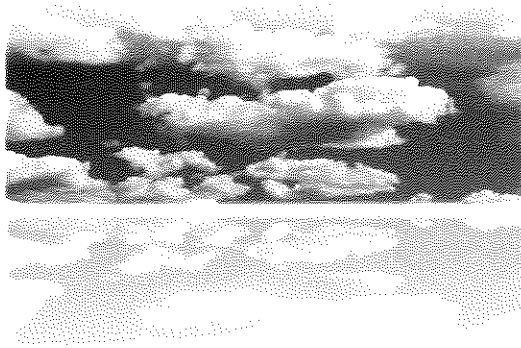




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SEP 20 2018

AIR QUALITY DIVISION



REPORT ON COMPLIANCE &
RATA TESTING

Detroit Refinery

Complex 2 SRU Incinerator Stack

Marathon Petroleum Company LP
1300 South Fort Street
Detroit, MI 48217
Client Reference No. 4101379616

CleanAir Project No. 13624-1
A2LA ISO 17025 Certificate No. 4342.01
A2LA / STAC Certificate No. 4342.02
Revision 0, Final Report
September 7, 2018

RECEIVED**SEP 20 2018****1. PROJECT OVERVIEW****AIR QUALITY DIVISION****Test Program Summary**

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing at the Complex 2 (East) SRU Incinerator (EU42-SULRECOV-S1) at the Detroit Refinery located in Detroit, Michigan. The test program included following objectives:

- Perform sulfuric acid mist (H₂SO₄) testing to demonstrate compliance with the Michigan Department of Environmental Quality (DEQ) Permit No. MI-ROP-A9831-2012c;
- Perform a relative accuracy test audit (RATA) on the facility continuous emissions monitoring system (CEMS) for oxygen (O₂) and sulfur dioxide (SO₂).

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 (USEPA)	Average Emission	Permit Limit¹
C2 SRU Incinerator Stack			
H ₂ SO ₄ (lb/MMBtu)	Draft ASTM CCM	0.025	N/A

¹ Permit limits obtained from MDEQ Renewable Operating Permit No. MI-ROP-A9831-2012c.

**Table 1-2:
Summary of RATA Results**

Source Constituent (Units)	Reference Method	Relative Accuracy (%)	Applicable Specification	Specification Limit¹
C2 SRU Incinerator				
O ₂ (% dv)	USEPA 3A	0.03	PS3	±1.0% of RM
SO ₂ (ppm dv @ 0% O ₂)	USEPA 6C / 3A	9.9	PS2	10% of Standard ²

¹ Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

² Standard = 250 ppm @ 0% O₂.

Test Program Details

Parameters

The test program included the following emissions measurements:

- sulfuric acid mist (H₂SO₄)
- sulfur dioxide (SO₂)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed on July 24 and 26, 2018. The on-site schedule followed during the test program is outlined in Table 1-3.

**Table 1-3:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
0	C2 SRU Incinerator	Draft ASTM CCM	Sulfuric Acid	07/24/18	09:18	10:18
1	C2 SRU Incinerator	Draft ASTM CCM	Sulfuric Acid	07/24/18	11:16	12:16
2	C2 SRU Incinerator	Draft ASTM CCM	Sulfuric Acid	07/24/18	13:05	14:05
3	C2 SRU Incinerator	Draft ASTM CCM	Sulfuric Acid	07/24/18	14:28	15:42
1	C2 SRU Incinerator	USEPA Method 2	Velocity & temperature	07/24/18	11:45	11:56
2	C2 SRU Incinerator	USEPA Method 2	Velocity & temperature	07/24/18	13:31	13:39
3	C2 SRU Incinerator	USEPA Method 2	Velocity & temperature	07/24/18	14:50	15:00
1	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	08:01	08:22
2	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	08:33	08:54
3	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	09:05	09:26
4	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	09:36	09:57
5	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	10:06	10:27
6	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	10:39	11:00
7	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	11:10	11:31
8	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	11:40	12:01
9	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	12:13	12:34
10	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	12:45	13:06
11	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	13:18	13:39
12	C2 SRU Incinerator	USEPA Method 3A / 6C	O ₂ / CO ₂ / SO ₂	07/26/18	13:52	14:13

Discussion

Test Scope Synopsis

H₂SO₄ Testing – Draft ASTM Controlled Condensation Method

H₂SO₄ emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM). Three (3) 60-minute Draft ASTM CCM test runs were performed. H₂SO₄ emission results were reported in units of lb/MMBtu calculated from emission rate (lb/hr) and heat input (MMBtu/hr) from auxiliary fuel (natural gas) to the unit supplied by MPC. The H₂SO₄ final results were expressed as the average of three (3) valid runs.

Three (3) EPA Method 2 velocity and temperature traverses were conducted during testing; one traverse was conducted per Draft ASTM CCM run. The traverses were utilized to convert H₂SO₄ concentrations from units of ppmdv to emission rates in units of lb/hr.

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.

