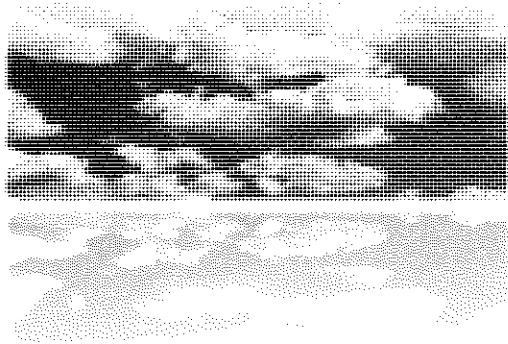




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REPORT ON COMPLIANCE &  
RATA TESTING

Detroit Refinery

B&W Boiler Stack (SV-B&WBoiler1)

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

CleanAir Project No. 13517-2  
A2LA ISO 17025 Certificate No. 4342.01  
A2LA / STAC Certificate No. 4342.02  
Revision 1, Final Report  
April 26, 2018

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# 1. PROJECT OVERVIEW

## Test Program Summary

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

- Perform particulate matter (PM), sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>), 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 (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 Compliance Results**

Source Constituent (Units)	Sampling Method (USEPA)	Average Emission	Permit Limit <sup>1</sup>
<i>B&amp;W Boiler Stack</i>			
PM (lb/MMBtu)	5	0.0011	0.0019
PM <sub>10</sub> (lb/MMBtu)	5 / 202	0.0026	0.0076
H <sub>2</sub> SO <sub>4</sub> (lb/MMBtu)	Draft ASTM CCM	0.00035	N/A
VOC (lb/MMBtu)	18 / 25A	<0.00068	0.0055

<sup>1</sup> Permit limits obtained from MDEQ Permit No: MI-ROP-A9831-2012c.

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

Source Constituent (Units)	Reference Method (USEPA)	Relative Accuracy (%) <sup>1</sup>	Applicable Specification	Standard Used	Specification Limit
<i>B&amp;W Boiler Stack</i>					
O <sub>2</sub> (% dv)	3A	0.38	40 CFR 75, APP. A	abs. diff.	± 1.0% <sup>2</sup>
NO <sub>x</sub> (ppmdv)	7E	5.7	40 CFR 75, APP. A	% of RM	10% <sup>3</sup>
NO <sub>x</sub> (lb/MMBtu)	7E	0.005	40 CFR 75, APP. A	abs. diff.	±0.020 <sup>4</sup>

<sup>1</sup> Relative Accuracy is expressed in terms of comparison to the reference method (% RM) or avg. absolute difference. The specific expression used depends on the specification limit cited.

<sup>2</sup> If RA is ≤ 7.5% or ±0.7% O<sub>2</sub>, the frequency of RATA may be reduced from semi-annually to annually.

<sup>3</sup> For any source emitting less than 250.0 ppm of NO<sub>x</sub>, the limit is either < 10% of RM or ± 15.0 ppm.

If RA is ≤ 7.5% or ±12.0 ppm NO<sub>x</sub>, the frequency of RATA may be reduced from semi-annually to annually.

<sup>4</sup> For any source emitting less than 0.200 lb/MMBtu of NO<sub>x</sub>, the limit is either < 10% of RM or ± 0.020 lb/MMBtu.

If RA is ≤ 7.5% or ±0.015 lb/MMBtu NO<sub>x</sub>, the frequency of RATA may be reduced from semi-annually to annually.

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## Test Program Details

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### Parameters

The test program included the following emissions measurements:

- total particulate matter less than 10 microns in diameter ( $PM_{10}$ ), assumed equivalent to the sum of the following constituents:
  - filterable particulate matter (FPM)
  - condensable particulate matter (CPM)
- nitrogen oxides ( $NO_x$ )
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents
  - methane ( $CH_4$ )
  - ethane ( $C_2H_6$ )
- sulfuric acid mist ( $H_2SO_4$ )
- flue gas composition (e.g.,  $O_2$ ,  $CO_2$ ,  $H_2O$ )
- flue gas temperature
- flue gas flow rate

## Schedule

Testing was performed on March 15 and 16, 2018. The on-site schedule followed during the test program is outlined in Table 1-3.

