CleanAir Engineering
500 W. Wood Street
Palatine, IL 60067-4975
cleanair.com

RECEIVED

JUL 21 2017

AIR QUALITY DIV.

REPORT FOR COMPLIANCE TESTING

Detroit Refinery
KHT Charge Heater Stack

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

CleanAir Project No. 13265-1
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 KHT Charge Heater (EU19-KHTCHARHTR-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_{10}), sulfuric acid (H_2SO_4), nitrogen oxides (NO_X) 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

Source **Constituent**	**Sampling Method**	**Average Emission**	**Permit Limit**[1]
KHT Charge Heater			
PM (lb/MMBtu)	USEPA 5	0.0013	0.0019
PM_{10} (lb/MMBtu)	USEPA 5/202	0.0028	0.0076
H_2SO_4 (lb/MMBtu)	Draft ASTM CCM	8.2E-04	N/A
NOx (lb/MMBtu)	USEPA 7E	0.15	0.20
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 (PM_{10}), assumed equivalent to the sum of the following constituents:
    - filterable particulate matter (FPM)
    - condensable particulate matter (CPM)
- nitrogen oxides (NO_X)
- carbon monoxide (CO)
- 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 May 22 and 23, 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	KHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/22/17	09:40	11:46
2	KHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/22/17	12:18	14:21
3	KHT Charge Heater	USEPA Method 5/202	FPM/CPM	05/22/17	16:38	18:42
1	KHT Charge Heater	USEPA Method 3A/7E/10	$O_2/CO_2/NO_X/CO$	05/22/17	10:01	11:06
2	KHT Charge Heater	USEPA Method 3A/7E/10	$O_2/CO_2/NO_X/CO$	05/22/17	11:32	12:32
3	KHT Charge Heater	USEPA Method 3A/7E/10	$O_2/CO_2/NO_X/CO$	05/22/17	12:57	14:05
0	KHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/23/17	09:54	10:54
1	KHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/23/17	11:09	12:09
2	KHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/23/17	12:38	13:38
3	KHT Charge Heater	Draft ASTM CCM	Sulfuric Acid	05/23/17	13:55	14:55

Discussion

Test Scope Synopsis

FPM & PM_{10} 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_{10} is assumed equivalent to the sum of FPM less than 10 micrometers (µm) in diameter (FPM_{10}) 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_{10} since Method 5 collects all FPM present in the flue gas (regardless of particle size).

O_2, CO_2, NO_X & CO Testing

Minute-average data points for O_2, CO_2, NO_X 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_2SO_4 Testing

H_2SO_4 emissions were determined referencing the Draft ASTM Controlled Condensation Method.

Three (3) 60-minute Draft ASTM CCM test runs were performed. H_2SO_4 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_2SO_4-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, ppmdv) 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 above 8,200 barrels/day (bpd) during NO_X and CO emissions compliance testing, and during Runs 1 and 2 of particulate emission testing. During H_2SO_4 emission testing and Run 3 of particulate emission testing, the unit was operated at 5,600-5,700 bpd. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in this test report.

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:
KHT Charge Heater Stack – FPM & PM_{10} Emissions

