

1. PROJECT OVERVIEW

TEST PROGRAM SUMMARY

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to perform emission measurements on the Fluid Catalytic Cracking Unit (FCCU) Regenerator Stack at the Detroit Refinery to demonstrate compliance status.

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.

**Table 1-1:
 Summary of NSFPM, CPM, and Total PM₁₀ Results (EPA Method 5F/202)**

FCCU Regenerator Stack		NSFPM Rate (lb/Mlb coke)	Method 5F/202	
			CPM Rate (lb/Mlb coke)	Total PM ₁₀ Rate (lb/Mlb coke)
Test Date	03/03/21			
Coke Burn Rate (Mlb coke/hr)	22.3	Run 1	0.22	0.60
FCC Rate (bpd)	41,000	Run 2	0.20	0.45
Aqueous NH ₃ Injection (lb/hr)	48.1	Run 3	0.22	0.66
		Average	0.21	0.57
		Limit	0.80	1.1

**Table 1-2:
 Summary of NH₃ Results (CTM-027)**

FCCU Regenerator Stack		NH ₃ Conc. (ppmdv)	Mod. CTM-027	
			NH ₃ Slip (lb/hr)	NH ₃ Slip (lb/Mlb coke)
Test Date	03/03/21			
Coke Burn Rate (Mlb coke/hr)	22.3	Run 1	13	2.5
FCC Rate (bpd)	41,000	Run 2	17	3.3
Aqueous NH ₃ Injection (lb/hr)	48.1	Run 3	12	2.4
		Average	14	2.7
		Limit	10.9	0.12

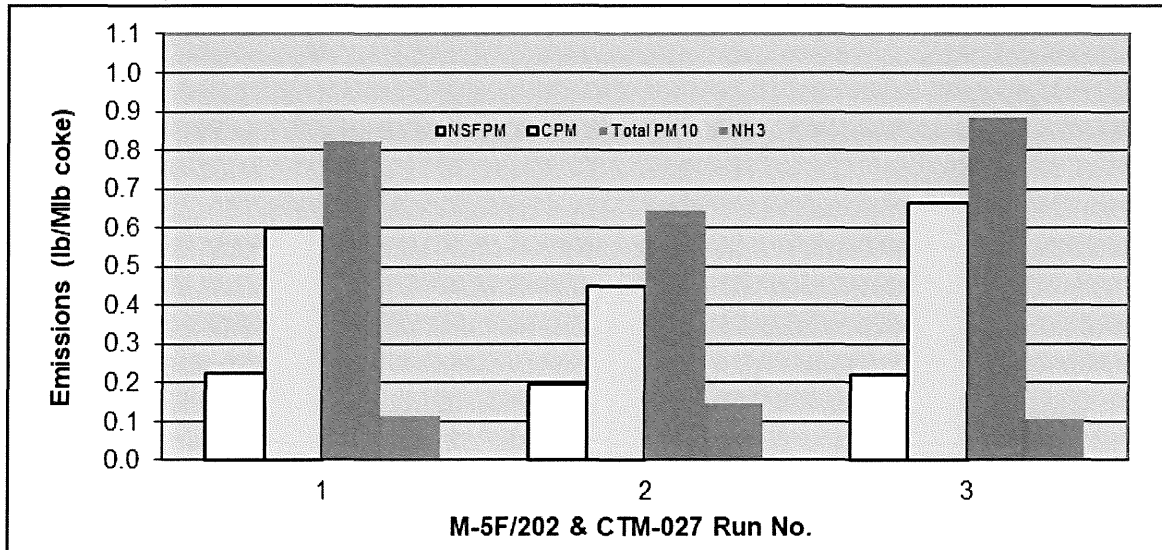
**Table 1-3:
 Summary of H₂SO₄ Results (CTM-013)**