**Table 1-3:  
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	B & W Stack	USEPA Method 5/202	FPM/CPM	03/15/18	08:07	10:10
2	B & W Stack	USEPA Method 5/202	FPM/CPM	03/15/18	10:47	12:54
3	B & W Stack	USEPA Method 5/202	FPM/CPM	03/15/18	15:49	17:53
1	B & W Stack	USEPA Method 25A/18	VOC	03/15/18	08:43	09:43
2	B & W Stack	USEPA Method 25A/18	VOC	03/15/18	12:00	13:00
3	B & W Stack	USEPA Method 25A/18	VOC	03/15/18	16:00	17:00
1	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/15/18	12:00	13:00
2	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/15/18	14:00	15:00
3	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/15/18	16:00	17:00
4	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/15/18	18:00	19:00
5	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/15/18	20:00	21:00
6	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/16/18	08:00	09:00
7	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/16/18	10:00	11:00
8	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/16/18	12:00	13:00
9	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/16/18	14:00	15:00
10	B & W Stack	USEPA Method 3A/7E	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub>	03/16/18	16:00	17:00
0	B & W Stack	Draft ASTM CCM	Sulfuric Acid	03/16/18	10:01	11:01
1	B & W Stack	Draft ASTM CCM	Sulfuric Acid	03/16/18	11:15	12:15
3	B & W Stack	Draft ASTM CCM	Sulfuric Acid	03/16/18	13:35	14:35
4	B & W Stack	Draft ASTM CCM	Sulfuric Acid	03/16/18	14:45	15:45

## Discussion

### *Project Synopsis*

### *PM & PM<sub>10</sub> 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.

PM<sub>10</sub> 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 PM<sub>10</sub> since Method 5 collects all FPM present in the flue gas (regardless of particle size).

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

H<sub>2</sub>SO<sub>4</sub> emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM). Three (3) 60-minute Draft ASTM CCM test runs were performed. H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub>-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.

Run 2 was aborted and deemed invalid. While leak checking the sample train after a sample flow blockage, the sample train was compromised when the condenser was broken. Consequently, the final results are an average of Runs 1, 3 and 4.

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

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

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. VOC Runs 2 and 3 coincide with RATA Runs 1 and 3. During the bias calibration check of RATA Run 2, the Method 18 bag was contaminated with calibration gas. Consequently, RATA Run 2 was deemed invalid as a VOC run.

THCs, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emission results were calculated in units of lb/MMBtu as propane. O<sub>2</sub> concentrations from concurrent Method 3A runs were utilized to convert VOC results to lb/MMBtu. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from nearly concurrent Method 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 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.

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.

### RATA Testing – USEPA Methods 3A and 7E

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 60 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 final result was expressed as the average of nine (9) of the ten (10) RATA runs performed.

The RATA for NO<sub>x</sub> and O<sub>2</sub> was conducted per 40 CFR Part 75.

MPC performed a linearity test following the test program on April 3, 2018.

All tests were completed while the facility CEMS was operated in a hands-off manner. The unit was operated above maximum normal operating capacity which is about 137 MMBtu/hr.

The facility CEMS data acquisition system used for NO<sub>x</sub> (Cirrus System) is different than the "normal" data acquisition systems. The Cirrus System is restricted to taking a reading every hour on the hour. This realization was not made on-site until approximately 50 minutes into the second RM run. Consequently, the second RM run was aborted and the first RM run was only utilized as VOC Run 1. The third attempted RM run is considered to be RATA Run 1.

In lieu of performing a stratification test, sampling was performed at the three points along the "long measurement line", as described in 40 CFR 60, Appendix B, PS 2, §8.1.3 (16.7%, 50.0% and 83.3% of the way across the stack), for each test run.

Bias tests were performed on all of the NO<sub>x</sub> RATA data sets. The CEMS data was found to be biased high in comparison to the RM data in all instances. Since the mean difference between the RM and CEMS data was less than or equal to the absolute value of the confidence coefficient for all runs, the CEMS passed the bias test and a bias adjustment factor (BAF) was not applied to any of the emissions results. Per 40 CFR Part 75, bias is only applicable when the CEMS data is biased low in relation to the RM data.

### Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppm<sub>dv</sub>) were converted to units of pounds per million Btu (lb/MMBtu) by calculating a combination oxygen-based fuel factor (F<sub>d</sub>) for natural gas and refinery gas per EPA Method 19 specifications.

- For natural gas, the volume-based gross heat content (GCV<sub>v</sub>) was obtained from a gas analysis report provided by MPC. The natural gas F<sub>d</sub> factor was obtained from 40 CFR Part 75, Appendix F, Table 1. This approach should yield worst-case calculated emission results.
- For refinery gas, the heat content and F<sub>d</sub> factor were calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents.