Run No.		1	2	3	Average
Date (2017)		May 22	May 22	May 22	
Start Time (approx.)		09:40	12:18	16:38	
Stop Time (approx.)		11:46	14:21	18:42	
Process Conditions					
P_1	Fuel gas flow rate (Mscf/day)	340	329	214	**294**
P_2	Charge rate (bpd)	8,308	8,077	5,655	**7,347**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,315	8,315	8,315	**8,315**
Gas Conditions					
O_2	Oxygen (dry volume %)	7.0	7.3	8.3	**7.5**
CO_2	Carbon dioxide (dry volume %)	8.1	7.9	7.3	**7.8**
T_s	Sample temperature (°F)	816	810	678	**768**
B_w	Actual water vapor in gas (% by volume)	13.3	12.7	12.7	**12.9**
Gas Flow Rate					
Q_a	Volumetric flow rate, actual (acfm)	10,100	10,100	6,600	**8,930**
Q_s	Volumetric flow rate, standard (scfm)	4,160	4,150	3,040	**3,780**
Q_{std}	Volumetric flow rate, dry standard (dscfm)	3,610	3,620	2,650	**3,290**
Sampling Data					
V_{mstd}	Volume metered, standard (dscf)	73.41	73.71	82.88	**76.67**
%I	Isokinetic sampling (%)	100.6	100.6	102.2	**101.1**
Laboratory Data					
m_{FPM}	Total FPM (g)	0.00421	0.00364	0.00269	
m_{CPM}	Total CPM (g)	0.00400	0.00412	0.00370	
m_{Part}	Total particulate matter (as PM_{10}) (g)	0.00821	0.00776	0.00639	
FPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	1.26E-07	1.09E-07	7.16E-08	**1.02E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.0274	0.0237	0.0114	**0.0208**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.00158	0.00139	0.00099	**0.00132**
CPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	1.20E-07	1.23E-07	9.85E-08	**1.14E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.0260	0.0268	0.0157	**0.0228**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.00150	0.00158	0.00136	**0.00148**
Total Particulate Matter (as PM_{10}) Results					
C_{sd}	Particulate Concentration (lb/dscf)	2.47E-07	2.32E-07	1.70E-07	**2.16E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.0534	0.0505	0.0271	**0.0436**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.00308	0.00297	0.00235	**0.00280**

Table 2-2:
KHT Charge Heater Stack – CO & NO$_X$ Emissions

Run No.		**1**	**2**	**3**	**Average**
Date (2017)		May 22	May 22	May 22	
Start Time (approx.)		10:01	11:32	12:57	
Stop Time (approx.)		11:06	12:32	14:05	
Process Conditions					
P_1	Fuel gas flow rate (Mscf/day)	339	341	331	**337**
P_2	Charge rate (bpd)	8,308	8,301	8,079	**8,229**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,315	8,315	8,315	**8,315**
Gas Conditions					
O_2	Oxygen (dry volume %)	6.3	6.4	6.7	**6.5**
CO_2	Carbon dioxide (dry volume %)	8.7	8.7	8.5	**8.6**
Carbon Monoxide Results					
C_{sd}	Concentration (ppmdv)[1]	<0.479	<0.479	<0.479	**<0.479**
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)	<4.15E-04	<4.17E-04	<4.26E-04	**<4.20E-04**
Nitrogen Oxides Results					
C_{sd}	Concentration (ppmdv)	107	107	107	**107**
C_{sd}	Concentration (lb/dscf)	1.28E-05	1.28E-05	1.28E-05	**1.28E-05**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	0.152	0.154	0.157	**0.154**

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

Table 2-3:
KHT Charge Heater Stack – H_2SO_4 Emissions

Run No.		**1**	**2**	**3**	**Average**
Date (2017)		May 23	May 23	May 23	
Start Time (approx.)		11:09	12:38	13:55	
Stop Time (approx.)		12:09	13:38	14:55	
Process Conditions					
P_1	Fuel gas flow rate (Mscf/day)	197	195	196	**196**
P_2	Charge rate (bpd)	5,646	5,625	5,608	**5,626**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,337	8,337	8,337	**8,337**
Gas Conditions					
O_2	Oxygen (dry volume %)	7.0	7.1	6.6	**6.9**
CO_2	Carbon dioxide (dry volume %)	8.0	7.9	8.2	**8.0**
T_s	Sample temperature (°F)	588	590	584	**587**
B_w	Actual water vapor in gas (% by volume)	13.4	13.5	14.1	**13.7**
Sampling Data					
V_{mstd}	Volume metered, standard (dscf)	28.19	27.81	27.81	**27.94**
Laboratory Data (Ion Chromatography)					
m_n	Total H2SO4 collected (mg)	0.7425	0.8560	0.9088	
Sulfuric Acid Vapor (H_2SO_4) Results					
C_{sd}	H_2SO_4 Concentration (lb/dscf)	5.81E-08	6.79E-08	7.21E-08	**6.60E-08**
C_{sd}	H_2SO_4 Concentration (ppmdv)	0.228	0.267	0.283	**0.259**
E_{Fd}	H_2SO_4 Rate - Fd-based (lb/MMBtu)	7.28E-04	8.57E-04	8.78E-04	**8.21E-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 Kerosene Hydrotreater unit uses hydrogen to remove sulfur and nitrogen from kerosene (and occasionally Naphtha). This process, known as hydrotreating, uses a catalyst with hydrogen and temperature to promote the desulfurization reaction. The KHT unit consists of process vessels (including exchangers, a reactor, a receiver, separators and a stripper column), a heater, tanks, containers, pumps, compressors, piping, drains and various components (pump and compressors, seals, process valves, pressure relief valves, flanges, connectors, etc.).

