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REPORT FOR COMPLIANCE
TESTING

Detroit Refinery
NHT Stripper/Reboiler Stack

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

CleanAir Project No. 13263
STAC Certificate No. 2007.002.0113.1217
Revision 0, Final Report
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Marathon Petroleum Company LP
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1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing on the NHT Stripper/Reboiler (EU16-NHTSTRIPREBOIL-S-1) 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 (PM₁₀), sulfuric acid (H₂SO₄), and carbon monoxide (CO) testing to demonstrate compliance with the 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**

Source Constituent	Sampling Method	Average Emission	Permit Limit ¹
<i>NHT Stripper/Reboiler</i>			
PM (lb/MMBtu)	USEPA 5	0.0010	0.0019
PM ₁₀ (lb/MMBtu)	USEPA 5/202	0.0019	0.0076
H ₂ SO ₄ (lb/MMBtu)	Draft ASTM CCM	4.1E-04	N/A
CO (lb/MMBtu)	USEPA 10	<0.0004	0.02

¹ 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 (PM₁₀), assumed equivalent to the sum of the following constituents:
 - filterable particulate matter (FPM)
 - condensable particulate matter (CPM)
- carbon monoxide (CO)
- sulfuric acid mist (H₂SO₄)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed the week of May 15, 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 ¹	NHT Stripper/Reboiler Stack	USEPA Method 5/202	FPM/CPM	05/16/17	10:26	11:45
2 ¹	NHT Stripper/Reboiler Stack	USEPA Method 5/202	FPM/CPM	05/16/17	12:41	14:46
3	NHT Stripper/Reboiler Stack	USEPA Method 5/202	FPM/CPM	05/16/17	15:28	17:34
4	NHT Stripper/Reboiler Stack	USEPA Method 5/202	FPM/CPM	05/16/17	18:16	20:23
5	NHT Stripper/Reboiler Stack	USEPA Method 5/202	FPM/CPM	05/17/17	08:00	10:37
1	NHT Stripper/Reboiler Stack	USEPA Method 3A/10	O ₂ /CO ₂ /CO	05/16/17	10:37	11:43
2	NHT Stripper/Reboiler Stack	USEPA Method 3A/10	O ₂ /CO ₂ /CO	05/16/17	12:14	13:14
3	NHT Stripper/Reboiler Stack	USEPA Method 3A/10	O ₂ /CO ₂ /CO	05/16/17	13:48	14:48
0	NHT Stripper/Reboiler Stack	Draft ASTM CCM	Sulfuric Acid	05/17/17	11:42	12:42
1	NHT Stripper/Reboiler Stack	Draft ASTM CCM	Sulfuric Acid	05/17/17	13:08	14:08
2	NHT Stripper/Reboiler Stack	Draft ASTM CCM	Sulfuric Acid	05/17/17	14:38	15:38
3	NHT Stripper/Reboiler Stack	Draft ASTM CCM	Sulfuric Acid	05/17/17	16:01	17:01

¹Test run was aborted/invalid. See *Discussion* for details.

Discussion

Test Scope Synopsis

FPM & PM₁₀ Testing

A total of three (3) valid 120-minute Method 5/202 test runs (Runs 3-5) were performed. Runs 1 and 2 were deemed invalid. 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. PM₁₀ is assumed equivalent to the sum of FPM less than 10 micrometers (μm) in diameter (FPM₁₀) and CPM. The Method 5/202 sample train yields a front-half, FPM result and a back-half, CPM result. The total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of total PM₁₀ since Method 5 collects all FPM present in the flue gas (regardless of particle size).

O₂, CO₂, & CO Testing

Minute-average data points for O₂, CO₂ and CO (dry basis) were collected over a period of 60 minutes for each RATA run.

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.

H₂SO₄ Testing

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

Three (3) 60-minute Draft ASTM CCM test runs were performed. H₂SO₄ emission results were calculated in units of lb/MMBtu. The final results were expressed as the average of three (3) valid runs.

Prior to the first official test run, a 60-minute sample conditioning run (Run 0) was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H₂SO₄-collecting portion of the sample train). The conditioning run was recovered in the same manner as the official test runs, but the condenser rinse and SAM filter were not analyzed.