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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:  
B&W Stack – PM & PM<sub>10</sub> Emissions**

Run No.	1	2	3	Average
Date (2018)	Mar 15	Mar 15	Mar 15	
Start Time (approx.)	08:07	10:47	15:49	
Stop Time (approx.)	10:10	12:54	17:53	
<b>Process Conditions</b>				
P <sub>1</sub> Steam production (mlb/hr)	144	145	144	144
F <sub>d</sub> Oxygen-based F-factor (dscf/MMBtu)	8,370	8,370	8,370	
H <sub>i</sub> Actual heat input (MMBtu/hr) <sup>1</sup>	163	163	165	164
<b>Gas Conditions</b>				
O <sub>2</sub> Oxygen (dry volume %)	5.0	5.1	5.0	5.0
CO <sub>2</sub> Carbon dioxide (dry volume %)	9.5	9.5	9.5	9.5
T <sub>s</sub> Sample temperature (°F)	338	339	340	339
B <sub>w</sub> Actual water vapor in gas (% by volume)	16.7	16.7	16.7	16.7
<b>Gas Flow Rate</b>				
Q <sub>a</sub> Volumetric flow rate, actual (acfm)	72,000	72,000	72,700	72,200
Q <sub>s</sub> Volumetric flow rate, standard (scfm)	46,100	46,100	46,500	46,300
Q <sub>std</sub> Volumetric flow rate, dry standard (dscfm)	38,400	38,400	38,800	38,500
<b>Sampling Data</b>				
V <sub>std</sub> Volume metered, standard (dscf)	77.49	76.09	75.89	76.49
%I Isokinetic sampling (%)	103.4	101.6	100.4	101.8
<b>Laboratory Data</b>				
m <sub>FPM</sub> Total FPM (g)	0.00315	0.00335	0.00386	
m <sub>CPM</sub> Total CPM (g)	0.00519	0.00421	0.00443	
m <sub>Part</sub> Total particulate matter (as PM <sub>10</sub> ) (g)	0.00834	0.00756	0.00829	
<b>FPM Results</b>				
C <sub>sd</sub> Particulate Concentration (lb/dscf)	8.96E-08	9.71E-08	1.12E-07	9.96E-08
E <sub>lb/hr</sub> Particulate Rate (lb/hr)	0.207	0.224	0.261	0.230
E <sub>Fd</sub> Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.000986	0.00107	0.00123	0.00110
<b>CPM Results</b>				
C <sub>sd</sub> Particulate Concentration (lb/dscf)	1.48E-07	1.22E-07	1.29E-07	1.33E-07
E <sub>lb/hr</sub> Particulate Rate (lb/hr)	0.340	0.281	0.299	0.307
E <sub>Fd</sub> Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00162	0.00135	0.00142	0.00146
<b>Total Particulate Matter (as PM<sub>10</sub>) Results</b>				
C <sub>sd</sub> Particulate Concentration (lb/dscf)	2.37E-07	2.19E-07	2.41E-07	2.32E-07
E <sub>lb/hr</sub> Particulate Rate (lb/hr)	0.547	0.505	0.560	0.537
E <sub>Fd</sub> Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00261	0.00242	0.00265	0.00256

<sup>1</sup> Calculated from fuel gas flow rates provided by MPC.

**Table 2-2:  
B&W Stack – H<sub>2</sub>SO<sub>4</sub> Emissions**

Run No.	1	3 <sup>1</sup>	4	Average
Date (2018)	Mar 16	Mar 16	Mar 16	
Start Time (approx.)	11:15	13:35	14:45	
Stop Time (approx.)	12:15	14:35	15:45	
<b>Process Conditions</b>				
P <sub>1</sub> Steam production (mlb/hr)	158	152	149	153
F <sub>d</sub> Oxygen-based F-factor (dscf/MMBtu)	8,432	8,436	8,437	8,435
H <sub>i</sub> Actual heat input (MMBtu/hr) <sup>2</sup>	175	167	166	169
<b>Gas Conditions</b>				
O <sub>2</sub> Oxygen (dry volume %)	5.7	5.3	4.6	5.2
CO <sub>2</sub> Carbon dioxide (dry volume %)	9.0	9.2	9.7	9.3
T <sub>s</sub> Sample temperature (°F)	347	345	344	345
B <sub>w</sub> Actual water vapor in gas (% by volume)	16.0	16.3	16.4	16.2
<b>Sampling Data</b>				
V <sub>mstd</sub> Volume metered, standard (dscf)	28.66	28.73	28.49	28.63
<b>Laboratory Data (Ion Chromatography)</b>				
m <sub>n</sub> Total H <sub>2</sub> SO <sub>4</sub> collected (mg)	0.3038	0.3856	0.4968	
<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)	2.34E-08	2.96E-08	3.84E-08	3.05E-08
C <sub>sd</sub> H <sub>2</sub> SO <sub>4</sub> Concentration (ppmdv)	0.092	0.116	0.151	0.120
E <sub>Fd</sub> H <sub>2</sub> SO <sub>4</sub> Rate - F <sub>d</sub> -based (lb/MMBtu)	0.000271	0.000335	0.000416	0.000340

<sup>1</sup> Run 2 aborted due to compromised sample train and deemed invalid.

<sup>2</sup> Calculated from fuel gas flow rates provided by MPC.