FCCU Regenerator Stack		Mod. CTM-013		
		H ₂ SO ₄ Conc. (ppmdv)	H ₂ SO ₄ Rate (lb/hr)	H ₂ SO ₄ Rate (lb/Mlb coke)
Test Date	3/2/2021			
Coke Burn Rate (Mlb coke/hr)	22.1	Run 1	3.2	0.16
FCC Rate (bpd)	41,000	Run 2	1.0	0.053
NH ₃ Injection (lb/hr)	46.2	Run 3	0.39	0.019
		Average	1.6	0.078
		Limit		

**Table 1-4:
 Summary of VOC Results (EPA Method 18/25A)**

FCCU Regenerator Stack		Method 25A		
		VOC Conc. (lb/hr)	VOC Rate (Ton/yr)	VOC Rate (lb/Mlb coke)
Test Date	03/02/21			
Coke Burn Rate (Mlb coke/hr)	22.1	Run 1	0.49	0.022
FCC Rate (bpd)	41,000	Run 2	0.70	0.032
NH ₃ Injection (lb/hr)	46.2	Run 3	0.55	0.025
		Average	0.58	0.026
		Limit	21	

**Figure 1-1:
 NSFPM, CPM, Total PM₁₀, and NH₃ Results**



TEST PROGRAM DETAILS

PARAMETERS

The test program included the following measurements:

- particulate matter (PM) assumed to be equivalent to nonsulfate particulate matter (NSFPM)
- condensable particulate matter (CPM)
- total particulate matter less than or equal to 10 microns (μm) in diameter (Total PM_{10}) assumed equivalent to the sum of the two preceding constituents
- ammonia (NH_3)
- sulfuric acid mist (H_2SO_4)
- volatile organic compounds (VOC) assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
 - methane (CH_4)
 - ethane (C_2H_6)
- flue gas composition (e.g., O_2 , CO_2 , H_2O)
- flue gas temperature
- flue gas flow rate

SCHEDULE

Testing was performed on March 2 & 3, 2021. Table 1-5 outlines the on-site schedule followed during the test program.

**Table 1-5:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	FCCU Regen Stack	USEPA Method 3A/25A	O ₂ / CO ₂ / VOC	03/02/21	08:45	09:48
1	FCCU Regen Stack	CTM-013 (mod)	Acid Vapor (as H ₂ SO ₄)	03/02/21	08:47	09:47
1	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/02/21	08:53	09:06
2	FCCU Regen Stack	USEPA Method 3A/25A	O ₂ / CO ₂ / VOC	03/02/21	10:11	11:13
2	FCCU Regen Stack	CTM-013 (mod)	Acid Vapor (as H ₂ SO ₄)	03/02/21	10:12	11:12
2	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/02/21	10:14	10:26
3	FCCU Regen Stack	USEPA Method 3A/25A	O ₂ / CO ₂ / VOC	03/02/21	11:35	12:39
3	FCCU Regen Stack	CTM-013 (mod)	Acid Vapor (as H ₂ SO ₄)	03/02/21	11:35	12:35
3	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/02/21	11:35	11:49
1	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/03/21	08:01	08:12
1	FCCU Regen Stack	CTM-027	Ammonia	03/03/21	08:48	09:57
1	FCCU Regen Stack	USEPA Method 5F/202	Nonsulfate FPM/CPM	03/03/21	08:48	09:57
1	FCCU Regen Stack	USEPA Method 3A	O ₂ / CO ₂	03/03/21	08:48	09:57
2	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/03/21	10:40	10:48
2	FCCU Regen Stack	CTM-027	Ammonia	03/03/21	10:58	12:05
2	FCCU Regen Stack	USEPA Method 5F/202	Nonsulfate FPM/CPM	03/03/21	10:58	12:05
2	FCCU Regen Stack	USEPA Method 3A	O ₂ / CO ₂	03/03/21	10:58	12:05
3	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/03/21	12:39	12:48
3	FCCU Regen Stack	CTM-027	Ammonia	03/03/21	13:11	14:18
3	FCCU Regen Stack	USEPA Method 5F/202	Nonsulfate FPM/CPM	03/03/21	13:11	14:18
3	FCCU Regen Stack	USEPA Method 3A	O ₂ / CO ₂	03/03/21	13:11	14:18
4	FCCU Regen Stack	USEPA Method 2F	3-D Velocity & Flow Rate	03/03/21	14:39	14:48

DISCUSSION

Flow Rate Measurements

Three-dimensional (3-D) flow traverses, per EPA Method 2F, were performed before and after each EPA Method 5F/202 and Conditional Test Method (CTM) 027 test run and during each EPA Method 18/25A and CTM-013 test run.

