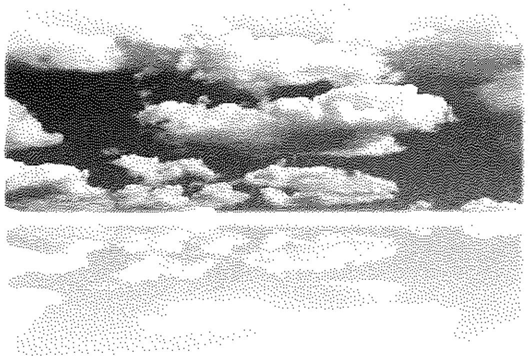
CleanAir Engineering
500 W. Wood Street
Palatine, IL 60067-4975
cleanair.com

RECEIVED
AUG 07 2017
AIR QUALITY DIVISION



REPORT ON COMPLIANCE TESTING

Detroit Refinery
Crude/Vacuum Heater Stack

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

CleanAir Project No. 13276-2
STAC Certificate No. 2007.002.0113.1217
Revision 0, Final Report
August 3, 2017

1. *PROJECT OVERVIEW*

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing on the Crude/Vacuum Heater (EU05-CRUDEHTR-S1) at the Detroit Refinery, located in Detroit, Michigan. The test program included the following objective:

- Perform particulate matter (PM), volatile organic compounds (VOCs) and sulfuric acid mist (H_2SO_4) testing to demonstrate compliance with the Michigan Department of Environmental Quality (DEQ) 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, begins on page 2.

Table 1-1:
Summary of Compliance Results

Source **Constituent**	**Sampling Method**	**Average Emission**	**Permit Limit[1]**
Crude Vacuum Heater Stack			
PM (lb/MMBtu)	USEPA M5	0.0021	0.0019
PM_{10} (lb/MMBtu)	USEPA M5 / 202	0.0036	0.0076
H_2SO_4 (lb/MMBtu)	ASTM Draft CCM	0.0012	N/A
VOC (lb/MMBtu)	USEPA M18 / 25A	< 0.0019	0.0055

[1] Permit limits obtained from MDEQ Renewable Operation 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)
- 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 from June 7 and 8, 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	Crude/Vacuum Heater Stack	USEPA Method 25A	THC	06/07/17	07:53	09:18
2	Crude/Vacuum Heater Stack	USEPA Method 25A	THC	06/07/17	09:28	11:08
3	Crude/Vacuum Heater Stack	USEPA Method 25A	THC	06/07/17	11:21	12:45
1	Crude/Vacuum Heater Stack	USEPA Method 5/202	FPM/CPM	06/07/17	08:05	10:17
2	Crude/Vacuum Heater Stack	USEPA Method 5/202	FPM/CPM	06/07/17	10:44	12:56
3	Crude/Vacuum Heater Stack	USEPA Method 5/202	FPM/CPM	06/07/17	13:20	15:32
0	Crude/Vacuum Heater Stack	Draft ASTM CCM	Sulfuric Acid	06/08/17	08:42	09:42
1	Crude/Vacuum Heater Stack	Draft ASTM CCM	Sulfuric Acid	06/08/17	10:13	11:13
2	Crude/Vacuum Heater Stack	Draft ASTM CCM	Sulfuric Acid	06/08/17	11:27	12:27
3	Crude/Vacuum Heater Stack	Draft ASTM CCM	Sulfuric Acid	06/08/17	12:37	13:37

Discussion

Test Scope Synopsis

FPM & PM_{10} 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.

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).

VOC Testing

VOC emissions were determined using EPA Method 25A to quantify THC emissions and EPA Method 18 to quantify methane (CH_4) and ethane (C_2H_6) emissions. VOC emissions are assumed equivalent to THC emissions, minus CH_4 and C_2H_6.

Nine (9) 21-minute Method 25A test runs were performed concurrently with three (3) 63-minute Method 18 bag collections. The final result for each THC run was expressed as the average of three (3) consecutive 21-minute runs. Other CEMS methods referencing EPA 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_4 and C_2H_6 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 runs.

For Run 2 and Run 3, the calculated emission rate of CH_4 and C_2H_6 detected through analysis of each Method 18 sample bag exceeded the amount of THC measured by the online THC analyzer. This is likely due to variations in the calibration standards, measurement and analytical technique. Therefore, VOC emissions are reported as a value "less than" 1% of the calibration span of the THC instrument.

H_2SO_4 Testing

H_2SO_4 emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM). 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 EPA 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 the test reports.