**Table 2-3:  
B&W Stack – VOC Emissions**

Run No.		1	2	3	Average
Date (2018)		Mar 15	Mar 15	Mar 15	
Start Time (approx.)		08:43	12:00	16:00	
Stop Time (approx.)		09:43	13:00	17:00	
<b>Process Conditions</b>					
P <sub>1</sub>	Steam production (mlb/hr)	145	145	144	145
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,370	8,370	8,370	8,370
H <sub>i</sub>	Actual heat input (MMBtu/hr) <sup>1</sup>	163	163	165	163
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	4.8	4.5	4.5	4.6
CO <sub>2</sub>	Carbon dioxide (dry volume %)	9.7	10.0	10.1	9.9
B <sub>w</sub>	Actual water vapor in gas (% by volume) <sup>2</sup>	16.7	16.7	16.7	16.7
<b>THC Results<sup>3</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	<0.553	<0.553	<0.553	<0.553
C <sub>sd</sub>	Concentration (lb/dscf)	<6.33E-08	<6.33E-08	<6.33E-08	<6.33E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	< 0.000690	< 0.000677	< 0.000675	< 0.000680
<b>Methane Results</b>					
C <sub>sd</sub>	Concentration (ppmdv)	5.70	5.41	5.79	5.63
C <sub>sd</sub>	Concentration (lb/dscf)	2.37E-07	2.25E-07	2.41E-07	2.35E-07
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	2.58E-03	2.41E-03	2.57E-03	2.52E-03
<b>Ethane Results</b>					
C <sub>sd</sub>	Concentration (ppmdv)	1.41	0.76	1.70	1.29
C <sub>sd</sub>	Concentration (lb/dscf)	1.10E-07	5.93E-08	1.33E-07	1.01E-07
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	1.20E-03	6.34E-04	1.41E-03	1.08E-03
<b>VOC Results<sup>4</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	< 0.553	< 0.553	< 0.553	< 0.553
C <sub>sd</sub>	Concentration (lb/dscf)	<6.33E-08	<6.33E-08	<6.33E-08	<6.33E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	< 0.000690	< 0.000677	< 0.000675	< 0.000680

<sup>1</sup> Calculated from fuel gas flow rates provided by MPC.<sup>2</sup> Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent M-5/202 runs.<sup>3</sup> For THC, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).<sup>4</sup> For VOCs, '<' indicates at least one non-detectable fraction was used in the calculations.

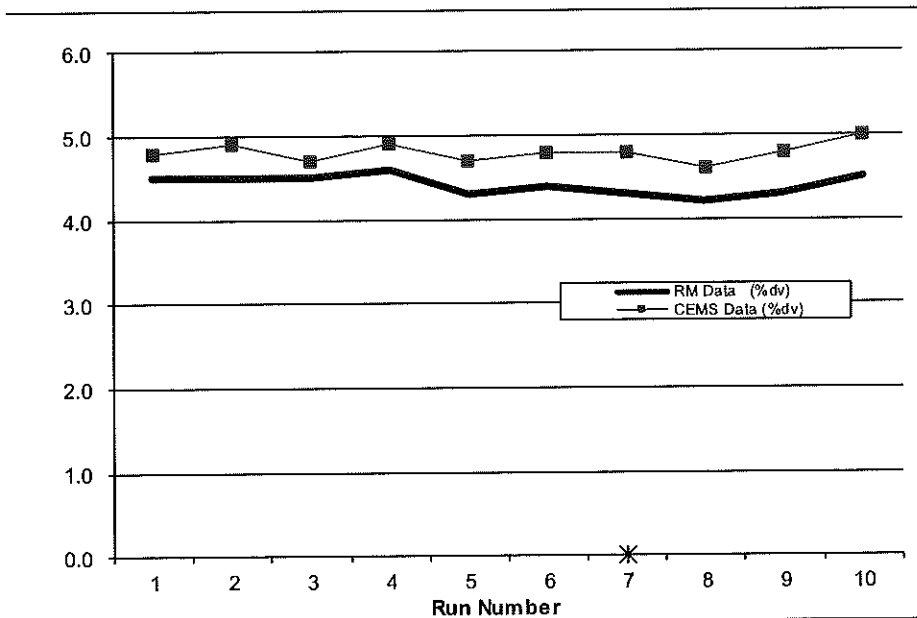
**Table 2-4:  
 B&W Stack – O<sub>2</sub> (%dv) Relative Accuracy**

Run No.	Start Time	Date (2018)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	12:00	Mar 15	4.5	4.8	-0.3	-6.7%
2	14:00	Mar 15	4.5	4.9	-0.4	-8.9%
3	16:00	Mar 15	4.5	4.7	-0.2	-4.4%
4	18:00	Mar 15	4.6	4.9	-0.3	-6.5%
5	20:00	Mar 15	4.3	4.7	-0.4	-9.3%
6	08:00	Mar 16	4.4	4.8	-0.4	-9.1%
7 *	10:00	Mar 16	4.3	4.8	-0.5	-11.6%
8	12:00	Mar 16	4.2	4.6	-0.4	-9.5%
9	14:00	Mar 16	4.3	4.8	-0.5	-11.6%
10	16:00	Mar 16	4.5	5.0	-0.5	-11.1%
<b>Average</b>			<b>4.4</b>	<b>4.8</b>	<b>-0.4</b>	<b>-8.5%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.0972	
Confidence Coefficient (CC)	0.0747	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	<b>10.2%</b>	<b>10.0%</b>
Avg. Abs. Diff. (%dv)	<b>0.38</b>	<b>1.0</b>

