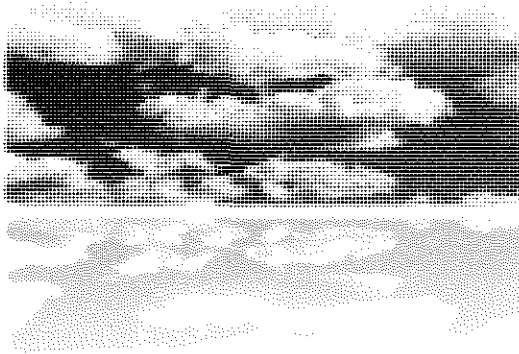




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AIR QUALITY DIVISION



REPORT ON COMPLIANCE &  
RATA TESTING

Detroit Refinery

Alky DIB Reboiler Heater

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

CleanAir Project No. 13420-1  
STAC Certificate No. 2007.002.0113.1217  
Revision 0, Final Report  
January 8, 2018

# 1. PROJECT OVERVIEW

## AIR QUALITY DIVISION

### Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing at the Alky DIB Reboiler Heater (EU09-ALKYDIBREBHTR-S1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), carbon monoxide (CO), volatile organic compounds (VOCs) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 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	Sampling Method	Average Emission	Permit Limit <sup>1</sup>
<u>Alky DIB Reboiler</u>			
PM (lb/MMBtu)	USEPA 5	0.0005	0.0019
PM <sub>2.5</sub> (lb/MMBtu)	USEPA 5 / 202	0.0017	0.0076
PM <sub>10</sub> (lb/MMBtu)	USEPA 5 / 202	0.0017	0.0076
NSFPM (lb/MMBtu)	USEPA 5B	0.0015	N/A
H <sub>2</sub> SO <sub>4</sub> (lb/MMBtu)	ASTM Draft CCM	0.0001	N/A
VOC (lb/MMBtu)	USEPA 18 / 25A	< 0.0007	0.0055
CO (lb/MMBtu)	USEPA 10	< 0.0004	0.02

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

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

Source Constituent (Units)	Reference Method	Relative Accuracy (%) <sup>1</sup>	Applicable Specification	Specification Limit <sup>1</sup>
<u>Alky DIB Reboiler</u>				
O <sub>2</sub> (% dv)	USEPA 3A	0.07	PS3	±1.0% dv
NO <sub>x</sub> (ppmdv @0%O <sub>2</sub> )	USEPA 7E / 3A	7.8	PS2	20% of RM
NO <sub>x</sub> (lb/MMBtu)	EPA 7E, 3A, 19	9.2	PS2	20% of RM

<sup>1</sup> Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

## Test Program Details

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### Parameters

The test program included the following emissions measurements:

- particulate matter (PM) assumed equivalent to filterable particulate matter (FPM)
- total particulate matter less than 2.5 microns in diameter ( $PM_{2.5}$ ) assumed equivalent to the sum of the following constituents:
  - filterable particulate matter (FPM)
  - condensable particulate matter (CPM)
- 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)
- non-sulfuric acid particulate matter (NSFPM)
- nitrogen oxides ( $NO_x$ )
- carbon monoxide (CO)
- 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 November 30 and December 1, 2017. 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	Alky DIB Reboiler	USEPA Method 5/202	FPM/CPM	11/30/17	12:43	15:00
2	Alky DIB Reboiler	USEPA Method 5/202	FPM/CPM	11/30/17	15:55	18:04
3	Alky DIB Reboiler	USEPA Method 5/202	FPM/CPM	12/01/17	08:25	10:33
1	Alky DIB Reboiler	USEPA Method 5B	NSFPM	11/30/17	12:43	15:00
2	Alky DIB Reboiler	USEPA Method 5B	NSFPM	11/30/17	15:55	18:04
3	Alky DIB Reboiler	USEPA Method 5B	NSFPM	12/01/17	08:25	10:33
1	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	10:08	10:29
2	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	12:30	12:51
3	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	13:09	13:30
4	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	13:47	14:08
5	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	14:09	14:30
6	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	14:51	15:12
7	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	15:31	15:52
8	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	16:09	16:30
9	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	16:32	16:53
10	Alky DIB Reboiler	USEPA Method 3A/7E/10	O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO	12/01/17	17:06	17:27
1	Alky DIB Reboiler	USEPA Method 25A/18	VOC	12/01/17	12:30	14:08
2	Alky DIB Reboiler	USEPA Method 25A/18	VOC	12/01/17	14:09	15:52
3	Alky DIB Reboiler	USEPA Method 25A/18	VOC	12/01/17	16:09	17:27
0	Alky DIB Reboiler	Draft ASTM CCM	Sulfuric Acid	12/01/17	12:50	13:50
1	Alky DIB Reboiler	Draft ASTM CCM	Sulfuric Acid	12/01/17	13:59	14:59
2	Alky DIB Reboiler	Draft ASTM CCM	Sulfuric Acid	12/01/17	15:07	16:07
3	Alky DIB Reboiler	Draft ASTM CCM	Sulfuric Acid	12/01/17	16:17	17:17

## Discussion

### *Test Scope Synopsis*

#### PM, PM<sub>2.5</sub> & 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>2.5</sub> and PM<sub>10</sub> are 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>2.5</sub> and PM<sub>10</sub> since Method 5 collects all FPM present in the flue gas (regardless of particle size).