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of pound per million BTU (lb/MMBtu) by calculating an oxygen-based fuel factor (F_d) for refinery gas per USEPA Method 19 specifications. The F_d factor was calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents.

Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions compliance test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in this test report.

Notable Occurrences

EPA Method 5/202 Run 1 was aborted midway through the test run when the realization was made that minimum criteria for sample volume would not be met due to the nozzle diameter being too small.

EPA Method 5/202 Run 2 was deemed invalid after the CPM filter of the back half portion of the sample train was contaminated.

The silica impinger of the sample train for EPA Method 5/202 Run 5 broke during the run. This was immediately realized, the run was paused, and the impinger was replaced. The moisture content utilized for calculations for Run 5 is an average of Runs 3 and 4. The silica weight presented on the datasheets for Run 5 represents a number that was extrapolated from the silica impinger weights from Runs 3 and 4. This weight was not used in the calculation for moisture content for Run 5.

All data is included in the appendices.

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:
NHT Stripper/Reboiler Stack – FPM & PM₁₀ Emissions**

Run No.		3	4	5	Average
Date (2017)		May 16	May 16	May 17	
Start Time (approx.)		15:28	18:16	08:00	
Stop Time (approx.)		17:34	20:23	10:37	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	756	761	779	765
P ₂	Charge rate (bpd)	28,027	28,030	28,044	28,034
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,304	8,304	8,268	8,292
Gas Conditions					
O ₂	Oxygen (dry volume %)	3.9	4.1	5.1	4.4
CO ₂	Carbon dioxide (dry volume %)	9.3	9.2	8.8	9.1
T _s	Sample temperature (°F)	599	602	620	607
B _w	Actual water vapor in gas (% by volume) ¹	15.3	15.2	15.2	15.2
Gas Flow Rate					
Q _a	Volumetric flow rate, actual (acfm)	12,900	12,600	14,800	13,433
Q _s	Volumetric flow rate, standard (scfm)	6,370	6,220	7,120	6,570
Q _{std}	Volumetric flow rate, dry standard (dscfm)	5,400	5,280	6,040	5,573
Sampling Data					
V _{msld}	Volume metered, standard (dscf)	63.24	60.44	71.00	64.89
%I	Isokinetic sampling (%)	103.7	101.4	104.1	103.0
Laboratory Data					
m _{FPM}	Total FPM (g)	0.00290	0.00269	0.00254	
m _{CPM}	Total CPM (g)	0.00262	0.00275	0.00263	
m _{Part}	Total particulate matter (as PM ₁₀) (g)	0.00552	0.00544	0.00517	
FPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	1.01E-07	9.82E-08	7.88E-08	9.27E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.0328	0.0311	0.0285	0.0308
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00103	0.00101	0.000861	0.000970
CPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	9.12E-08	1.00E-07	8.17E-08	9.11E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.0295	0.0317	0.0296	0.0303
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00093	0.00104	0.000894	0.000954
Total Particulate Matter (as PM₁₀) Results					
C _{sd}	Particulate Concentration (lb/dscf)	1.92E-07	1.98E-07	1.60E-07	1.84E-07
E _{lb/hr}	Particulate Rate (lb/hr)	0.0623	0.0628	0.0581	0.0611
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00197	0.00205	0.00176	0.00192

Note: Run 1 was aborted midway through the run and Run 2 was deemed invalid.

¹Run 5 moisture content an average of Runs 3 and 4.

**Table 2-2:
NHT Stripper/Reboiler Stack – CO Emissions**

Run No.		1	2	3	Average
Date (2017)		May 16	May 16	May 16	
Start Time (approx.)		10:37	12:14	13:48	
Stop Time (approx.)		11:43	13:14	14:48	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	727	733	775	745
P ₂	Charge rate (bpd)	27,974	27,974	28,024	27,991
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,304	8,304	8,304	8,304
Gas Conditions					
O ₂	Oxygen (dry volume %)	4.3	4.2	3.9	4.14
CO ₂	Carbon dioxide (dry volume %)	9.7	9.8	10.0	9.8
Carbon Monoxide Results					
C _{sd}	Concentration (ppmdv) ¹	<0.479	<0.479	<0.479	<0.48
C _{sd}	Concentration (lb/dscf)	<3.48E-08	<3.48E-08	<3.48E-08	<3.48E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	<3.64E-04	<3.62E-04	<3.55E-04	<3.61E-04

¹Resultant concentrations were less than 1% of instrument calibration span.