O₂ & SO₂ RATA Testing

Minute-average data points for O₂ and SO₂ (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A and 6C. Relative accuracy was determined based on nine (9) of 12 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4, unless there were no significant statistical relevance to exclude runs (O₂). Carbon dioxide (CO₂) was collected for supplemental purposes.

Sampling occurred at the three (3) points as specified in Section 8.1.3.2 of PS 2 during each run. The average result for each run was converted to identical units of measurement as the facility CEMs and compared for relative accuracy.

Test Conditions

The unit was operated at no less than the maximum normal operating capacity during 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:
C2 SRU Incinerator – H₂SO₄ Emissions**

Run No.	1	2	3	Average
Date (2018)	Jul 24	Jul 24	Jul 24	
Start Time (approx.)	11:16	13:05	14:28	
Stop Time (approx.)	12:16	14:05	15:42	
Process Conditions				
H _i Actual heat input (MMBtu/hr)	11.5	11.5	11.5	11.5
Gas Conditions				
O ₂ Oxygen (dry volume %)	6.9	7.4	8.1	7.5
CO ₂ Carbon dioxide (dry volume %)	3.5	3.4	3.2	3.4
T _s Sample temperature (°F)	1304	1299	1296	1299
B _w Actual water vapor in gas (% by volume)	11.5	11.0	11.0	11.2
Gas Flow Rate				
Q _a Volumetric flow rate, actual (acfm)	47,100	43,300	44,800	45,100
Q _s Volumetric flow rate, standard (scfm)	13,800	12,700	13,200	13,200
Q _{std} Volumetric flow rate, dry standard (dscfm)	12,200	11,300	11,700	11,700
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	27.38	27.44	27.54	27.45
Laboratory Data (Ion Chromatography)				
m _n Total H ₂ SO ₄ collected (mg)	5.1647	5.2669	5.0903	
Sulfuric Acid Vapor (H₂SO₄) Results				
C _{sdl} H ₂ SO ₄ Concentration (lb/dscf)	4.16E-07	4.23E-07	4.08E-07	4.16E-07
C _{sdl} H ₂ SO ₄ Concentration (ppmdv)	1.63	1.66	1.60	1.63
E _{lb/hr} H ₂ SO ₄ Rate (lb/hr)	0.305	0.287	0.287	0.293
E _{Hi} H ₂ SO ₄ Rate - Heat Input-based (lb/MMBtu)	0.0264	0.0250	0.0250	0.0255

**Table 2-2:
 C2 SRU Incinerator – O₂ (% dv) RATA**

Run No.	Start Time	Date (2018)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	08:01	Jul 26	6.58	6.62	-0.04	-0.6%
2	08:33	Jul 26	6.53	6.56	-0.03	-0.5%
3	09:05	Jul 26	6.41	6.46	-0.05	-0.8%
4	09:36	Jul 26	6.27	6.29	-0.02	-0.3%
5	10:06	Jul 26	6.37	6.41	-0.04	-0.6%
6	10:39	Jul 26	6.12	6.13	-0.01	-0.2%
7	11:10	Jul 26	6.29	6.33	-0.04	-0.6%
8	11:40	Jul 26	6.14	6.17	-0.03	-0.5%
9	12:13	Jul 26	6.15	6.21	-0.06	-1.0%
10	12:45	Jul 26	5.96	6.00	-0.04	-0.7%
11	13:18	Jul 26	6.21	6.25	-0.04	-0.6%
12	13:52	Jul 26	6.33	6.34	-0.01	-0.2%
Average			6.28	6.31	-0.03	-0.5%

Relative Accuracy Test Audit Results

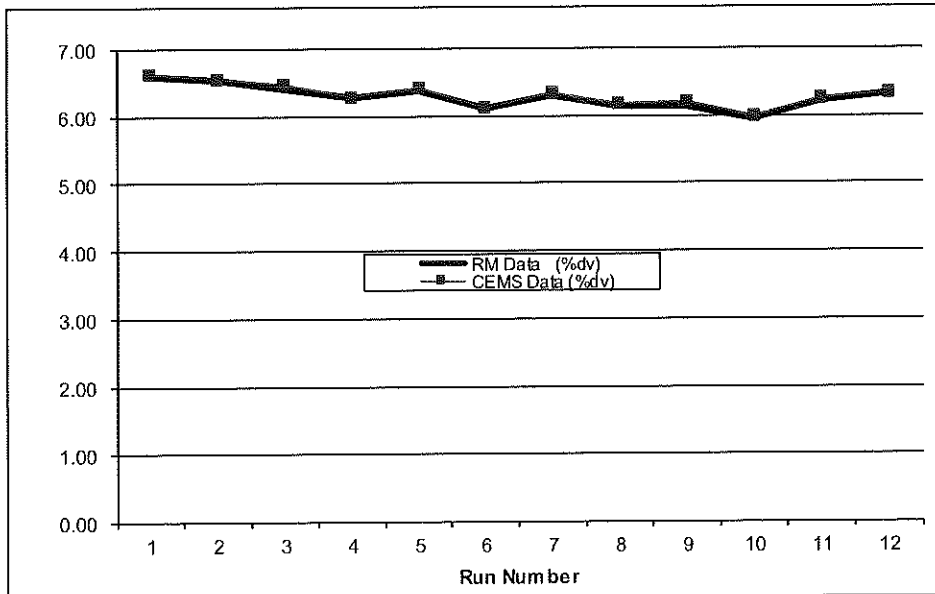
Standard Deviation of Differences	0.01505	
Confidence Coefficient (CC)	0.00956	
t-Value for 12 Data Sets	2.201	
Avg. Abs. Diff. (%dv)	0.03	Limit 1.0

RM = Reference Method (CleanAir Data)

080918 16408

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on all 12 runs.