RM = Reference Method (CleanAir Data) 040418 110437  
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-5:  
 B&W Stack – NO<sub>x</sub> (ppmdv) Relative Accuracy**

Run No.	Start Time	Date (2018)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	12:00	Mar 15	48.7	50.8	-2.1	-4.3%
2	14:00	Mar 15	49.1	52.4	-3.3	-6.7%
3 *	16:00	Mar 15	49.3	54.1	-4.8	-9.7%
4	18:00	Mar 15	51.3	55.8	-4.5	-8.8%
5	20:00	Mar 15	57.6	56.6	1.0	1.7%
6	08:00	Mar 16	53.3	54.5	-1.2	-2.3%
7	10:00	Mar 16	52.3	53.6	-1.3	-2.5%
8	12:00	Mar 16	50.3	51.5	-1.2	-2.4%
9	14:00	Mar 16	50.0	50.4	-0.4	-0.8%
10	16:00	Mar 16	50.1	52.3	-2.2	-4.4%
<b>Average</b>			<b>51.4</b>	<b>53.1</b>	<b>-1.7</b>	<b>-3.3%</b>

**Relative Accuracy Test Audit Results**

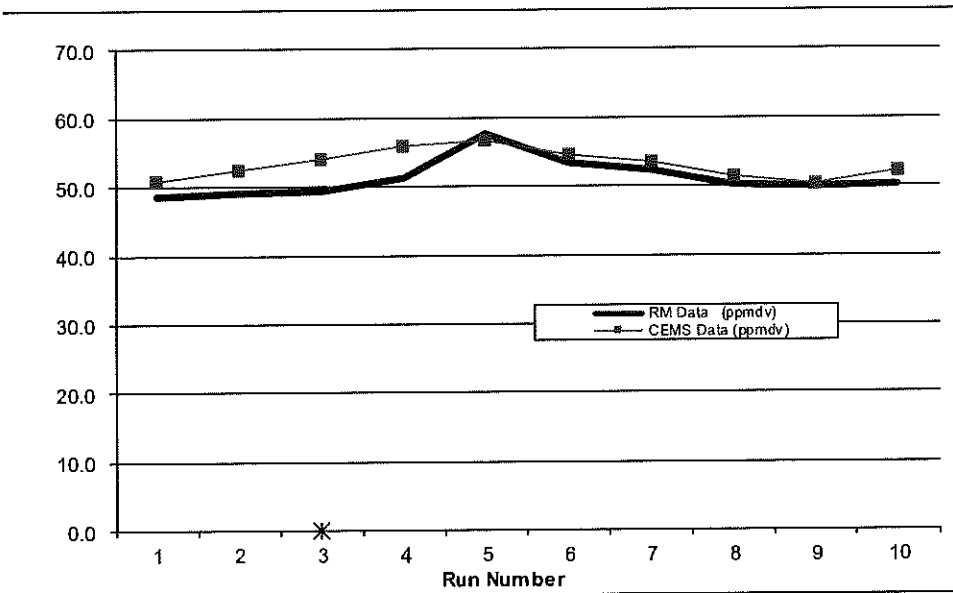
Standard Deviation of Differences	1.5988	
Confidence Coefficient (CC)	1.2289	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	5.7%	10.0%
Avg. Abs. Diff. (ppmdv)	1.9	15.0
Bias Test	-1.689 ≤ 1.229	
Bias Test Status	<b>Pass</b>	

RM = Reference Method (CleanAir Data)