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**Table 2-3:
NHT Stripper/Reboiler Stack – H₂SO₄ Emissions**

Run No.		1	2	3	Average
Date (2017)		May 17	May 17	May 17	
Start Time (approx.)		13:08	14:38	16:01	
Stop Time (approx.)		14:08	15:38	17:01	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	792	783	788	788
P ₂	Charge rate (bpd)	28,040	28,002	27,967	28,003
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,268	8,268	8,268	8,268
Gas Conditions					
O ₂	Oxygen (dry volume %)	5.1	5.7	5.4	5.4
CO ₂	Carbon dioxide (dry volume %)	8.8	8.5	8.5	8.6
T _s	Sample temperature (°F)	620	614	614	616
B _w	Actual water vapor in gas (% by volume)	15.0	14.8	15.4	15.1
Sampling Data					
V _{msld}	Volume metered, standard (dscf)	27.36	27.26	27.11	27.24
Laboratory Data (Ion Chromatography)					
m _n	Total H ₂ SO ₄ collected (mg)	0.503	0.421	0.436	
Sulfuric Acid Vapor (H₂SO₄) Results					
C _{sd}	H ₂ SO ₄ Concentration (lb/dscf)	4.05E-08	3.40E-08	3.55E-08	3.67E-08
C _{sd}	H ₂ SO ₄ Concentration (ppmdv)	0.159	0.134	0.140	0.144
E _{Fd}	H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	4.43E-04	3.87E-04	3.96E-04	4.09E-04

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 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 Stripper/Reboiler (EU16-NHTSTRIPREBOIL-S1) heats the liquid from the bottom of the stripper column. The vapors that form are returned to the top of the stripper column; the liquid vapor is removed as a product stream. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the NHT Stripper/Reboiler Stack (SV16-H3) where testing was performed.

Test Location

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

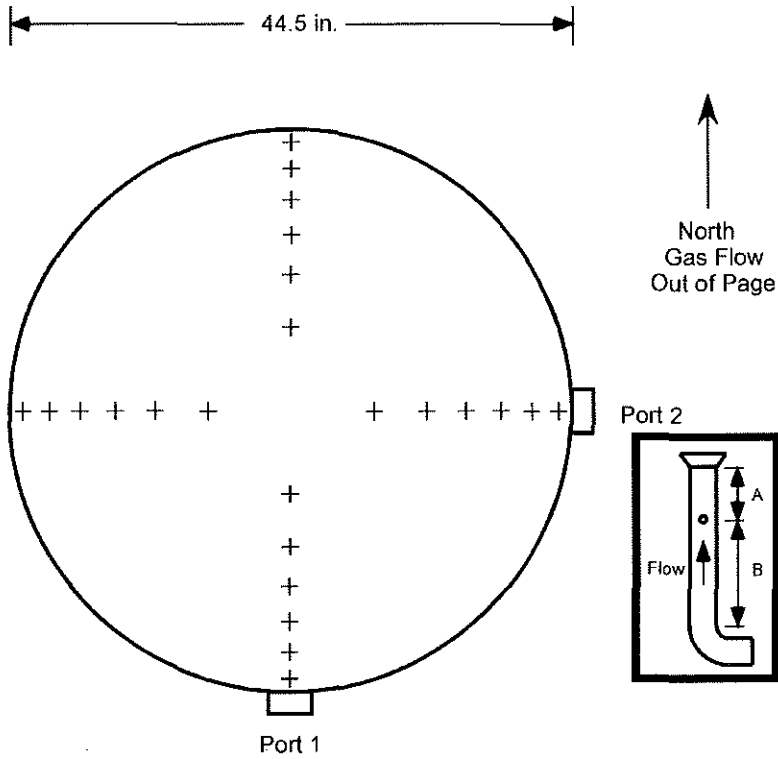
**Table 3-1:
Sampling Point Information**