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:
Crude/Vacuum Heater Stack – FPM & PM$_{10}$ Emissions

Run No.		**1**	**2**	**3**	**Average**
Date (2017)		Jun 7	Jun 7	Jun 7	
Start Time (approx.)		08:05	10:44	13:20	
Stop Time (approx.)		10:17	12:56	15:32	
Process Conditions					
P_2	Charge rate (bpd)	136,028	139,434	138,951	**138,138**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,289	8,289	8,289	**8,289**
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	**8,760**
Gas Conditions					
O_2	Oxygen (dry volume %)	8.7	8.8	8.8	**8.8**
CO_2	Carbon dioxide (dry volume %)	6.9	6.9	7.0	**6.9**
T_s	Sample temperature (°F)	276	278	281	**278**
B_w	Actual water vapor in gas (% by volume)	12.1	12.0	12.4	**12.2**
Gas Flow Rate					
Q_a	Volumetric flow rate, actual (acfm)	109,000	107,000	113,000	**110,000**
Q_s	Volumetric flow rate, standard (scfm)	76,800	75,500	79,000	**77,100**
Q_{std}	Volumetric flow rate, dry standard (dscfm)	67,500	66,500	69,200	**67,700**
Sampling Data					
V_{mstd}	Volume metered, standard (dscf)	82.49	81.23	84.52	**82.75**
%I	Isokinetic sampling (%)	100.7	100.7	100.6	**100.6**
Laboratory Data					
m_{FPM}	Total FPM (g)	0.00465	0.00560	0.00663	
m_{CPM}	Total CPM (g)	0.00247	0.00422	0.00473	
m_{Part}	Total particulate matter (as PM$_{10}$) (g)	0.00712	0.00982	0.01136	
FPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	1.24E-07	1.52E-07	1.73E-07	**1.50E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.503	0.606	0.718	**0.609**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.00176	0.00218	0.00248	**0.00214**
CPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	6.61E-08	1.15E-07	1.23E-07	**1.01E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.268	0.457	0.512	**0.412**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.000939	0.00164	0.00177	**0.00145**
Total Particulate Matter (as PM$_{10}$) Results					
C_{sd}	Particulate Concentration (lb/dscf)	1.90E-07	2.67E-07	2.96E-07	**2.51E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.771	1.06	1.23	**1.02**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.00270	0.00382	0.00424	**0.00359**

Table 2-2:
Crude/Vacuum Heater Stack – VOCs Emissions

Run No.		**1**	**2**	**3**	**Average**
Date (2017)		Jun 7	Jun 7	Jun 7	
Start Time (approx.)		07:53	09:28	11:21	
Stop Time (approx.)		09:18	11:08	12:45	
Process Conditions					
P_1	Charge rate (bpd)	136,812	134,513	141,034	**137,453**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,289	8,289	8,289	**8,289**
Gas Conditions					
O_2	Oxygen (dry volume %)	8.1	8.2	7.9	**8.1**
CO_2	Carbon dioxide (dry volume %)	7.5	7.5	7.7	**7.6**
B_w	Actual water vapor in gas (% by volume)[1]	12.1	12.1	12.0	**12.1**
THC Results					
C_{sd}	Concentration (ppmdv as C_3H_8)	3.69	0.36	0.19	**1.41**
C_{sd}	Concentration (lb/dscf)	4.22E-07	4.10E-08	2.22E-08	**1.62E-07**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	0.00573	0.00056	0.00030	**0.00219**
Methane Results					
C_{sd}	Concentration (ppmdv)	2.3	2.6	2.9	**2.6**
C_{sd}	Concentration (lb/dscf)	9.6E-08	1.1E-07	1.2E-07	**1.1E-07**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	0.0013	0.0015	0.0016	**0.0015**
Ethane Results					
C_{sd}	Concentration (ppmdv)	<0.15	<0.15	<0.15	**<0.15**
C_{sd}	Concentration (lb/dscf)	<1.2E-08	<1.2E-08	<1.2E-08	**<1.2E-08**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	< 0.00016	< 0.00016	< 0.00016	**< 0.00016**
VOC Results					
C_{sd}	Concentration (ppmdv as C_3H_8)	<2.8	<0.45	<0.45	**<1.24**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	< 0.0044	< 0.00070	< 0.00069	**< 0.0019**

---

[1] Moisture data used for ppmwv to ppmdv correction obtained from an average of overlapping M5/202 runs.