### Non-Sulfuric Acid Filterable Particulate Matter Testing

A total of three (3) 120-minute EPA Method 5B test runs were performed for diagnostic purposes. NSFPM emission results were calculated in units of lb/MMBtu. The final result was expressed as the average of the three (3) valid runs.

Atypically, final results for NSFPM were higher than FPM results. All QA/QC practices were checked and verified. There is no overt explanation for this occurrence; however, further investigation is ongoing.

### O<sub>2</sub> and NO<sub>x</sub> RATA Testing

Minute-average data points for O<sub>2</sub> and NO<sub>x</sub> (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A and 7E. Relative accuracy was determined based on nine (9) of 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

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.

### CO Testing

CO emissions were determined using EPA Method 10. CO testing was comprised of three (3) 63-minute test runs with each test run comprised of three (3) 21-minute segments. Test runs were performed concurrently with O<sub>2</sub> and NO<sub>x</sub> RATA testing. Run 1 was concurrent with RATA Runs 2 through 4, Run 2 was concurrent with RATA Runs 5 through 7 and Run 3 was concurrent with RATA Runs 8 through 10. CO emission results were calculated in units of lb/MMBtu. The final result was expressed as the average of the three (3) valid runs.

For all 21-minute segments of Method 10 runs, the measured concentrations of CO were below the detection limit defined as 'less than 1%' of the calibration span of the CO instrument. For runs resulting in non-detects, the final result is treated as 'less than' the entire value of the detection limit.

### VOC Testing

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) 63-minute test runs with each test run comprised of three (3) 21-minute segments. The Method 25A test runs were performed concurrently with three (3) 63-minute Method 18 bag collections. VOC testing was also performed concurrently with O<sub>2</sub> and NO<sub>x</sub> RATA testing. VOC Run 1 (Method 25A and Method 18) were concurrent with RATA Runs 2 through 4, Run 2 was concurrent with RATA Runs 5 through 7 and Run 3 was concurrent with RATA Runs 8 through 10. The final result for each VOC run was expressed as the average of three (3) consecutive 21-minute runs. Other CEMS methods referencing Method 7E were performed simultaneously using the same sampling system. Data was collected from all of the required Method 7E points rather than from the centroid of the duct, as specified by Method 25A.

THC, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emission results were calculated in units of lb/MMBtu as propane. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from averaging overlapping Method 5/202 and Draft ASTM Controlled Condensation Method (CCM) runs.

For all 21-minute 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, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> 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.

### H<sub>2</sub>SO<sub>4</sub> Testing

H<sub>2</sub>SO<sub>4</sub> emissions were determined referencing the Draft ASTM 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.

### Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm<sub>dv</sub>) were converted into units of lb/MMBtu by calculating an oxygen-based fuel factor (F<sub>d</sub>) for refinery gas per EPA Method 19 specifications. The F<sub>d</sub> 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.

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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:  
Alky DIB Reboiler – PM, PM<sub>2.5</sub> & PM<sub>10</sub> Emissions**