The KHT Heater (EU19-KHTCHARHTR-S1) preheats the feed to the reactor. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the KHT Charge Heater Stack (SV19-H2) 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 9 and 10 represent the layout of the test location.

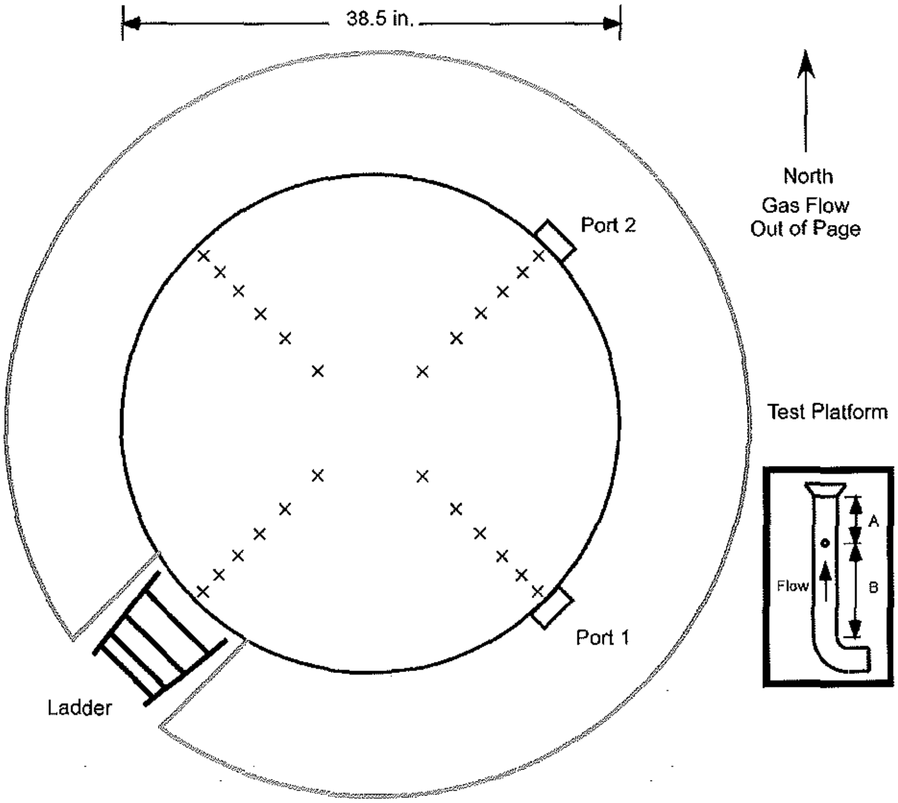
Table 3-1:
Sampling Point Information

Source Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
KHT Charge Heater							
FPM/CPM (PM_{10})	EPA M5/202	1-3	2	12	5	120	3-1
H_2SO_4	Draft ASTM CCM	1-3	1	1	60	60	N/A[1]
O_2 / CO_2 / NO_X/CO	EPA M3A/7E/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.

