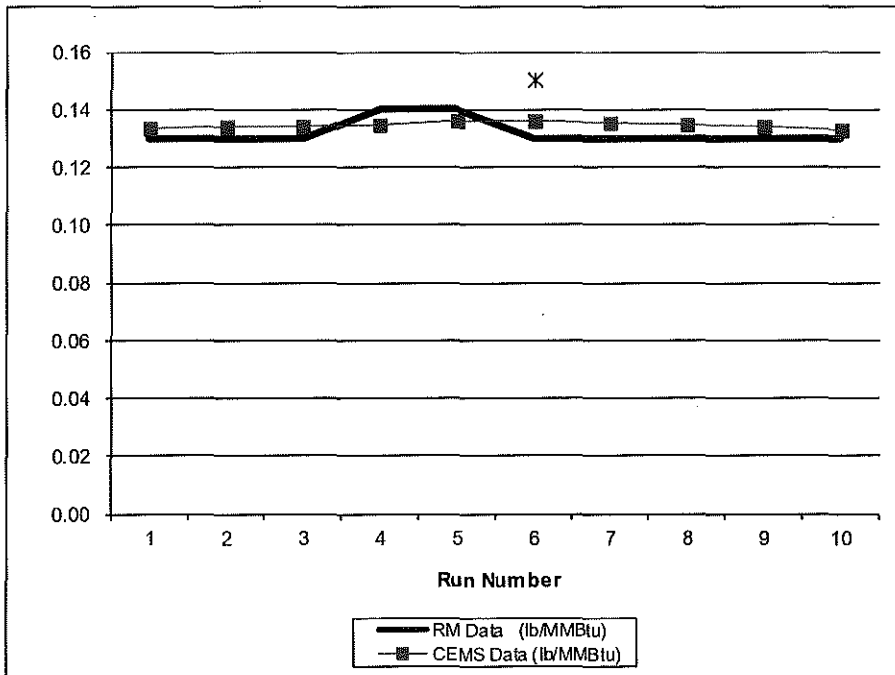
Relative Accuracy (as % of RM)          **3.8%**      **Limit 20.0%**

RM = Reference Method (CleanAir Data)

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CEMS = Continuous Emissions Monitoring System (MPC Data)

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



### 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 Zurn Boiler (EG27-ZURNBOILER) 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).

#### Test Locations

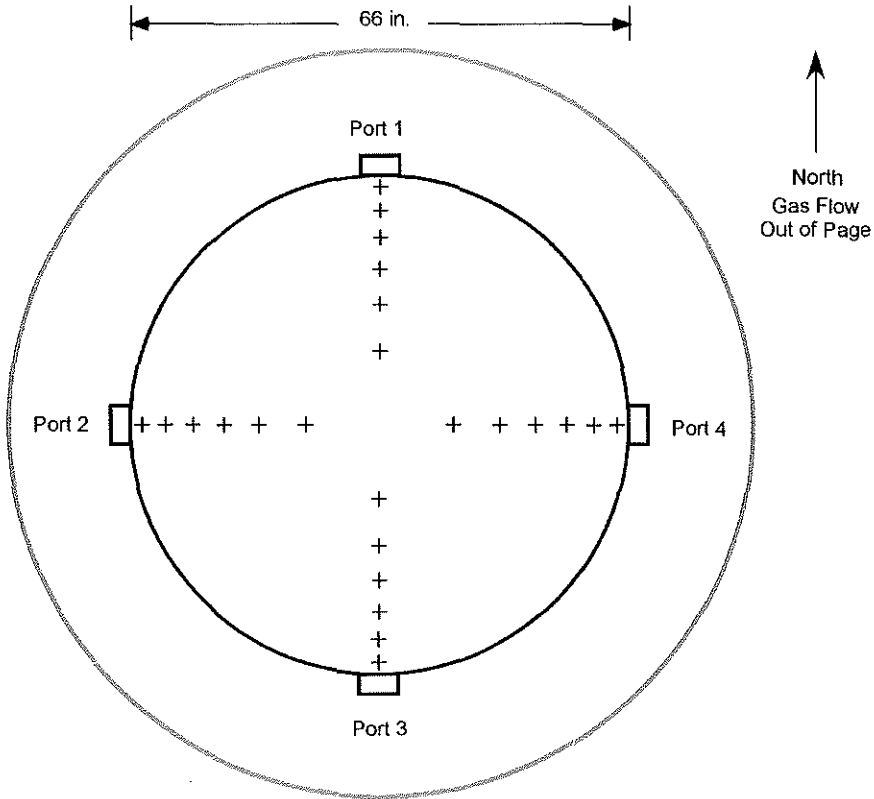
Sampling point locations were determined via EPA Method 1 and Performance Specification 2. Table 3-1 presents the sampling information for the test locations. The figures shown on pages 12 and 13 represent the layout of the test location.

