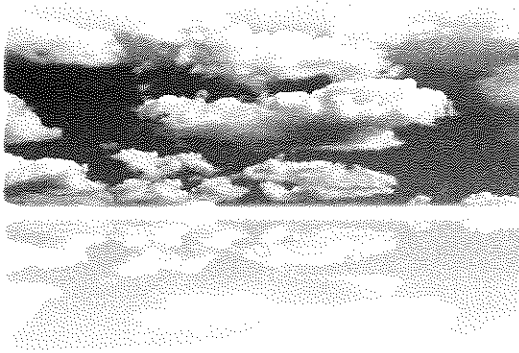




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REPORT FOR COMPLIANCE  
TESTING

Detroit Refinery  
NHT Charge Heater Stack

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

CleanAir Project No. 13265-2  
STAC Certificate No. 2007.002.0113.1217  
Revision 0, Final Report  
July 13, 2017

## 1. PROJECT OVERVIEW

### Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing on the NHT Charge Heater (EU16-NHTCHARHTR-S1) at the Detroit Refinery located in Detroit, Michigan. The objective of the test program was to perform particulate matter (PM), total particulate matter less than 10 microns in diameter (PM<sub>10</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and carbon monoxide (CO) testing to demonstrate compliance with the Michigan Department of Environmental Quality (MDEQ) Permit No. MI-ROP-A9831-2012c.

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, begin on page 2.

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

<u>Source</u> Constituent	<u>Sampling</u> Method	<u>Average</u> Emission	<u>Permit Limit</u> <sup>1</sup>
<i>NHT Charge Heater</i>			
PM (lb/MMBtu)	USEPA 5	0.0011	0.0019
PM <sub>10</sub> (lb/MMBtu)	USEPA 5/202	0.0024	0.0076
H <sub>2</sub> SO <sub>4</sub> (lb/MMBtu)	Draft ASTM CCM	7.4E-04	N/A
CO (lb/MMBtu)	USEPA 10	<0.0004	0.02

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

## Test Program Details

### Parameters

The test program included the following emissions measurements:

- particulate matter (PM), assumed equivalent to filterable particulate matter (FPM) only
- total particulate matter less than 10 microns in diameter (PM<sub>10</sub>), assumed equivalent to the sum of the following constituents:
  - filterable particulate matter (FPM)
  - condensable particulate matter (CPM)
- carbon monoxide (CO)
- 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

Testing was performed on May 24 and 25, 2017. The on-site schedule followed during the test program is outlined in Table 1-2.

**Table 1-2:  
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	NHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/24/17	09:10	11:21
2	NHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/24/17	11:55	14:09
3	NHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/24/17	14:41	16:50
1	NHT Charge Heater	USEPA Method 3A/10	O <sub>2</sub> /CO <sub>2</sub> /CO	05/24/17	09:20	10:26
2	NHT Charge Heater	USEPA Method 3A/10	O <sub>2</sub> /CO <sub>2</sub> /CO	05/24/17	10:45	11:45
3	NHT Charge Heater	USEPA Method 3A/10	O <sub>2</sub> /CO <sub>2</sub> /CO	05/24/17	12:07	13:15
0	NHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/25/17	09:15	10:15
1	NHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/25/17	10:37	11:37
2	NHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/25/17	12:00	13:00
3	NHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/25/17	13:21	14:21

## Discussion

### *Test Scope Synopsis*

#### FPM & PM<sub>10</sub> Testing

A total of three (3) valid 120-minute 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.

For this test program, PM emission rate is assumed equivalent to FPM. PM<sub>10</sub> is assumed 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. 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).

#### O<sub>2</sub>, CO<sub>2</sub>, & CO Testing

Minute-average data points for O<sub>2</sub>, CO<sub>2</sub>, and CO (dry basis) were collected over a period of 60 minutes for each run utilizing EPA Methods 3A, 7E and 10.

For all three (3) runs, the CO concentration was below 1% of the instrument calibration span. As such, CO emission rates are expressed as "less than" the emission rate calculated using an assumed concentration equivalent to 1% of the instrument calibration span.

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

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

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 pound per million BTU (lb/MMBtu) by calculating an oxygen-based fuel factor (F<sub>d</sub>) for refinery gas per USEPA 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. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in this test report.