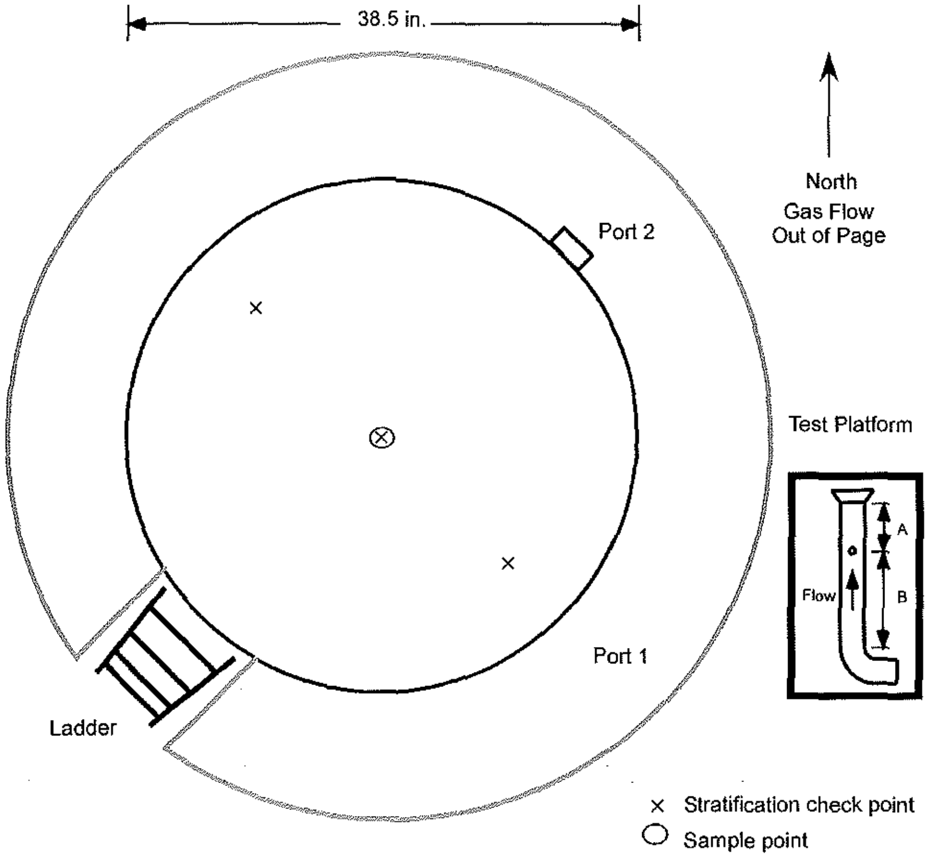
Figure 3-1:
FPM & PM_{10} Sample Point Layout (EPA Method 1)



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	97.9	37.5
2	93.3	35.9
3	88.2	34.0
4	82.3	31.7
5	75.0	28.9
6	64.4	24.8
7	35.6	13.7
8	25.0	9.6
9	17.7	6.8
10	11.8	4.5
11	6.7	2.6
12	2.1	1.0

Duct diameters upstream from flow disturbance (A): 5.0 Limit: 0.5
Duct diameters downstream from flow disturbance (B): 3.7 Limit: 2.0

Figure 3-2:
CO & NO_X Sample Point Layout (EPA Method 7E)



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	32.1
2	50.0	19.3
3	16.7	6.4

Duct diameters upstream from flow disturbance (A): 5.0 Limit: 0.5

Duct diameters downstream from flow disturbance (B): 3.7 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 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 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
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 PM_{10} 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_2) and NO_X interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water and SO_2 and NO_X were absorbed and partially oxidized before they could be purged out with nitrogen (N_2).

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_2) 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_2, CO_2, NO_X and CO Testing – USEPA Methods 3A and 10

Reference method oxygen (O_2) and carbon dioxide (CO_2) 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. Reference method NO_X emissions were determined using a chemiluminescent analyzer per EPA Method 7E.

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

Calibration error checks were performed by introducing zero N_2, 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 and 10, the average results for each run were drift-corrected.

H_2SO_4 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_2SO_4-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H_2O as the recovery/extraction solvent; any H_2SO_4 disassociates into sulfate ion (SO_4^{2-}) and is stabilized in the H_2O matrix until analysis.

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

End of Section