**Table 3-1:  
Sampling Information**

<b>Source</b>		<b>Run</b>		<b>Points per</b>	<b>Minutes</b>	<b>Total</b>	
<b>Constituent</b>	<b>Method</b>	<b>No.</b>	<b>Ports</b>	<b>Port</b>	<b>per Point</b>	<b>Minutes</b>	<b>Figure</b>
<u>Zurn Boiler Stack</u>							
PM	EPAM5	1-2, 4	4	6	5	120	3-1
H <sub>2</sub> SO <sub>4</sub>	Draft ASTM CCM	1-3	1	1	60	60	N/A <sup>1</sup>
O <sub>2</sub> / CO <sub>2</sub> / CH <sub>4</sub> / C <sub>2</sub> H <sub>6</sub> / THC	3A, 18, 25A	1-3	1	3	20	60	3-2
O <sub>2</sub> / No <sub>x</sub>	3A+PS3, 7E+PS2	1-10	1	3	7	21	3-2

<sup>1</sup> Sampling occurred at a single point near the center of the duct.

**Figure 3-1:  
 Zurn Boiler Stack Sample Point Layout (EPA Method 1)**

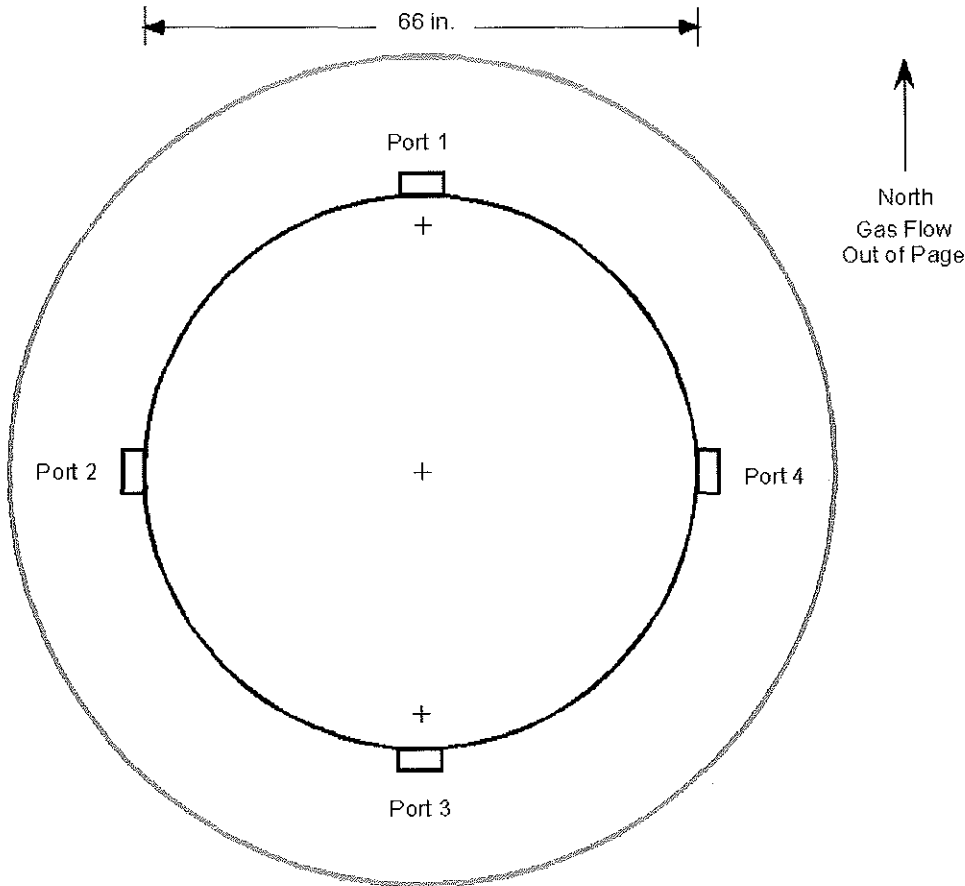


Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	23.5
2	25.0	16.5
3	17.7	11.7
4	11.8	7.8
5	6.7	4.4
6	2.1	1.4

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:  
 Zurn Boiler Stack 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

## 4. METHODOLOGY

### Procedures and Regulations

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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 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 <sub>2</sub> and NO <sub>x</sub> Continuous Emission Monitoring Systems in Stationary Sources"
PS3	"Specifications and Test Procedures for O <sub>2</sub> and CO <sub>2</sub> Continuous Emission Monitoring Systems in 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

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### PM Testing - EPA Method 5

The front-half 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.