Source Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
NHT Stripper/Reboiler Stack							
FPM/CPM (PM ₁₀)	EPAM5/202	3-5	2	12	5	120	3-1
H ₂ SO ₄	Draft ASTM CCM	1-3	1	1	60	60	N/A ¹
O ₂ /CO ₂ /CO	EPAM3A/10	1-3	1	1 ²	60	60	3-2

¹ Sampling occurred at a single point near the center of the duct.

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

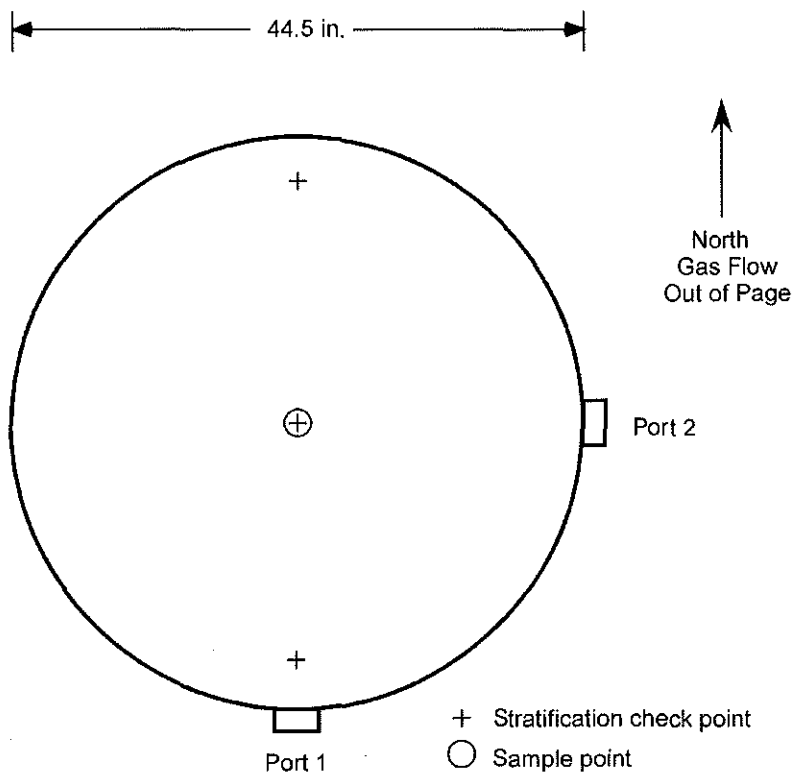
**Figure 3-1:
 FPM & PM₁₀ Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	97.9	43.5
2	93.3	41.5
3	88.2	39.2
4	82.3	36.6
5	75.0	33.4
6	64.4	28.7
7	35.6	15.8
8	25.0	11.1
9	17.7	7.9
10	11.8	5.3
11	6.7	3.2
12	2.1	1.0

Duct diameters upstream from flow disturbance (A): 6.7 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	37.1
2	50.0	22.3
3	16.7	7.4

Duct diameters upstream from flow disturbance (A): 6.7 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 3.1 Limit: 2.0

End of Section

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the USEPA and State Agency Name. 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 1A "Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts"
- 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

FPM and PM₁₀ 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 (SO₂) and nitrogen oxide (NO_x) interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water and SO₂ and NO_x were absorbed and partially oxidized before they could be purged out with nitrogen (N₂).

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 tetrafluoroethylene (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 (N₂) 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.

O₂, CO₂, and CO Testing – USEPA Methods 3A and 10

Reference method oxygen (O₂) and carbon dioxide (CO₂) 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_{dv}).

Calibration error checks were performed by introducing zero N₂, 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.

H₂SO₄ 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 H₂SO₄-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H₂O as the recovery/extraction solvent; any H₂SO₄ disassociates into sulfate ion (SO₄²⁻) and is stabilized in the H₂O matrix until analysis.

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

End of Section