Table 2-3:
Crude/Vacuum Heater Stack – H_2SO_4 Emissions

Run No.		**1**	**2**	**3**	**Average**
Date (2017)		Jun 8	Jun 8	Jun 8	
Start Time (approx.)		10:13	11:27	12:37	
Stop Time (approx.)		11:13	12:27	13:37	
Process Conditions					
P_2	Charge rate (bpd)	125,035	125,989	127,147	**126,057**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,332	8,332	8,332	**8,332**
Gas Conditions					
O_2	Oxygen (dry volume %)	9.1	8.5	8.5	**8.7**
CO_2	Carbon dioxide (dry volume %)	7.1	7.4	7.3	**7.3**
T_s	Sample temperature (°F)	288	287	287	**287**
B_w	Actual water vapor in gas (% by volume)	11.8	11.9	12.2	**12.0**
Sampling Data					
V_{mstd}	Volume metered, standard (dscf)	25.54	25.57	25.59	**25.57**
Laboratory Data (Ion Chromatography)					
m_n	Total H_2SO_4 collected (mg)	1.1848	0.9867	0.8083	
Sulfuric Acid Vapor (H_2SO_4) Results					
C_{sd}	H_2SO_4 Concentration (lb/dscf)	1.02E-07	8.51E-08	6.97E-08	**8.57E-08**
C_{sd}	H_2SO_4 Concentration (ppmdv)	0.402	0.334	0.274	**0.337**
E_{Fd}	H_2SO_4 Rate - Fd-based (lb/MMBtu)	0.00151	0.00120	0.00098	**0.00123**

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 Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to other units in the refinery for further processing. The Crude Unit consists of process vessels (including heat exchangers and fractionation columns), the Alcorn heater (EG05-CRUDEHTR), tanks, containers, compressors, pumps, piping, drains, and various components (pump and compressors seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Crude Heater (EU05-CRUDEHTR-S1) is fired by refinery fuel gas. Emissions are vented to the atmosphere via a common stack known as the Crude/Vacuum Heater Stack (SV04-H1-05-H1), where testing was performed.

Test Location

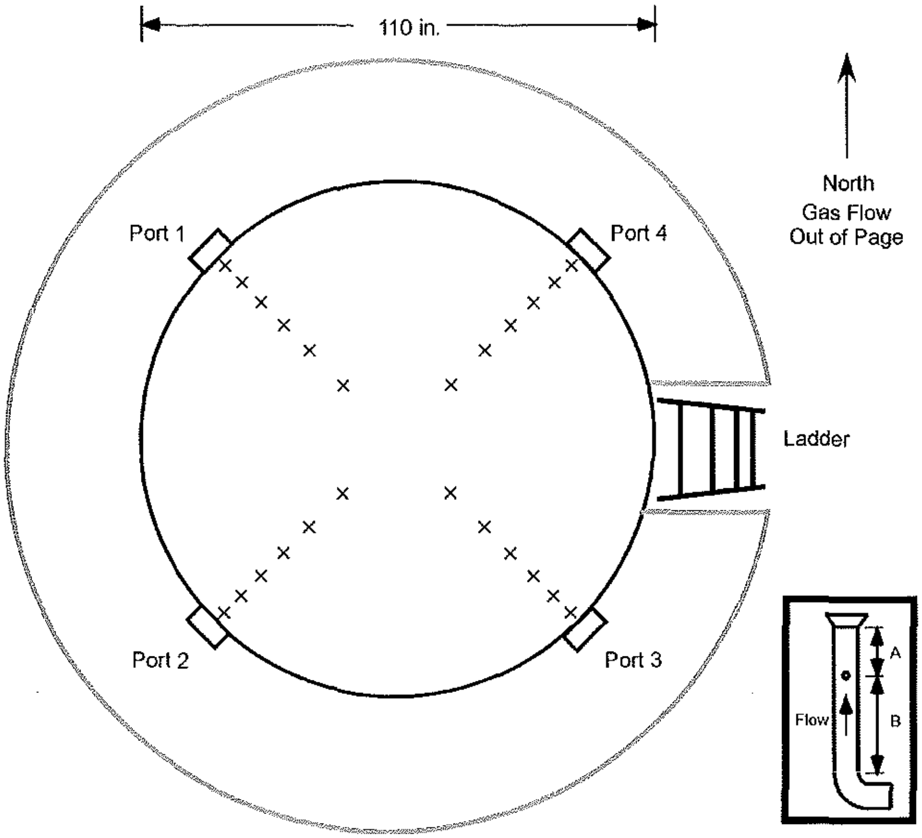
The sample point locations were determined by EPA Methods 1 and 25A (with references to 7E specifications). Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 9 and 10 represent the layout of the test location.

Table 3-1:
Sampling Point Information

Source Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
Crude Vacuum Heater Stack							
FPM / CPM	M5 / 202	1-3	4	6	5	120	3-1
H_2SO_4	Draft ASTM CCM	1-3	1	1	60	60	N/A
O_2 / CO_2 / CH_4 / C_2H_6 / THC	3A / 18 / 25A	1-3	1	3	21	63	3-2

[1] Draft STM CCM sampling occurred at a single point near the center of the duct.