During the first flow traverse performed on March 2, there appeared to be a data communication error from the stack temperature thermocouple. The results of Run 1 were calculated using the average stack temperature measured at each point from Runs 2 & 3.

NSFPM and CPM Testing

Three (3) 60-minute Method 5F/202 test runs were performed on March 3.

For this test program, PM emission rate is assumed equivalent to NSFPM emission rate, and PM₁₀ emission rate is assumed equivalent to the sum of NSFPM and CPM emission rates (units of lb/hr, ton/yr, or lb/Mlb coke for all constituents). For emissions inventory purposes, MPC applies a correction factor to NSFPM to eliminate particles with a diameter less than 10 microns. Application of that correction factor is not included in this test report.

NH₃ Testing

Three (3) 60-minute CTM-027 test runs were performed on March 3. Each test run was performed concurrently with Method 5F/202 testing. The results are the average of all runs.

H₂SO₄ Testing

Three (3) 60-minute modified CTM-013 test runs were performed on March 2. The results were expressed as the average of three test runs.

VOC Testing

Three (3) 60-minute Method 25A test runs for THCs were performed concurrently with three (3) 60-minute Method 18 integrated gas sample (IGS) collections for CH₄ and C₂H₆.

VOC emission rate is normally equivalent to THC emission rate minus CH₄ and C₂H₆ emission rate (units of lb/hr, Ton/yr, or lb/Mlb coke for all constituents). Since THC emission rates were already less than the limit for VOC, CH₄, and C₂H₆ analysis was not conducted and VOC emissions for Runs 1 through 3 were considered equivalent to THC emissions only. The final VOC results were expressed as the average of three runs.

Calculation of Final Results

Sample flow rates measured during the run, as determined by EPA Method 2, were used to calculate isokinetic sampling conditions. Mass-based emission rates in units of pounds per hour (lb/hr) for Method 5F/202 and CTM-027 were calculated using the applicable average pre-run and post-run flow rate determined by EPA Method 2F. Mass-based emission rates in units of lb/hr for Method EPA 25A and modified CTM-013 were calculated using the applicable concurrent flow rate determined by Method 2F.

Wall-effects adjustment factor (WAF) correction respective to specifications outlined in EPA Method 2H produced negligible effects and were not included in final calculations for flow rates.

Emission rates in units of tons per year (Ton/yr) were calculated using an assumed capacity factor of 8,760 operating hours per year. Emission rates in units of pounds per 1,000 pounds of coke burn (lb/Mlb coke) were calculated using coke burn rate data provided by MPC.

NH₃ injection rates, shown in Tables 2-1 through 2-4, are the aqueous NH₃ (11FC2032) multiplied by a factor of 0.2.

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices.