Run No.		1	2	3	Average
Date (2017)		Nov 30	Nov 30	Dec 1	
Start Time (approx.)		12:43	15:55	08:25	
Stop Time (approx.)		15:00	18:04	10:33	
<b>Process Conditions</b>					
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	7,639	7,639	7,997	
H <sub>i</sub>	Actual heat input (MMBtu/hr)	51.1	51.2	49.3	50.5
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.6	7.0	5.8	6.5
CO <sub>2</sub>	Carbon dioxide (dry volume %)	6.8	6.9	6.8	6.8
T <sub>s</sub>	Sample temperature (°F)	522	523	503	516
B <sub>w</sub>	Actual water vapor in gas (% by volume)	16.1	15.8	18.4	16.8
<b>Gas Flow Rate</b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	23,400	23,700	22,700	23,200
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	12,400	12,500	12,300	12,400
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	10,400	10,500	10,000	10,300
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	72.02	73.03	70.89	71.98
%I	Isokinetic sampling (%)	101.1	101.1	102.9	101.7
<b>Laboratory Data</b>					
m <sub>FPM</sub>	Total FPM(g)	0.00125	0.00110	0.00169	
m <sub>CPM</sub>	Total CPM(g)	0.00538	0.00250	0.00309	
m <sub>Part</sub>	Total particulate matter (as PM <sub>10</sub> )(g)	0.00663	0.00360	0.00478	
<b>FPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	3.83E-08	3.32E-08	5.26E-08	4.13E-08
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.0238	0.0209	0.0316	0.0254
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.000427	0.000381	0.000582	0.000464
<b>CPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	1.65E-07	7.55E-08	9.62E-08	1.12E-07
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.102	0.0476	0.0579	0.0693
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00184	0.000867	0.00106	0.00126
<b>Total Particulate Matter (as PM<sub>10</sub> &amp; PM<sub>2.5</sub>) Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	2.03E-07	1.09E-07	1.49E-07	1.53E-07
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.126	0.0685	0.0895	0.0947
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00227	0.00125	0.00165	0.00172

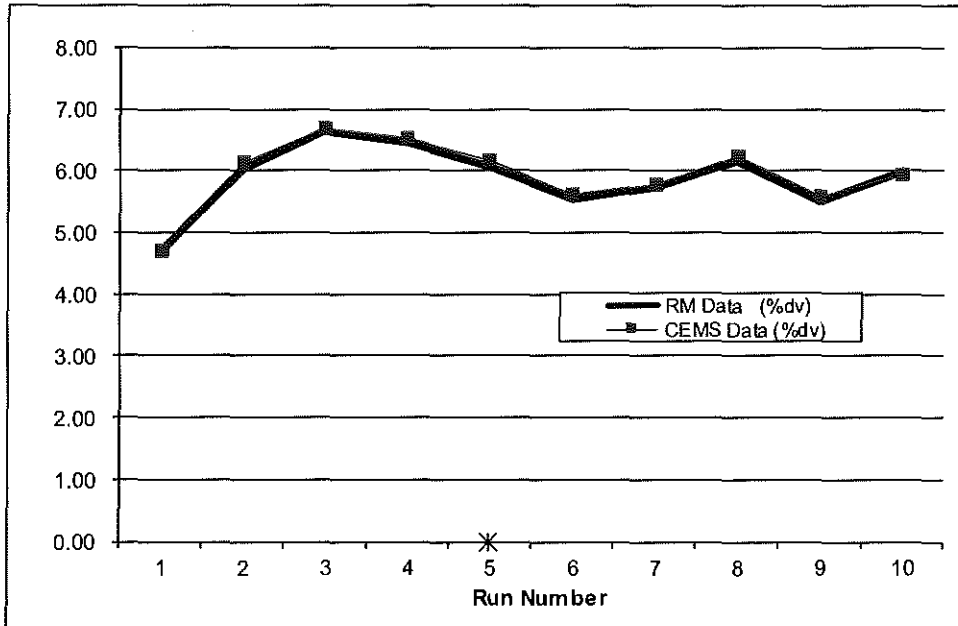
**Table 2-2:  
 Alky DIB Reboiler – O<sub>2</sub> (% dv) RATA**

Run No.	Start Time	Date (2017)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	10:08	Dec 1	4.68	4.72	-0.04	-0.9%
2	12:30	Dec 1	6.03	6.14	-0.11	-1.8%
3	13:09	Dec 1	6.63	6.69	-0.06	-0.9%
4	13:47	Dec 1	6.44	6.52	-0.08	-1.2%
5 *	14:09	Dec 1	6.07	6.18	-0.11	-1.8%
6	14:51	Dec 1	5.54	5.61	-0.07	-1.3%
7	15:31	Dec 1	5.73	5.79	-0.06	-1.0%
8	16:09	Dec 1	6.15	6.25	-0.10	-1.6%
9	16:32	Dec 1	5.51	5.58	-0.07	-1.3%
10	17:06	Dec 1	6.00	5.95	0.05	0.8%
<b>Average</b>			<b>5.86</b>	<b>5.92</b>	<b>-0.06</b>	<b>-1.0%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.0464
Confidence Coefficient (CC)	0.0356
t-Value for 9 Data Sets	2.306
<b>Avg. Abs. Diff. (%dv)</b>	<b>0.07</b>
<b>Limit</b>	<b>1.0</b>

RM = Reference Method (CleanAir Data) 122717 110056  
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.