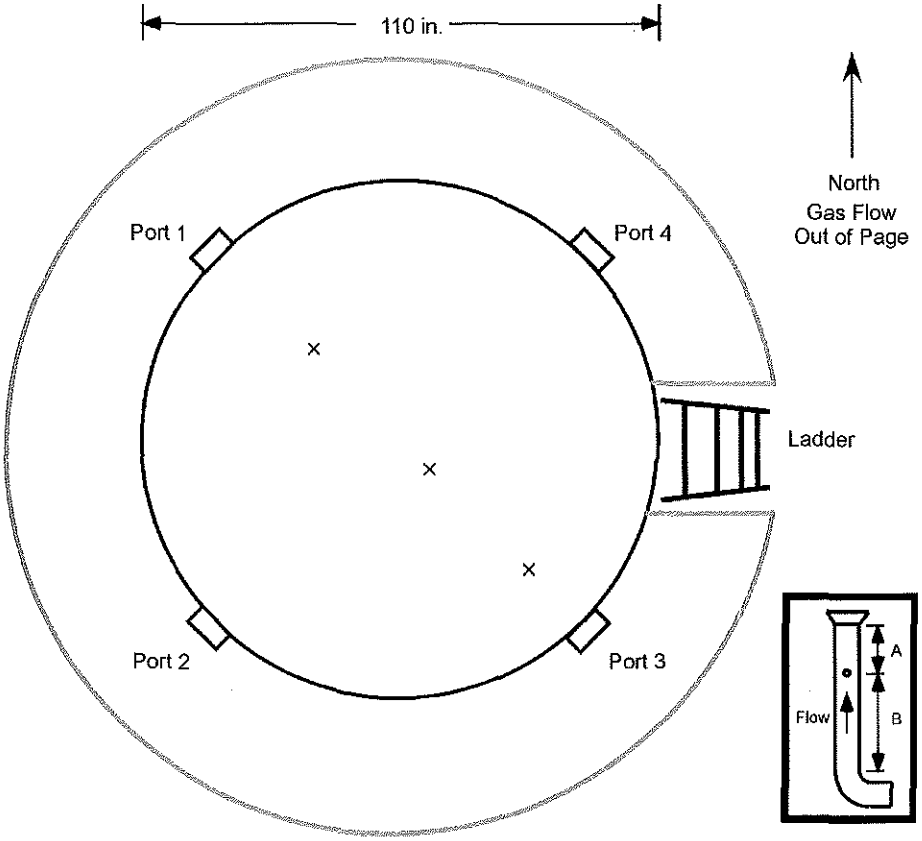
Figure 3-1:
FPM & PM_{10} Sample Point Layout (EPA Method 1)



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	39.2
2	25.0	27.5
3	17.7	19.5
4	11.8	13.0
5	6.7	7.4
6	2.1	2.3

Duct diameters upstream from flow disturbance (A): 5.3	Limit: 0.5
Duct diameters downstream from flow disturbance (B): 2.4	Limit: 2.0

Figure 3-2:
THC Sample Point Layout (EPA Method 25A)



Sampling Point	Port to Point Distance (meters)	Port to Point Distance (inches)
1	2.0	78.7
2	1.2	47.2
3	0.4	15.7

Duct diameters upstream from flow disturbance (A): 5.3	Limit: 0.5
Duct diameters downstream from flow disturbance (B): 2.4	Limit: 2.0

End of Section

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the U.S. 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 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 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"
Method 18	"Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"

Title 40 CFR Part 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 (EPA 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 (EPA 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 nitrogen oxide (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 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.

VOCs Testing – USEPA Methods 25A & 18

The Method 25A sampling system consists of a heated probe, heated filter and heated sample line. Flue gas was delivered at 250°F to a flame ionization analyzer (FIA), which continuously measures minute-average THC concentration expressed in terms of propane (C_3H_8) on an actual (wet) basis. FIA calibration was performed by introducing zero air, high, mid- and low range C_3H_8 calibration gases to the inlet of the sampling system's heated filter. Bias checks were performed before and after each sampling run in a similar manner.

The Method 18 sampling system consists of a gas conditioner (for moisture removal), TFE sample lines, TFE-coated diaphragm pump and a mass flow meter ("Direct Pump Sampling Procedure"). This system 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_4 and C_2H_6 are insoluble in water.

Analysis for CH_4 and C_2H_6 was performed off-site by CleanAir Analytical Services using gas chromatography (GC). Since moisture was removed from the sample prior to collection, the GC analyzer 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_4 and C_2H_6 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_4 and C_2H_6, 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_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 deionized (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