## 2. RESULTS

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

**Table 2-1:  
NHT Charge Heater Stack – FPM & PM<sub>10</sub> Emissions**

Run No.		1	2	3	Average
Date (2017)		May 24	May 24	May 24	
Start Time (approx.)		09:10	11:55	14:41	
Stop Time (approx.)		11:21	14:09	16:50	
<b>Process Conditions</b>					
P <sub>1</sub>	Fuel gas flow rate (Mscf/day)	1,150	1,149	1,159	1,153
P <sub>2</sub>	Charge rate (bpd)	34,053	34,033	34,025	34,037
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,341	8,341	8,341	8,341
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.1	5.9	5.2	5.7
CO <sub>2</sub>	Carbon dioxide (dry volume %)	8.5	8.7	9.1	8.8
T <sub>s</sub>	Sample temperature (°F)	877	874	873	875
B <sub>w</sub>	Actual water vapor in gas (% by volume)	12.1	14.3	14.2	13.5
<b>Gas Flow Rate</b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	34,400	33,800	32,700	33,600
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	13,300	13,100	12,700	13,000
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	11,700	11,300	10,900	11,300
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	68.24	65.89	64.35	66.16
%I	Isokinetic sampling (%)	102.7	103.1	104.0	103.3
<b>Laboratory Data</b>					
m <sub>FPM</sub>	Total FPM (g)	0.00277	0.00294	0.00312	
m <sub>CPM</sub>	Total CPM (g)	0.00324	0.00329	0.00305	
m <sub>part</sub>	Total particulate matter (as PM <sub>10</sub> ) (g)	0.00601	0.00623	0.00617	
<b>FPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	8.95E-08	9.84E-08	1.07E-07	9.83E-08
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.0628	0.0664	0.0699	0.0664
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00105	0.00114	0.00119	0.00113
<b>CPM Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	1.05E-07	1.10E-07	1.05E-07	1.06E-07
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.0734	0.0743	0.0683	0.0720
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00123	0.00128	0.00116	0.00122
<b>Total Particulate Matter (as PM<sub>10</sub>) Results</b>					
C <sub>sd</sub>	Particulate Concentration (lb/dscf)	1.94E-07	2.08E-07	2.11E-07	2.05E-07
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.136	0.141	0.138	0.138
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00229	0.00242	0.00235	0.00235

**Table 2-2:  
NHT Charge Heater Stack – CO & NO<sub>x</sub> Emissions**

Run No.		1	2	3	Average
Date (2017)		May 24	May 24	May 24	
Start Time (approx.)		09:20	10:45	12:07	
Stop Time (approx.)		10:26	11:45	13:15	
<b>Process Conditions</b>					
P <sub>1</sub>	Fuel gas flow rate (Mscf/day)	1,149	1,156	1,141	1,149
P <sub>2</sub>	Charge rate (bpd)	34,055	34,046	34,035	34,045
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,341	8,341	8,341	8,341
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	5.3	5.2	5.1	5.2
CO <sub>2</sub>	Carbon dioxide (dry volume %)	9.4	9.4	9.5	9.4
<b>Carbon Monoxide Results</b>					
C <sub>sd</sub>	Concentration (ppm dv) <sup>1</sup>	<0.479	<0.479	<0.479	<0.479
C <sub>sd</sub>	Concentration (lb/dscf)	<3.48E-08	<3.48E-08	<3.48E-08	<3.48E-08
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<3.89E-04	<3.87E-04	<3.85E-04	<3.87E-04

<sup>1</sup>Resultant concentrations were less than 1% of instrument calibration span.