**Table 2-3:  
 Alky DIB Reboiler – NO<sub>x</sub> (ppm @ 0% O<sub>2</sub>) RATA**

Run No.	Start Time	Date (2017)	RM Data (ppm@0%O <sub>2</sub> )	CEMS Data (ppm@0%O <sub>2</sub> )	Difference (ppm@0%O <sub>2</sub> )	Difference Percent
1	10:08	Dec 1	25.66	23.57	2.09	8.1%
2	12:30	Dec 1	28.10	26.07	2.03	7.2%
3	13:09	Dec 1	29.17	27.27	1.90	6.5%
4	13:47	Dec 1	28.95	26.80	2.15	7.4%
5	14:09	Dec 1	28.34	26.13	2.21	7.8%
6	14:51	Dec 1	27.02	24.87	2.15	8.0%
7	15:31	Dec 1	27.12	25.02	2.10	7.7%
8	16:09	Dec 1	27.86	25.77	2.09	7.5%
9	16:32	Dec 1	26.79	24.66	2.13	8.0%
10 *	17:06	Dec 1	27.76	25.46	2.30	8.3%
<b>Average</b>			<b>27.67</b>	<b>25.57</b>	<b>2.09</b>	<b>7.6%</b>

**Relative Accuracy Test Audit Results**

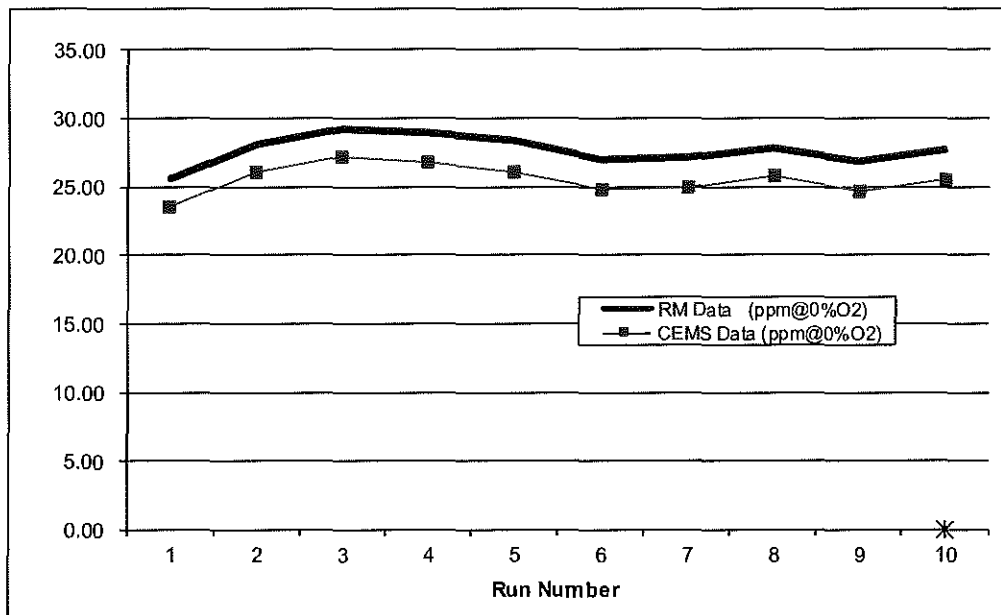
Standard Deviation of Differences	0.0886	
Confidence Coefficient (CC)	0.0681	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	7.8%	20.0%
Relative Accuracy (as % of Appl. Std.)	5.4%	10.0%
Appl. Std. = 40 ppm@0%O <sub>2</sub>		

RM = Reference Method (CleanAir Data)

122717 1646'6

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

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



**Table 2-4:  
 Alky DIB Reboiler – NO<sub>x</sub> (lb/MMBtu) RATA**

Run No.	Start Time	Date (2017)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1 *	10:08	Dec 1	0.0245	0.0222	0.0023	9.4%
2	12:30	Dec 1	0.0268	0.0246	0.0022	8.2%
3	13:09	Dec 1	0.0279	0.0257	0.0022	7.9%
4	13:47	Dec 1	0.0276	0.0252	0.0024	8.7%
5	14:09	Dec 1	0.0271	0.0246	0.0025	9.2%
6	14:51	Dec 1	0.0258	0.0234	0.0024	9.3%
7	15:31	Dec 1	0.0259	0.0236	0.0023	8.9%
8	16:09	Dec 1	0.0266	0.0243	0.0023	8.6%
9	16:32	Dec 1	0.0256	0.0232	0.0024	9.4%
10	17:06	Dec 1	0.0265	0.0240	0.0025	9.4%
<b>Average</b>			<b>0.0266</b>	<b>0.0243</b>	<b>0.0024</b>	<b>8.8%</b>