**Table 2-1:
Sulfuric Acid Vapor (H₂SO₄) Emission Results(CTM-013)**

Run No.	1	2	3	Average
Date (2021)	Mar 2	Mar 2	Mar 2	
Start Time (approx.)	08:47	10:12	11:35	
Stop Time (approx.)	09:47	11:12	12:35	
Process Conditions				
R _p Production rate (Mlb Coke/hr)	22.2	22.1	22.0	22.1
P ₁ FCCU charge rate (bpd)	41,000	41,000	41,000	41,000
P ₂ Ammonia Injection (lb/hr)	46.4	46.2	46.1	46.2
Gas Conditions				
O ₂ Oxygen (dry volume %)	1.75	1.68	1.72	1.72
CO ₂ Carbon dioxide (dry volume %)	16.2	16.3	16.2	16.2
T _s Stack temperature (°F)	523	522	522	522
B _w Actual water vapor in gas (% by volume)	10.4	10.9	9.9	10.4
Gas Flow Rate (from Method 2F data)				
Q _a Volumetric flow rate, actual (acfm)	150,000	153,000	150,000	151,000
Q _s Volumetric flow rate, standard (scfm)	81,000	82,700	80,800	81,500
Q _{std} Volumetric flow rate, dry standard (dscfm)	72,600	74,100	72,400	73,000
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	27.48	26.75	26.66	26.96
Laboratory Data (Ion Chromatography)				
m _n Total H ₂ SO ₄ collected (mg)	10.296	3.1845	1.1904	
Sulfuric Acid Vapor (H₂SO₄) Results				
C _{sd} H ₂ SO ₄ Concentration (ppmdv)	3.2	1.0	0.39	1.6
E _{lb/hr} H ₂ SO ₄ Rate (lb/hr)	3.6	1.2	0.43	1.7
E _{T/yr} H ₂ SO ₄ Rate (Ton/yr)	16	5.1	1.9	7.6
E _{Rp} H ₂ SO ₄ Rate - Production-based (lb/Mlb Coke)	0.16	0.053	0.019	0.078

**Table 2-2:
Volatile Organic Compounds (VOC) Emission Results (EPA Method 25A)**

Run No.		1	2	3	Average
Date (2021)		Mar 2	Mar 2	Mar 2	
Start Time (approx.)		08:45	10:11	11:35	
Stop Time (approx.)		09:48	11:13	12:39	
Process Conditions					
RP	Production rate (Mlb Coke/hr)	22.2	22.1	22.0	22.1
P1	FCCU charge rate (bpd)	41,000	41,000	41,000	41,000
P2	Ammonia Injection (lb/hr)	46.4	46.2	46.1	46.2
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760
Gas Conditions					
O ₂	Oxygen (dry volume %)	1.75	1.68	1.72	1.72
CO ₂	Carbon dioxide (dry volume %)	16.2	16.3	16.2	16.2
T _s	Sample temperature (°F)	509	506	512	509
B _w	Actual water vapor in gas (% by volume)	10.4	10.4	10.4	10.4
Gas Flow Rate (from Method 2F data)					
Q _a	Volumetric flow rate, actual (acfm)	150,000	153,000	150,000	151,000
Q _s	Volumetric flow rate, standard (scfm)	81,000	82,700	80,800	81,500
Q _{std}	Volumetric flow rate, dry standard (dscfm)	72,600	74,100	72,400	73,000
Volatile Organic Compounds (VOC) as Propane					
C _d	VOC Concentration (ppmdv)	0.99	1.4	1.1	1.2
E _{lb/hr}	VOC Mass Rate (lb/hr)	0.49	0.70	0.55	0.58
E _{T/yr}	VOC Mass Rate (Ton/yr)	2.2	3.1	2.4	2.5
E _{Rp}	VOC Mass Rate (lb/Mlb Coke)	0.022	0.032	0.025	0.026