**Table 2-3:  
NHT Charge Heater Stack – H<sub>2</sub>SO<sub>4</sub> Emissions**

Run No.		1	2	3	Average
Date (2017)		May 25	May 25	May 25	
Start Time (approx.)		10:37	12:00	13:21	
Stop Time (approx.)		11:37	13:00	14:21	
<b>Process Conditions</b>					
P <sub>1</sub>	Fuel gas flow rate (Mscf/day)	1,183	1,169	1,167	1,173
P <sub>2</sub>	Charge rate (bpd)	33,967	33,964	33,966	33,966
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,343	8,343	8,343	8,343
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	6.9	6.1	6.2	6.4
CO <sub>2</sub>	Carbon dioxide (dry volume %)	8.1	8.6	8.6	8.4
T <sub>s</sub>	Sample temperature (°F)	875	878	876	876
B <sub>w</sub>	Actual water vapor in gas (% by volume)	14.0	14.3	14.1	14.1
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	29.37	29.38	29.07	29.27
<b>Laboratory Data (Ion Chromatography)</b>					
m <sub>n</sub>	Total H <sub>2</sub> SO <sub>4</sub> collected (mg)	0.7116	0.8380	0.8987	
<b>Sulfuric Acid Vapor (H<sub>2</sub>SO<sub>4</sub>) Results</b>					
C <sub>sdc</sub>	H <sub>2</sub> SO <sub>4</sub> Concentration (lb/dscf)	5.34E-08	6.29E-08	6.82E-08	6.15E-08
C <sub>sdc</sub>	H <sub>2</sub> SO <sub>4</sub> Concentration (ppm dv)	0.210	0.247	0.268	0.242
E <sub>Fd</sub>	H <sub>2</sub> SO <sub>4</sub> Rate - Fd-based (lb/MMBtu)	6.65E-04	7.41E-04	8.09E-04	7.38E-04

End of Section

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### 3. DESCRIPTION OF INSTALLATION

#### Process Description

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Naphtha Hydrotreater unit uses hydrogen to remove sulfur and nitrogen from straight-run and coker naphthas. This process, known as hydrotreating, uses a catalyst to promote the desulfurization reaction. The desulfurized or sweet naphtha is blended into gasoline or used for platformer feed. The NHT unit consists of process vessels (including exchangers, reactors, receivers, separators, and a stripper column), heaters, tanks, containers, pumps, piping, drains, and various components (pump seals, process valves, pressure relief valves, flanges, connectors, etc.).

The NHT Heater (EU16-NHTCHARHTR-S1) preheats the feed to the reactor. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the NHT Charge Heater Stack (SV16-H4) where testing was performed.

#### Test Location

The sample point locations were determined by EPA Methods 1 and 10 specifications. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 8 and 9 represent the layout of the test location.

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

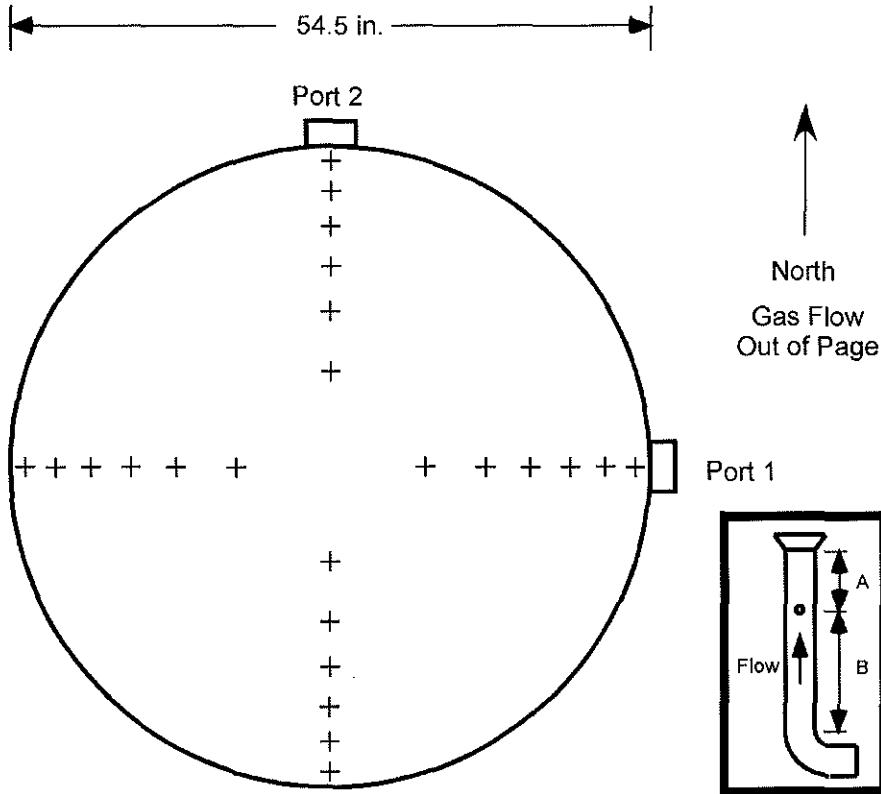
Source	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>NHT Charge Heater</u>							
FPM/CPM (PM <sub>10</sub> )	EPA M5/202	1-3	2	12	5	120	3-1
H <sub>2</sub> SO <sub>4</sub>	Draft ASTM CCM	1-3	1	1	60	60	N/A <sup>1</sup>
O <sub>2</sub> /CO <sub>2</sub> /CO	EPAM3A/10	1-3	1	1 <sup>2</sup>	60	60	3-2

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

<sup>2</sup> A stratification check conducted prior to Run 1 determined source met criteria for single point sampling.