**Relative Accuracy Test Audit Results**

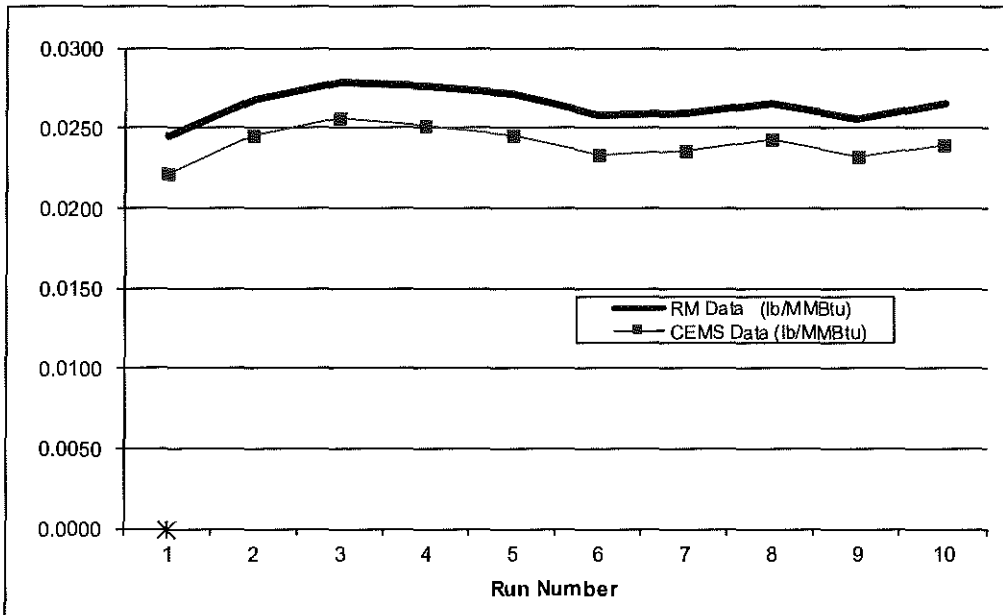
Standard Deviation of Differences	0.000113	
Confidence Coefficient (CC)	0.000087	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	9.2%	20.0%
Relative Accuracy (as % of Appl. Std.)	6.1%	10.0%
Appl. Std. = 0.04 lb/MMBtu		

RM = Reference Method (CleanAir Data)

122717 164616

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:  
Alky DIB Reboiler – CO & VOCs Emissions**

Run No.		1	2	3	Average
Date (2017)		Dec 1	Dec 1	Dec 1	
Start Time (approx.)		10:08	13:47	15:31	
Stop Time (approx.)		13:30	15:12	16:53	
<b>Process Conditions</b>					
F <sub>d</sub>	Oxygen-based F-factor (dsct/MMBtu)	7,997	7,997	7,997	7,997
H <sub>i</sub>	Actual heat input (MMBtu/hr)	42.3	43.5	44.2	
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.4	5.8	5.9	6.0
CO <sub>2</sub>	Carbon dioxide (dry volume %)	7.1	7.3	7.2	7.2
B <sub>w</sub>	Actual water vapor in gas (% by volume) <sup>1</sup>	16.1	16.8	17.4	16.8
<b>THC Results<sup>2</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	<0.542	<0.547	<0.551	<0.547
C <sub>sd</sub>	Concentration (lb/dscf)	<6.20E-08	<6.26E-08	<6.31E-08	<6.26E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<0.000714	<0.000692	<0.000702	<0.000703
<b>Methane Results<sup>3</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv)	<0.23	<0.23	<0.23	<0.23
C <sub>sd</sub>	Concentration (lb/dscf)	<9.58E-09	<9.58E-09	<9.58E-09	<9.58E-09
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<1.10E-04	<1.06E-04	<1.07E-04	<1.08E-04
<b>Ethane Results<sup>3</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv)	<0.12	<0.12	<0.12	<0.12
C <sub>sd</sub>	Concentration (lb/dscf)	<9.37E-09	<9.37E-09	<9.37E-09	<9.37E-09
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<1.08E-04	<1.04E-04	<1.04E-04	<1.05E-04
<b>VOC Results<sup>4</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> )	<0.542	<0.547	<0.551	<0.547
C <sub>sd</sub>	Concentration (lb/dscf)	<6.20E-08	<6.26E-08	<6.31E-08	<6.26E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<0.000714	<0.000692	<0.000702	<0.000703
<b>Carbon Monoxide Results</b>					
C <sub>sd</sub>	Concentration (ppmdv)	<0.478	<0.478	<0.478	<0.478
C <sub>sd</sub>	Concentration (lb/dscf)	<3.47E-08	<3.47E-08	<3.47E-08	<3.47E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<0.000400	<0.000384	<0.000387	<0.000390

<sup>1</sup> Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent M-5/202 and Draft ASTM CCM runs.