040418 110437

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

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



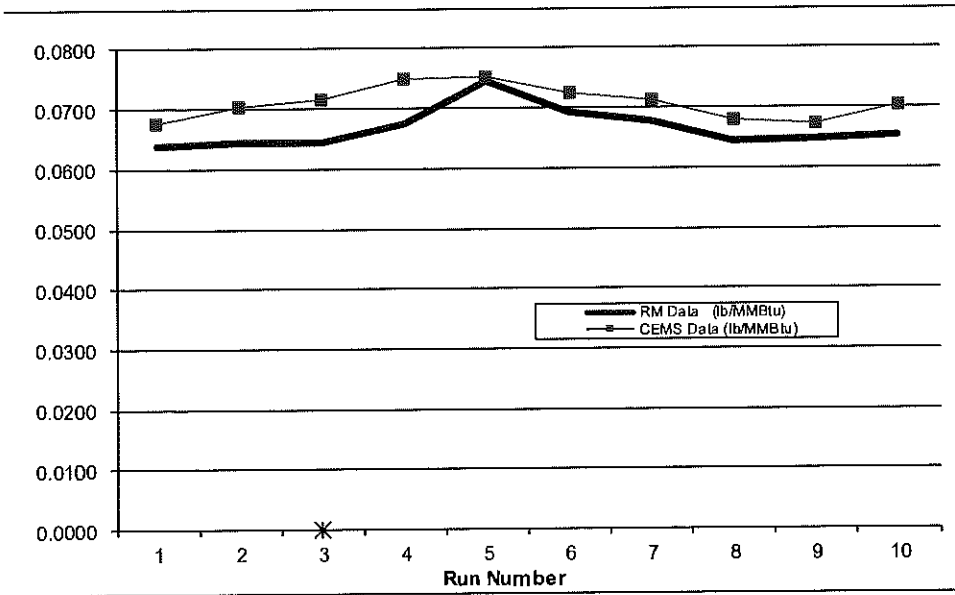
**Table 2-6:  
 B&W Stack – NO<sub>x</sub> (lb/MMBtu) Relative Accuracy**

Run No.	Start Time	Date (2018)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	12:00	Mar 15	0.0639	0.0676	-0.0037	-5.8%
2	14:00	Mar 15	0.0644	0.0702	-0.0058	-9.0%
3 *	16:00	Mar 15	0.0643	0.0717	-0.0074	-11.5%
4	18:00	Mar 15	0.0674	0.0748	-0.0074	-11.0%
5	20:00	Mar 15	0.0745	0.0751	-0.0006	-0.8%
6	08:00	Mar 16	0.0692	0.0726	-0.0034	-4.9%
7	10:00	Mar 16	0.0676	0.0712	-0.0036	-5.3%
8	12:00	Mar 16	0.0644	0.0679	-0.0035	-5.4%
9	14:00	Mar 16	0.0647	0.0673	-0.0026	-4.0%
10	16:00	Mar 16	0.0654	0.0704	-0.0050	-7.6%
<b>Average</b>			<b>0.0668</b>	<b>0.0708</b>	<b>-0.0040</b>	<b>-5.9%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.00194	
Confidence Coefficient (CC)	0.00149	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	8.2%	10.0%
Avg. Abs. Diff. (lb/MMBtu)	0.0040	0.020
Bias Test	$-0.00396 \leq 0.00149$	
Bias Test Status	Pass	

RM = Reference Method (CleanAir Data) 040418 110437  
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company 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 B&W Boiler (EU27-B&WBOILER1-S1) generates steam required by other refinery process components. The unit is fired by natural gas and refinery fuel gas. Emissions are vented to the atmosphere via the B&W Boiler Stack (SV-B&WBOILER1).

#### Test Location

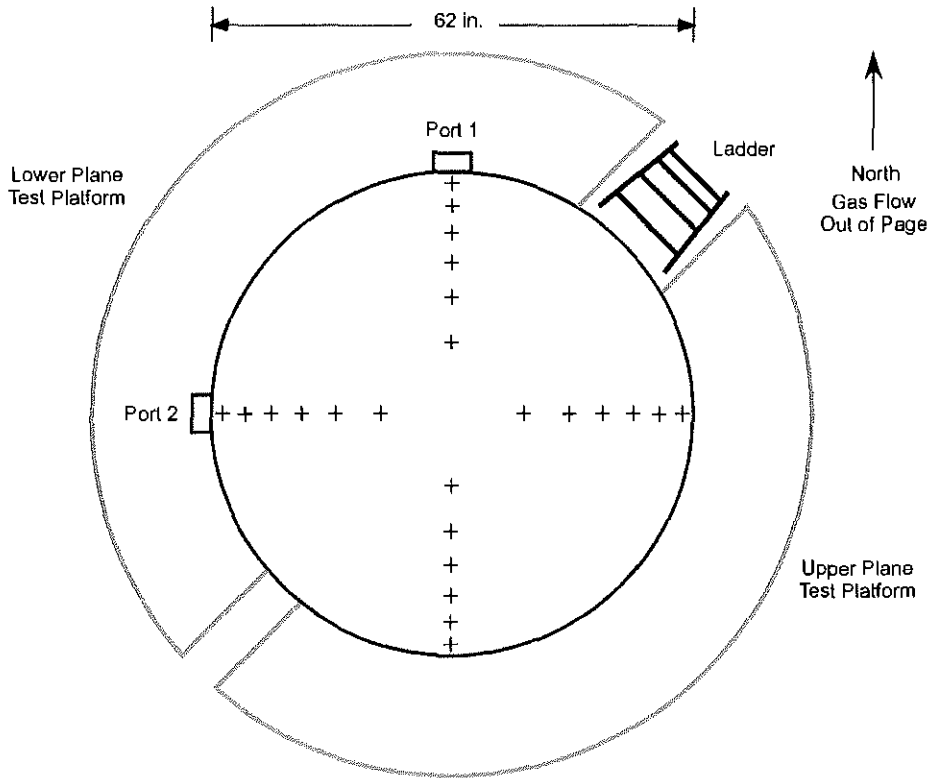
EPA Method 1 specifications determined the sample point locations for PM/PM<sub>10</sub> testing. Appendix A of 40 CFR 75, with references to Performance Specification (PS) 2 in 40 CFR 60, Appendix B and Method 7E in 40 CFR 60, Appendix A, determined the sample point locations for RATA testing. Table 3-1 presents the sampling point information for the test location. The figures shown on pages 13 and 14 represent the layout of the test location.