**Table 2-3:
Particulate (NSFPM, CPM, & Total PM₁₀) Emissions Results (EPA Method 5F/202)**

Run No.	1	2	3	Average
Date (2021)	Mar 3	Mar 3	Mar 3	
Start Time (approx.)	08:48	10:58	13:11	
Stop Time (approx.)	09:57	12:05	14:18	
Process Conditions				
R _p Production rate (Mlb Coke/hr)	22.4	22.3	22.2	22.3
P ₁ FCCU charge rate (bpd)	41,000	41,000	41,000	41,000
P ₂ Ammonia Injection (lb/hr)	46.4	48.4	49.4	48.1
Gas Conditions				
O ₂ Oxygen (dry volume %)	1.73	1.74	1.71	1.73
CO ₂ Carbon dioxide (dry volume %)	16.2	16.2	16.3	16.2
T _s Stack temperature (°F)	520	522	522	521
B _w Actual water vapor in gas (% by volume)	10.4	10.2	10.7	10.4
Gas Flow Rate (from Method 2F data)				
Q _a Volumetric flow rate, actual (acfm)	154,000	154,000	153,000	154,000
Q _s Volumetric flow rate, standard (scfm)	82,600	82,500	82,400	82,500
Q _{std} Volumetric flow rate, dry standard (dscfm)	73,900	73,700	73,700	73,800
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	36.79	37.13	36.74	36.89
%I Isokinetic sampling (%)	98.6	98.0	98.1	98.2
Laboratory Data				
m _n Total NSFPM (g)	0.0189	0.0167	0.0183	
m _{CPM} Total CPM (g)	0.0505	0.0382	0.0555	
m _{Part} Total particulate matter (g)	0.0694	0.0549	0.0738	
NSFPM Results				
C _{sd} Particulate Concentration (lb/dscf)	1.13E-06	9.91E-07	1.10E-06	1.07E-06
E _{lb/hr} Particulate Rate (lb/hr)	5.0	4.4	4.9	4.8
E _{T/yr} Particulate Rate (Ton/yr)	22	19	21	21
E _{Rp} Particulate Rate - Production-based (lb/Mlb Coke)	0.22	0.20	0.22	0.21
CPM Results				
C _{sd} Particulate Concentration (lb/dscf)	3.03E-06	2.27E-06	3.33E-06	2.88E-06
E _{lb/hr} Particulate Rate (lb/hr)	13	10	15	13
E _{T/yr} Particulate Rate (Ton/yr)	59	44	65	56
E _{Rp} Particulate Rate - Production-based (lb/Mlb Coke)	0.60	0.45	0.66	0.57
Total Particulate Matter Results				
C _{sd} Particulate Concentration (lb/dscf)	4.16E-06	3.26E-06	4.43E-06	3.95E-06
E _{lb/hr} Particulate Rate (lb/hr)	18	14	20	17
E _{T/yr} Particulate Rate (Ton/yr)	81	63	86	77
E _{Rp} Particulate Rate - Production-based (lb/Mlb Coke)	0.82	0.65	0.88	0.78

**Table 2-4:
Ammonia (NH₃) Emission Results (CTM-027)**

Run No.		1	2	3	Average
Date (2021)		Mar 3	Mar 3	Mar 3	
Start Time (approx.)		08:48	10:58	13:11	
Stop Time (approx.)		09:57	12:05	14:18	
Process Conditions					
R _P	Production rate (Mlb Coke/hr)	22.4	22.3	22.2	22.3
P ₁	FCCU charge rate (bpd)	41,000	41,000	41,000	41,000
P ₂	Ammonia Injection (lb/hr)	46.4	48.4	49.4	48.1
Gas Conditions					
O ₂	Oxygen (dry volume %)	1.73	1.74	1.71	1.73
CO ₂	Carbon dioxide (dry volume %)	16.2	16.2	16.3	16.2
T _s	Stack temperature (°F)	522	522	522	522
B _w	Actual water vapor in gas (% by volume)	10.6	11.0	10.6	10.7
Gas Flow Rate (from Method 2F data)					
Q _a	Volumetric flow rate, actual (acfm)	154,000	154,000	153,000	154,000
Q _s	Volumetric flow rate, standard (scfm)	82,600	82,500	82,400	82,500
Q _{std}	Volumetric flow rate, dry standard (dscfm)	73,900	73,700	73,700	73,800
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	39.89	38.83	39.74	39.49
%I	Isokinetic sampling (%)	99.7	99.6	100.0	99.8
Laboratory Data					
m _n	Total NH ₃ collected (mg)	10.38	13.15	9.63	
Ammonia (NH₃) Results					
C _{sd}	Ammonia Concentration (lb/dscf)	5.74E-07	7.47E-07	5.34E-07	6.18E-07
C _{sd}	Ammonia Concentration (ppmdv)	13.0	16.9	12.1	14.0
E _{lb/hr}	Ammonia Rate (lb/hr)	2.5	3.3	2.4	2.7
E _{T/yr}	Ammonia Rate (Ton/yr)	11	14	10	12
E _{Rp}	Ammonia Rate - Production-based (lb/Mlb coke)	0.11	0.15	0.11	0.12

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 compliant with permitted emission limits.