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

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

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

**Table 2-6:  
 Alky DIB Reboiler – H<sub>2</sub>SO<sub>4</sub> Emissions**

Run No.		1	2	3	Average
Date (2017)		Dec 1	Dec 1	Dec 1	
Start Time (approx.)		13:59	15:07	16:17	
Stop Time (approx.)		14:59	16:07	17:17	
<b>Process Conditions</b>					
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	7,997	7,997	7,997	
H <sub>i</sub>	Actual heat input (MMBtu/hr)	43.4	44.5	44.9	44.3
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.1	5.7	5.5	5.8
CO <sub>2</sub>	Carbon dioxide (dry volume %)	7.2	7.2	7.2	7.2
T <sub>s</sub>	Sample temperature (°F)	492	493	494	493
B <sub>w</sub>	Actual water vapor in gas (% by volume)	16.6	17.2	17.6	17.1
<b>Sampling Data</b>					
V <sub>std</sub>	Volume metered, standard (dscf)	26.96	27.41	27.69	27.35
<b>Laboratory Data (Ion Chromatography)</b>					
m <sub>n</sub>	Total H <sub>2</sub> SO <sub>4</sub> collected (mg)	0.1498	0.1461	0.1370	
<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)	1.23E-08	1.18E-08	1.09E-08	1.16E-08
C <sub>sd</sub>	H <sub>2</sub> SO <sub>4</sub> Concentration (ppmdv)	0.0481	0.0462	0.0429	0.0457
E <sub>Fd</sub>	H <sub>2</sub> SO <sub>4</sub> Rate - Fd-based (lb/MMBtu)	0.000138	0.000129	0.000118	0.000129

**Table 2-7:  
Alky DIB Reboiler – NSFPM Emissions**

Run No.		1	2	3	Average
Date (2017)		Nov 30	Nov 30	Dec 1	
Start Time (approx.)		12:43	15:55	08:25	
Stop Time (approx.)		15:00	18:04	10:33	
<b>Process Conditions</b>					
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	7,639	7,639	7,997	
H <sub>i</sub>	Actual heat input (MMBtu/hr)	51.1	51.2	49.3	50.5
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	7.6	7.3	5.8	6.9
CO <sub>2</sub>	Carbon dioxide (dry volume %)	6.5	6.8	6.8	6.7
T <sub>s</sub>	Sample temperature (°F)	524	524	502	517
B <sub>w</sub>	Actual water vapor in gas (% by volume)	16.3	16.2	18.3	17.0
<b>Gas Flow Rate</b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	23,200	23,400	22,600	23,100
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	12,200	12,300	12,200	12,300
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	10,200	10,300	9,970	10,200
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	72.57	73.87	71.97	72.80
%I	Isokinetic sampling (%)	103.4	103.9	105.0	104.1
<b>Laboratory Data</b>					
m <sub>FPM</sub>	Total NSFPM (g)	0.00534	0.00215	0.00513	
<b>NSFPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	1.62E-07	6.42E-08	1.57E-07	1.28E-07
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.0993	0.0398	0.0941	0.0778
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.001946	0.000754	0.001741	0.00148

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 Alkylation Unit (EU09-ALKYLATION) reacts isobutene with olefins in the presence of sulfuric acid to produce alkylate, a high octane gasoline blending component. Reaction products are sent for further processing and separation in the fractionating section. Products from the unit include off-gas, alkylate, butane, isobutene, and propane. Off-gas is routed to the refinery fuel gas system. Alkylate, butane, and propane are directed to storage; isobutene is recycled through the system for further processing. The alkylation unit consists of process vessels (including fractionators, reactor and caustic scrubber), the Alkylation Deisobutanizer (DIB) Reboiler heater (EU09-ALKYDIBREBHTR-S1), tanks, containers, cooling tower, flare, compressors, pumps, piping, drains, and other various components.

The Alky DIB Reboiler Heater is fired by refinery fuel gas. Emissions are vented to the atmosphere via the Alky DIB Reboiler Stack (SV09-H7), where testing was performed.