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

Source Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<i>B&amp;W Boiler Stack</i>							
FPM/CPM	5/202	1-3	2	12	5	120	3-1
H <sub>2</sub> SO <sub>4</sub>	Draft ASTM CCM	1-4	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> (RATA)	3A/7E	1-10	1	3	20	60	3-2

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

**Figure 3-1:  
 PM & PM<sub>10</sub> Sample Point Layout**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	97.9	60.7
2	93.3	57.8
3	88.2	54.7
4	82.3	51.0
5	75.0	46.5
6	64.4	39.9
7	35.6	22.1
8	25.0	15.5
9	17.7	11.0
10	11.8	7.3
11	6.7	4.2
12	2.1	1.3

Duct diameters upstream from flow disturbance (A): 9.5

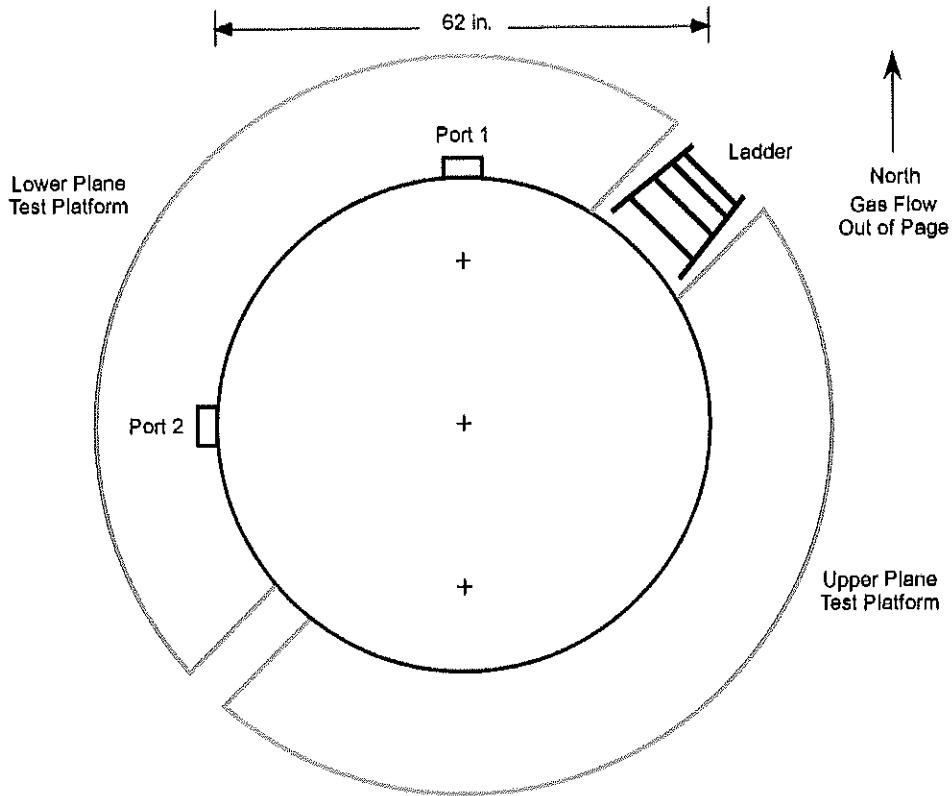
Limit: 0.5

Duct diameters downstream from flow disturbance (B): 2.3

Limit: 2.0

**Figure 3-2:**

**O<sub>2</sub>, CO<sub>2</sub>, VOC & NO<sub>x</sub> Sample Point Layout**



Note: RM test port selection may vary

Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	51.6
2	50.0	31.0
3	16.7	10.4

Duct diameters upstream from flow disturbance (A): 9.5

Limit: 0.5

Duct diameters downstream from flow disturbance (B): 2.3

Limit: 2.0

End of Section

## 4. METHODOLOGY

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### Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the DEQ. These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix.