The Fluid Catalytic Cracking Unit (EU11-FCCU-S1) utilizes a primary reactor, a distillation column, and a catalyst regeneration unit to continuously generate light hydrocarbon products from heavy oil feeds. The FCCU is equipped with an electrostatic precipitator (ESP) with two (2) bays and variable aqueous NH₃ injection to control emissions. Emissions are vented to the atmosphere via the FCCU Regenerator Stack (SVFCCU), where testing was conducted.

TEST LOCATION

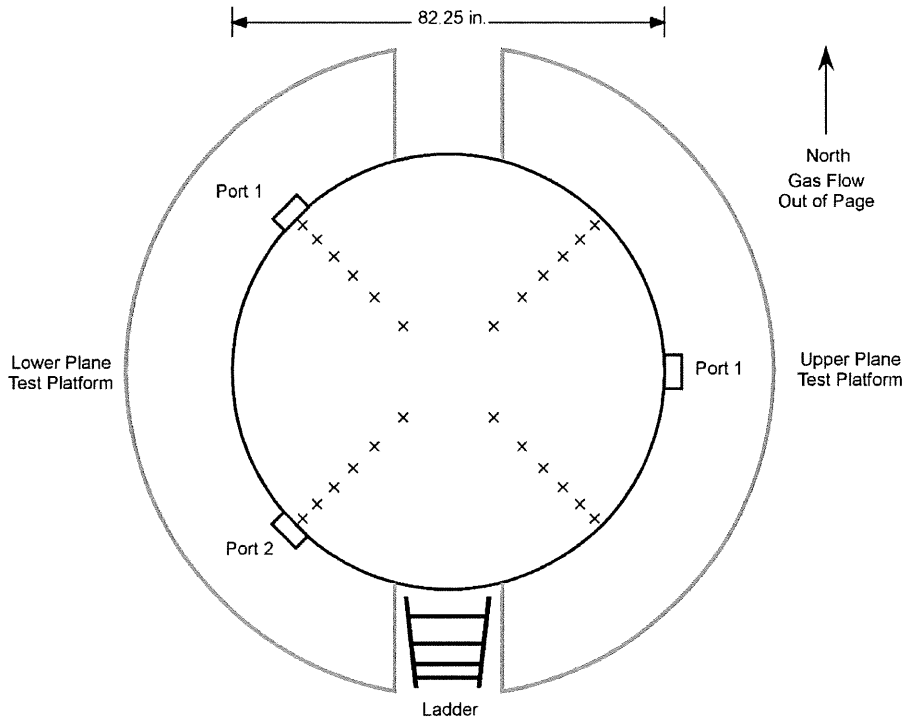
The sample point placement was determined by EPA Method 1 and 2 specifications. Table 3-1 presents the sampling information for the test location. The figure represents the layout of the test location.

**Table 3-1:
Sampling Information**

Source Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>FCCU Regenerator Stack</u>							
Flow Rate	USEPA 2F	1-4	2	12	varied	varied	3-1
NSFPM / CPM	USEPA 5F / 202	1-3	2	12	2.5	60	3-1
NH ₃	USEPA CTM-027	1-3	2	12	2.5	60	3-1
H ₂ SO ₄	USEPA CTM-013	1-3	1	1	60	60	N/A ¹
O ₂ / CO ₂ / CH ₄ / THC	USEPA 3A / 25A	1-3	1	1	60	60	N/A ¹

¹ Constituent sampled from the approximate center of the duct.

**Figure 3-1:
 FCCU Regenerator Stack Sample Point Layout (EPA Methods 2F, 5F/202, & CTM-O27)**



Note: Ports on the lower plane were used for these points.