#### Test Location

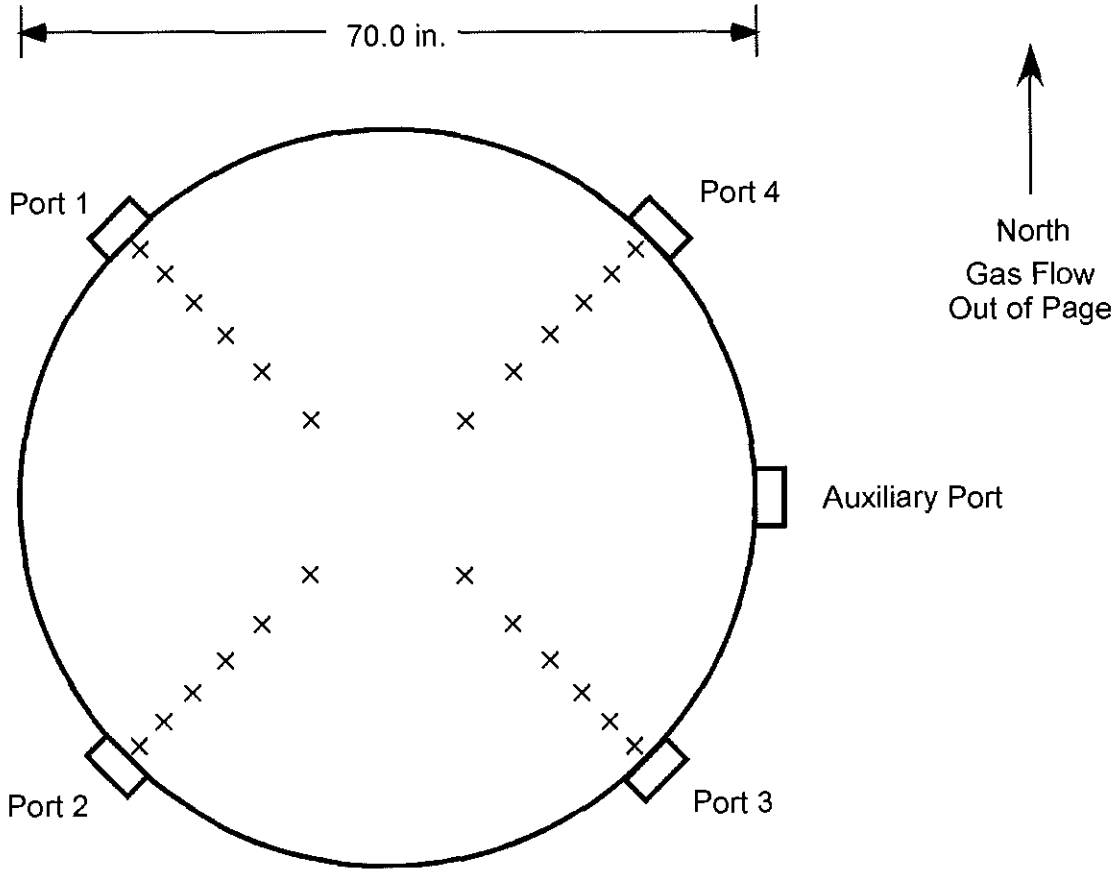
The sample point locations were determined by EPA Methods 1 and 7E specifications. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 14 and 15 represent the layout of the test location.

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

Source	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>Alky DIB Reboiler</u>							
FPM / CPM	5 / 202	1-3	4	6	5	120	3-1
NSFPM	5B	1-3	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> / NO <sub>x</sub> / CO	3A / 7E / 10	1-10	1	3	7	21	3-2
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	21	63	3-2

<sup>1</sup> Draft ASTM CCM sampling occurred at a single point near the center of the duct.