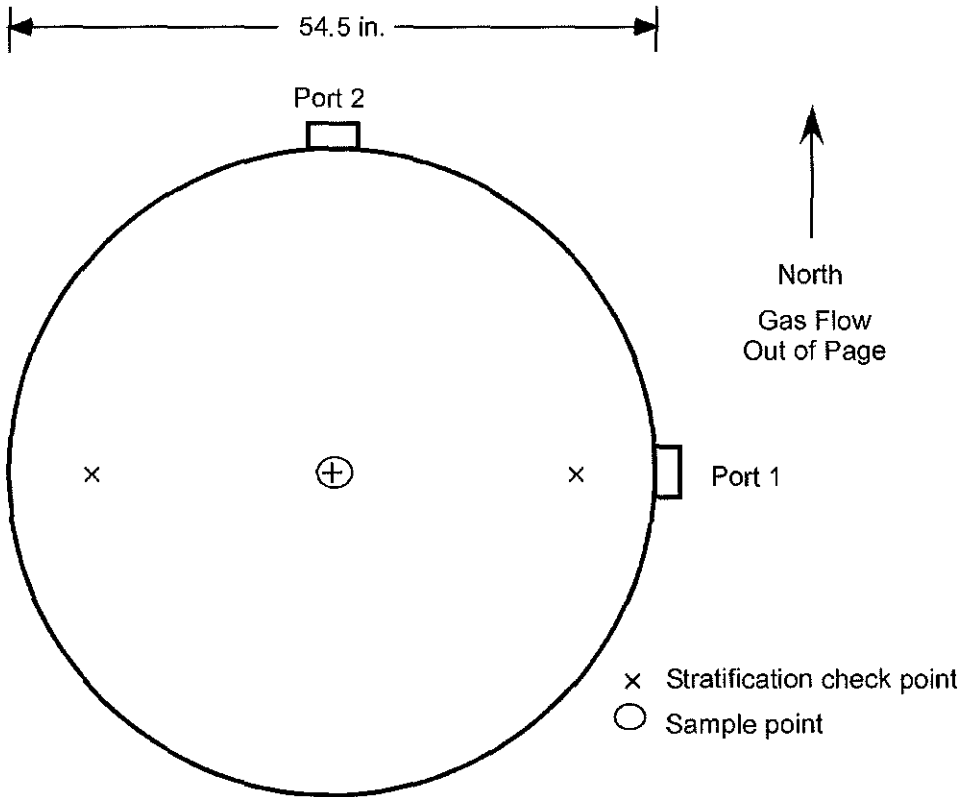
**Figure 3-1:  
 FPM & PM<sub>10</sub> Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	97.9	53.4
2	93.3	50.8
3	88.2	48.1
4	82.3	44.9
5	75.0	40.9
6	64.4	35.1
7	35.6	19.4
8	25.0	13.6
9	17.7	9.6
10	11.8	6.4
11	6.7	3.7
12	2.1	1.1

Duct diameters upstream from flow disturbance (A): 2.9      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 3.1      Limit: 2.0

**Figure 3-2:  
 CO Sample Point Layout (EPA Method 10)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	45.4
2	50.0	27.3
3	16.7	9.1

Duct diameters upstream from flow disturbance (A): 2.9      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 3.1      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 MDEQ. 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 3B "Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air"
- Method 4 "Determination of Moisture Content in Stack Gases"
- Method 5 "Determination of Particulate Matter Emissions from Stationary Sources"
- Method 10 "Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
- Method 19 "Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"

#### 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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### FPM 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 nitrogen oxide (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 nitrogen (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.

### O<sub>2</sub>, CO<sub>2</sub>, and CO Testing – USEPA Methods 3A and 10

Reference method oxygen (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 CO emissions were determined using an infrared 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 Method 3A and 10, the average results for each run were drift-corrected.

### 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 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 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 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*