Sampling Point	% of Stack Diameter	Port to Point Distance (in.)
1	97.9	80.5
2	93.3	76.7
3	88.2	72.5
4	82.3	67.7
5	75.0	61.7
6	64.4	53.0
7	35.6	29.3
8	25.0	20.6
9	17.7	14.6
10	11.8	9.7
11	6.7	5.5
12	2.1	1.7

Duct diameters upstream from flow disturbance (A): 2.2

Limit: 0.5

Duct diameters downstream from flow disturbance (B): 3.4

Limit: 2.0

4. METHODOLOGY

PROCEDURES AND REGULATIONS

The test program sampling measurements followed procedures and regulations outlined by the USEPA and Michigan Department of Environment, Great Lakes, and Energy (EGLE). 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. Any modifications to standard test methods are explicitly indicated in this appendix. In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

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 2F "Determination of Stack Gas Velocity and Volumetric Flow Rate with Three-Dimensional Probes"
- 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 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"

CONDITIONAL TEST METHODS

- CTM-013 "Determination of Sulfur Oxides Including Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Vapor and Mist from Stationary Sources Using a Controlled Condensation Sampling Apparatus"
- CTM-027 "Procedure for Collection and Analysis of Ammonia in Stationary Sources"

METHODOLOGY DISCUSSION

USEPA METHOD 5F/202

PM and PM₁₀ emissions were determined using EPA Method 5F/202.

- For this test program, PM is assumed equivalent to NSFPM. Per 40 CFR Subpart Ja §60.104a, EPA Method 5F is permitted for measuring front-half PM emissions from FCCUs.
- PM₁₀ is equivalent to the sum of filterable particulate matter less than 10 micrometers (µm) in diameter (FPM₁₀) and CPM. The Method 5F/202 sample train yields a front-half, non-sulfate FPM result and a back-half, CPM result. The total non-sulfate PM result (NSFPM plus CPM) from Method 5F/202 can be used as a worst-case estimation of Total PM₁₀ since Method 5F will collect all NSFPM present in the flue gas (regardless of particle size).

The front-half (Method 5F portion) of the sampling train consisted of a glass nozzle, glass liner, and filter holder heated to 320°F, and a quartz fiber filter heated to 320°F. Flue gas samples were extracted isokinetically; nozzle and probe liner recoveries were performed using de-ionized water (DI H₂O) as the recovery solvent.

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. Earlier versions of the method were utilized, 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. For this method, ambient temperature is defined as 65°F to 85°F. 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 was not analyzed for CPM and was only collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then ed through 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 5F requirements. 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 N₂ at a rate of 14 liters per minute (lpm) for one (1) hour following each test run prior to recovery.

A field train recovery 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 in Palatine, Illinois, for gravimetric analysis. Method 202 samples were maintained at a temperature < 85°F during transport to the laboratory.

The analytical procedures in EPA Method 202 include an ammonium titration of the inorganic sample fractions with pH less than 7.0 to neutralize acids with hygroscopic properties, such as H_2SO_4 , that may be present in the sample. This step speeds up the sample desiccation process and allows the samples to reach a constant weight prior to weighing. The weight of ammonium added to the sample as a result of the titration is subtracted from the analytical result. CleanAir Analytical Services in Palatine, Illinois, performed the gravimetric analysis and has determined that only samples with an initial pH less than 4.5 require a significant amount of ammonium neutralization, resulting in a correction more than 0.5 mg. Based on this observation, the laboratory has altered its procedures. Only samples with a pH lower than 4.5 are titrated.

Ammonium titration was not conducted because initial pHs for inorganic samples for all runs were greater than 4.5. All samples were observed to reach a constant weight without requiring the titration procedure.

CTM-027

NH_3 emissions were determined using a CTM-027 and an isokinetic, multi-point sample train. The sampling system consisted of a glass nozzle, in-stack quartz filter, glass-lined heated probe, impinger train (for NH_3 collection and H_2O removal and measurement), and a dry gas meter. The NH_3 -collecting impingers were charged with 0.1 N H_2SO_4 solution.