In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications, along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

#### Title 40 CFR Part 60, Appendix A

Method 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"

#### Title 40 CFR Part 51, Appendix M

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

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

### Methodology Discussion

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#### *PM and PM<sub>10</sub> Testing – USEPA Method 5/202*

PM<sub>10</sub> emissions were determined using EPA Method 5/202. PM<sub>10</sub> is equivalent to the sum of FPM less than 10 micrometers ( $\mu\text{m}$ ) in diameter (FPM<sub>10</sub>) and CPM. The Method 5/202 sample train yields a front-half, FPM result and a back-half, CPM result. Where appropriate, the total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of total PM<sub>10</sub> since Method 5 will collect all FPM present in the flue gas (regardless of particle size).

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 are 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<sub>2</sub>) and NO<sub>x</sub> interferences observed with earlier versions of the method, in which flue gas is bubbled through cold water, and SO<sub>2</sub> and NO<sub>x</sub> are absorbed and partially oxidized before they could be purged out with nitrogen (N<sub>2</sub>).

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 was 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 is not 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<sub>2</sub> at a rate of 14 liters per minute (LPM) for one (1) hour following each test run and prior to recovery.

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

#### *O<sub>2</sub> and NO<sub>x</sub> 40 CFR 75 RATA Testing – USEPA Methods 3A and 7E*

The RATA for NO<sub>x</sub> and O<sub>2</sub> were conducted per 40 CFR 75, Appendix A specifications.

Prior to conducting the RATA, MPC performed a linearity test which will be reported separately.

The following tests were performed by CleanAir on the applicable CEMS:

- RATA (NO<sub>x</sub> and O<sub>2</sub> CEMS) - The RATAs were performed using EPA Methods 3A and 7E as the RMs.
  - The RATA was performed while the unit was combusting the normal primary or back-up fuel.
  - The four (4) required range levels of calibration gas were utilized during calibration error checks:
    - “high-level” - 80% to 100% of span;
    - “mid-level” - 50% to 60% of span;
    - “low-level” - 20% to 30% of span;
    - “zero-level” - 0% to 20% of span.
  - For pre- and post-test system bias checks, the calibration gas that has a concentration closest to but greater than the actual flue gas concentration of the constituent was selected.
  - Minute-average data points for O<sub>2</sub> and NO<sub>x</sub> (dry basis) were collected over a period of 60 minutes for each RM run.
  - A minimum of nine (9) RM runs were performed.
  - The average result for each RM was calculated and compared to the average result from the facility CEMS over an identical time interval in order to calculate RA.
- Bias Test (NO<sub>x</sub> CEMS) - This is a calculation performed on the RATA results to determine whether the CEMS is biased low compared to the RM.

RM O<sub>2</sub> emissions were determined using a paramagnetic analyzer per EPA Method 3A. NO<sub>x</sub> emissions were determined using a chemiluminescent analyzer per EPA Method 7E.

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

Calibration error checks were performed by introducing “high-level”, “mid-level”, “low-level” and “zero-level” (if applicable) calibration gases to the inlet of each analyzer during calibration error checks. Bias checks were performed before and after each run by introducing calibration gas to the inlet of the sampling system’s heated filter. Documentation of interference checks and NO<sub>2</sub> converter efficiency checks are included in the report.

Minute-average data points for O<sub>2</sub> and NO<sub>x</sub> (dry basis) were collected over a period of 60 minutes for each RATA run. Sampling occurred at the three (3) points along the “long measurement line”, as described in 40 CFR 60, Appendix B, PS2, §8.1.3 (16.7%, 50.0% and 83.3% of the way across the stack). A single port was used for each run.

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

#### *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 CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emissions. VOC emissions are equivalent to THC emissions source, minus CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>.

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 (C<sub>3</sub>H<sub>8</sub>) on an actual (wet) basis.

FIA calibration was performed by introducing zero air, 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. Bias checks were performed before and after each sampling run in a similar manner.

The Method 18 sampling system consists of a gas conditioner (for moisture removal), TFE sample lines, TFE-coated diaphragm pump and a mass flow meter ("Direct Pump Sampling Procedure"). This system pulls a slipstream of the flue gas from the Method 25A sample delivery system and delivers it into a FlexFoil bag at a constant rate.

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 measures concentration on a dry basis. At least five 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 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 CCM*

H<sub>2</sub>SO<sub>4</sub> 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 SO<sub>2</sub> into the H<sub>2</sub>SO<sub>4</sub>-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 was maintained below 68°F. The sample gas then flowed into a dry gas meter, where the collected sample gas volume was determined by means of a calibrated, dry gas meter or an orifice-based flow meter.

The H<sub>2</sub>SO<sub>4</sub>-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H<sub>2</sub>O as the recovery/extraction solvent; any H<sub>2</sub>SO<sub>4</sub> disassociates into sulfate ion (SO<sub>4</sub><sup>2-</sup>) and is stabilized in the H<sub>2</sub>O matrix until analysis.

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

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*End of Section*