After exiting the filter, the flue gas passed through a Teflon line into a series of knockout jars surrounded by ice. The purpose of the knockout jars was to thoroughly remove the moisture from the gas stream and to determine the flue gas moisture. The sample gas then flowed through a calibrated dry gas meter to determine the sample gas volume.

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.

### VOC Testing - EPA Method 25A and Method 18

VOC emissions were determined using EPA Method 25A to quantify total hydrocarbon emissions (THC) and EPA Method 18 to quantify methane (CH<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) emissions.

The Method 25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted near the centroid of the duct or at a point no closer than one (1) meter to the duct wall at a constant rate and delivered at 250°F to a flame ionization analyzer (FIA) which continuously measured minute-average THC concentration expressed in terms of propane (C<sub>3</sub>H<sub>8</sub>) on an actual (wet) basis.

FIA calibration was performed by introducing a zero gas, high, mid- and low range C<sub>3</sub>H<sub>8</sub> calibration gases to the inlet of the sampling system's heated filter. Drift 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 allowed a slipstream of the flue gas from the Method 25A sample delivery system to be delivered into a FlexFoil® bag at a constant rate. The moisture condensate was not collected for analysis as CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are insoluble in water. A sample bag was filled during each 60-minute THC sampling run.

Analysis for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> 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. A minimum of 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 CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> concentrations introduced directly into the GC. Upon completion of calibration, a recovery study was performed by spiking one (1) of the bag samples with a known concentration of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, storing the bags for the same period of time prior to analysis as the field samples, and analyzing the bags to determine percent recovery.

### H<sub>2</sub>SO<sub>4</sub> Testing - Draft ASTM Controlled Condensation Method

H<sub>2</sub>SO<sub>4</sub> emissions are determined referencing the Draft ASTM Controlled Condensation Method.

A gas sample was extracted 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 was 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  $140^{\circ}\text{F} \pm 9^{\circ}\text{F}$  plus  $2^{\circ}\text{F}$  for each 1% moisture above 16% flue gas moisture. This keeps the gas temperature above the water dew point but below the sulfuric acid dew point. The absence of liquid water eliminates the oxidation of dissolved  $\text{SO}_2$  into the  $\text{H}_2\text{SO}_4$ -collecting fraction of the sample train.

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  $68^{\circ}\text{F}$ . The sample gas was then passed through a dry gas meter, where the collected sample gas volume is determined by means of a calibrated, dry gas meter.

The  $\text{H}_2\text{SO}_4$ -collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI  $\text{H}_2\text{O}$  as the recovery/extraction solvent; any  $\text{H}_2\text{SO}_4$  disassociates into sulfate ion ( $\text{SO}_4^{2-}$ ) and is stabilized in the  $\text{H}_2\text{O}$  matrix until analysis.

Prior to the first official test run, a 60-minute sample conditioning run was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the  $\text{H}_2\text{SO}_4$ -collecting portion of the sample train). The sample conditioning run is referred to as run zero (0). The conditioning run was recovered in the same manner as the official test runs, but the condenser rinse and SAM filter were not analyzed.

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

## $\text{O}_2$ and $\text{NO}_x$ RATA Testing - EPA Methods 3A and 7E

The RATA for  $\text{NO}_x$  and  $\text{O}_2$  was conducted per 40 CFR 75, Appendix A specifications.

RM  $\text{O}_2$  emissions were determined using a paramagnetic analyzer per EPA Method 3A.  $\text{NO}_x$  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 measures concentration on a dry basis (units of %dv or ppm<sub>dv</sub>).

Calibration error checks were performed by introducing "high-level", "mid-level", and "zero-level" calibration gases to the inlet of each analyzer during calibration error checks. Bias checks were performed before the first run and after at least every third run thereafter by introducing calibration gas to the inlet of the sampling system's heated filter. Documentation of interference checks and  $\text{NO}_2$  converter efficiency checks are included in Appendix D of this report.

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

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*End of Section*