The filter temperature, as noted on the raw data sheets, is the heated area between the probe outlet and impinger inlet of the sampling train. The actual filter was in-stack at stack temperature.

The sampling system traversed all Method 1 points during each run. A minimum volume of 0.9 dry standard cubic meters (dscm), or 31.8 dry standard cubic feet (dscf), were sampled during each 60-minute run.

The sample train was recovered per CTM-027 requirements. The front-half assembly (components prior to the in-stack filter) was not recovered or analyzed, as gaseous NH_3 passed through without reacting or changing state. The three (3) NH_3 -collecting impingers were recovered separately per CTM-027 requirements. The back-half of the sample train prior to Impinger 1 (heated probe and connecting glassware) was rinsed into Impinger 1.

Samples were brought back to CleanAir Analytical Services in Palatine, Illinois, for ion chromatography analysis.

CTM-013 (MOD.)

H_2SO_4 emissions were determined using modified CTM-013 Controlled Condensation Method (CCM).

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of $650^\circ\text{F} \pm 25^\circ\text{F}$ (depending on the required probe length) and a quartz fiber filter (to remove particulate matter) maintained at the same temperature as the probe. 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) is located at the condenser outlet for the collection of residual SAM not collected by the condenser. The condenser temperature is regulated by a water jacket and the SAM filter is regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at $140^\circ\text{F} \pm 9^\circ\text{F}$ plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved SO_2 into the H_2SO_4 -collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then 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 is maintained below 68°F. The sample gas then flowed into a dry gas meter, where the collected sample gas volume is 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 was stabilized in the H₂O matrix until analysis.

Samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for ion chromatography analysis.

USEPA METHODS 3A AND 25A

Oxygen (O₂) and carbon dioxide (CO₂) emissions were determined using a paramagnetic/non-dispersive infrared (NDIR) analyzer per EPA Method 3A. VOC emissions were determined using EPA Method 25A to quantify THC emissions.

The Method 3A/25A sampling system consisted of a heated probe, heated filter, and heated sample line. Flue gas was extracted at a constant rate and delivered at approximately 250°F to a tee at the end of the heated sample line.

- One leg of the tee was connected to a flame ionization analyzer (FIA), which continuously measured minute-average THC concentration expressed in terms of propane (C₃H₈) on an actual (wet) basis.
- The other leg of the tee was connected to a gas conditioner which removed moisture before delivering the gas to a flow panel, and the O₂/CO₂ analyzers which measured concentration on a dry basis (units of %dv or ppm_{dv}).
- The Method 18 gas sample was collected by pulling a slipstream from the flow panel and delivered it into a FlexFoil bag at a constant rate. The moisture condensate was not collected for analysis as CH₄ and C₂H₆ are insoluble in water. Each bag was filled over a period of approximately one hour for each test run. The bags were not analyzed.

THC analyzer calibration was performed by introducing zero air, high, mid-, and low range C₃H₈ 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.

O₂/CO₂ calibration error checks were performed by introducing zero N₂, high 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, the average results for each run were drift corrected.

GENERAL CONSIDERATIONS

A traditional verification of the absence of cyclonic flow following EPA Method 1 specifications was not performed. However, absence of cyclonic flow was demonstrated by measuring the resultant angle of flow during each EPA Method 2F flow traverse, which yielded a resultant angle of flow less than 20° in all instances. Data is included in Appendix G of this report.

H₂O data used for moisture correction of concentration data was obtained (when required) for Method 5F/202, CTM-027, and Draft ASTM CCM by Method 4 measurements incorporated into the sampling and recovery procedures. For Method 3A/18/25A, H₂O data was obtained from most concurrently operated Method 5F/202 and CTM-027 sample trains.

O₂, CO₂, and H₂O data used for Method 2F flow calculations were obtained from the concurrently operated sample trains.

End of Section