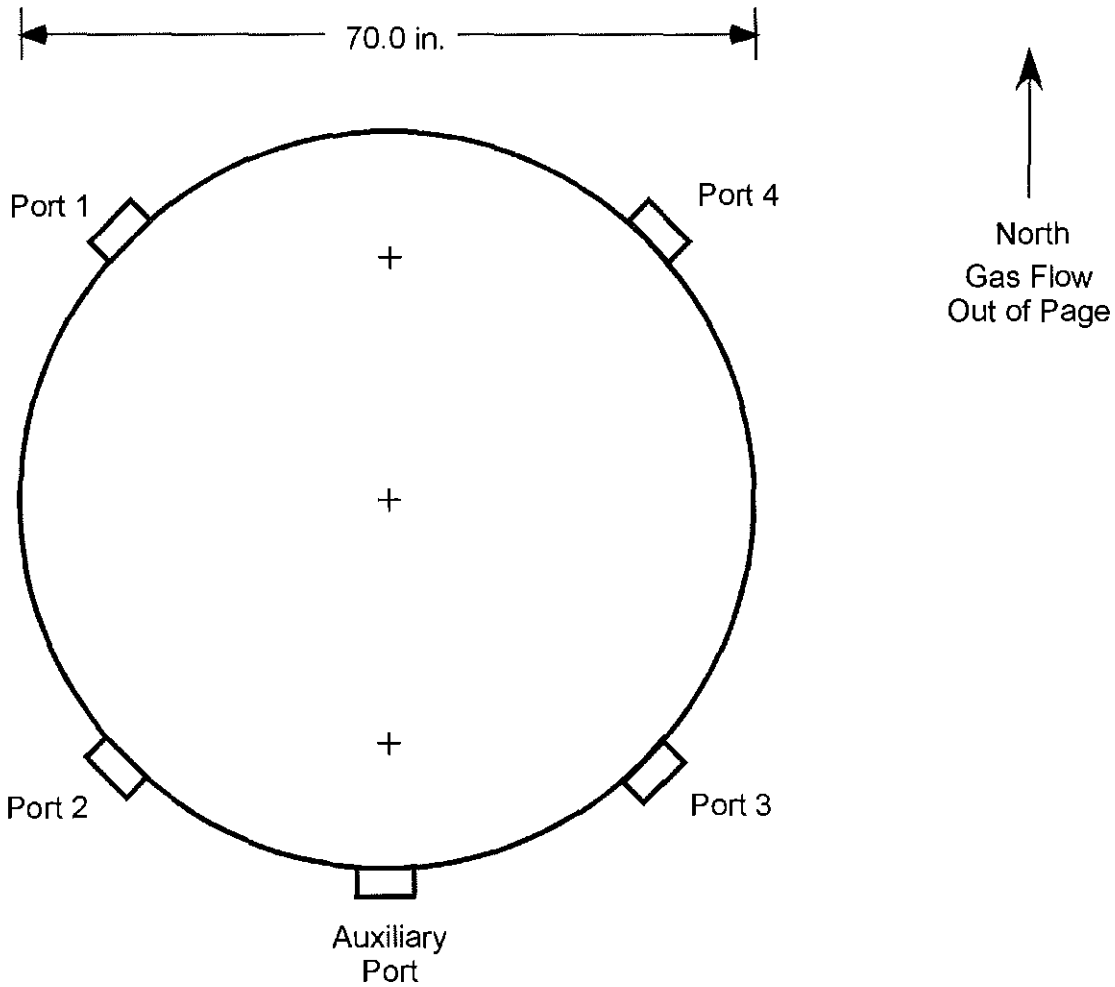
**Figure 3-1:  
 PM, PM<sub>2.5</sub>, PM<sub>10</sub> & NSFPM Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	24.9
2	25.0	17.5
3	17.7	12.4
4	11.8	8.3
5	6.7	4.7
6	2.1	1.5

Duct diameters upstream from flow disturbance (A): 20.0      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 4.0      Limit: 2.0

**Figure 3-2:**  
**O<sub>2</sub>, NO<sub>x</sub>, CO & THC Sample Point Layout (EPA Method 7E)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	58.3
2	50.0	35.0
3	16.7	11.7

Duct diameters upstream from flow disturbance (A): 20.0      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 4.0      Limit: 2.0



## 4. METHODOLOGY

### Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the Michigan 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 5B "Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources"
- Method 7E "Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer)"
- Method 10 "Determination of Carbon Monoxide Emissions from Stationary Sources"
- 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

- 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"

## 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, PM<sub>2.5</sub> and PM<sub>10</sub> Testing – USEPA Method 5/202

The front-half (Method 5 portion) 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.

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 was bubbled through cold water, and SO<sub>2</sub> and NO<sub>x</sub> were absorbed and partially oxidized before they could be purged out with nitrogen (N<sub>2</sub>).

Flue gas exiting the front-half heated filter passed 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 passed through a tetrafluoroethane (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 passed through two (2) additional impingers surrounded by ice in a “cold” section of the impinger bucket. The moisture collected in these impingers were not analyzed for CPM and was only collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent. 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 for gravimetric analysis. Method 202 samples were maintained at a temperature < 85°F during transport to the laboratory.

#### NSFPM Testing – USEPA Method 5B

The front-half (Method 5 portion) of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 320°F ± 25°F and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5B requirements.

The back-half of the sample train consisted of a series of knock-out jars. The moisture collected in these knock-out jars were only collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5B requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services for gravimetric analysis.

### O<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub> and CO Testing – USEPA Methods 3A, 7E and 10

Reference method O<sub>2</sub> and carbon dioxide (CO<sub>2</sub>) emissions were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. Reference method NO<sub>x</sub> emissions was determined using a chemiluminescent analyzer per EPA Method 7E. Reference method CO emissions was determined using a gas filter correlation IR analyzer per EPA Method 10.

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 zero N<sub>2</sub>, high range 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. Per Methods 3A, 7E and 10, the average results for each run were drift-corrected.

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

The EPA 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 measures 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 EPA 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 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 CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are insoluble in water.

Analysis for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were 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 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

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 maintained at the same temperature as the probe to remove particulate matter.

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) 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°F ± 9°F. 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°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 deionized (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 for ion chromatography (IC) analysis.

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*End of Section*