**Table 2-3:
 C2 SRU Incinerator – SO₂ (ppmdv @ 0%O₂) RATA**

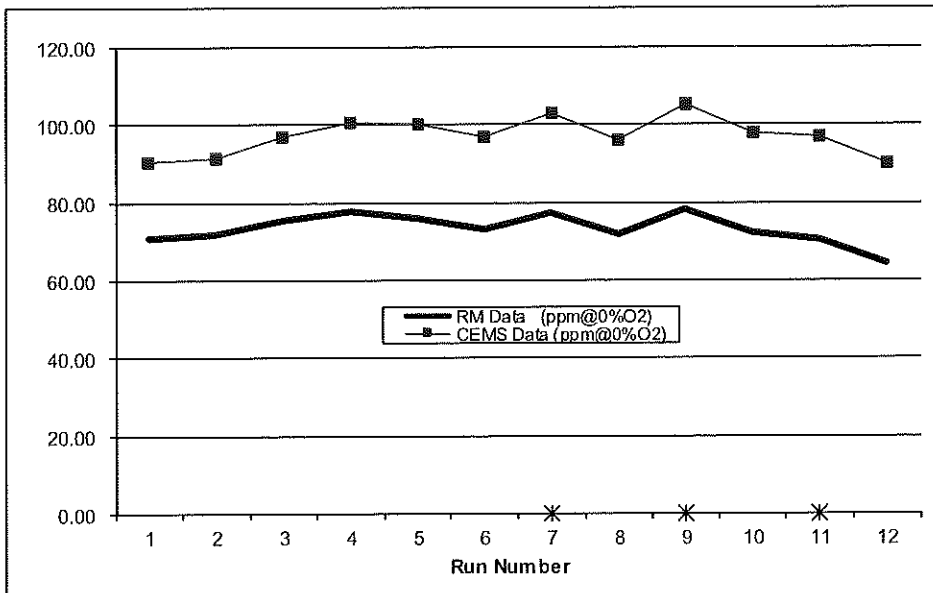
Run No.	Start Time	Date (2018)	RM Data (ppm@0%O ₂)	CEMS Data (ppm@0%O ₂)	Difference (ppm@0%O ₂)	Difference Percent
1	08:01	Jul 26	70.83	90.40	-19.57	-27.6%
2	08:33	Jul 26	71.89	91.32	-19.43	-27.0%
3	09:05	Jul 26	75.50	97.05	-21.55	-28.5%
4	09:36	Jul 26	77.79	100.88	-23.09	-29.7%
5	10:06	Jul 26	76.11	99.97	-23.86	-31.3%
6	10:39	Jul 26	73.29	96.85	-23.56	-32.1%
7 *	11:10	Jul 26	77.19	103.13	-25.94	-33.6%
8	11:40	Jul 26	72.01	96.26	-24.25	-33.7%
9 *	12:13	Jul 26	78.20	105.29	-27.09	-34.6%
10	12:45	Jul 26	72.24	98.02	-25.78	-35.7%
11 *	13:18	Jul 26	70.56	96.97	-26.41	-37.4%
12	13:52	Jul 26	64.48	89.91	-25.43	-39.4%
Average			72.68	95.63	-22.95	-31.6%

Relative Accuracy Test Audit Results

Standard Deviation of Differences 2.314
 Confidence Coefficient (CC) 1.779
 t-Value for 9 Data Sets 2.306

Relative Accuracy (as % of Appl. Std.) **9.9%** **Limit 10.0%**
 Appl. Std. = 250 ppm@0%O₂

RM = Reference Method (CleanAir Data) 082918 152643
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
 RATA calculations are based on 9 of 12 runs. * indicates the excluded runs.



AIR QUALITY DIVISION

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 Sulfur Recovery Unit (EU42-43SULRECOV-S1) removes hydrogen sulfide (H₂S) from acid gas and converts it to elemental sulfur using the Claus Process (Trains A, B, and C), the SCOT Tail Gas Treating Unit process (Trains No. 1 and No. 2) and associated amine treating equipment. Tail gas is routed to a thermal oxidizer, or incinerator, which oxidizes the remaining H₂S in the tail gas to SO₂ before exhausting to the atmosphere via the SRU Incinerator Stack (SV43-H2). The emission group also consists of process vessels (including thermal reactors, an absorbing tower and a stripping tower), heaters, tanks, containers, compressors, seals, process valves, flanges, connectors, etc.).

The testing reported in this document was performed at the Complex 2 SRU Incinerator Stack.

Test Location

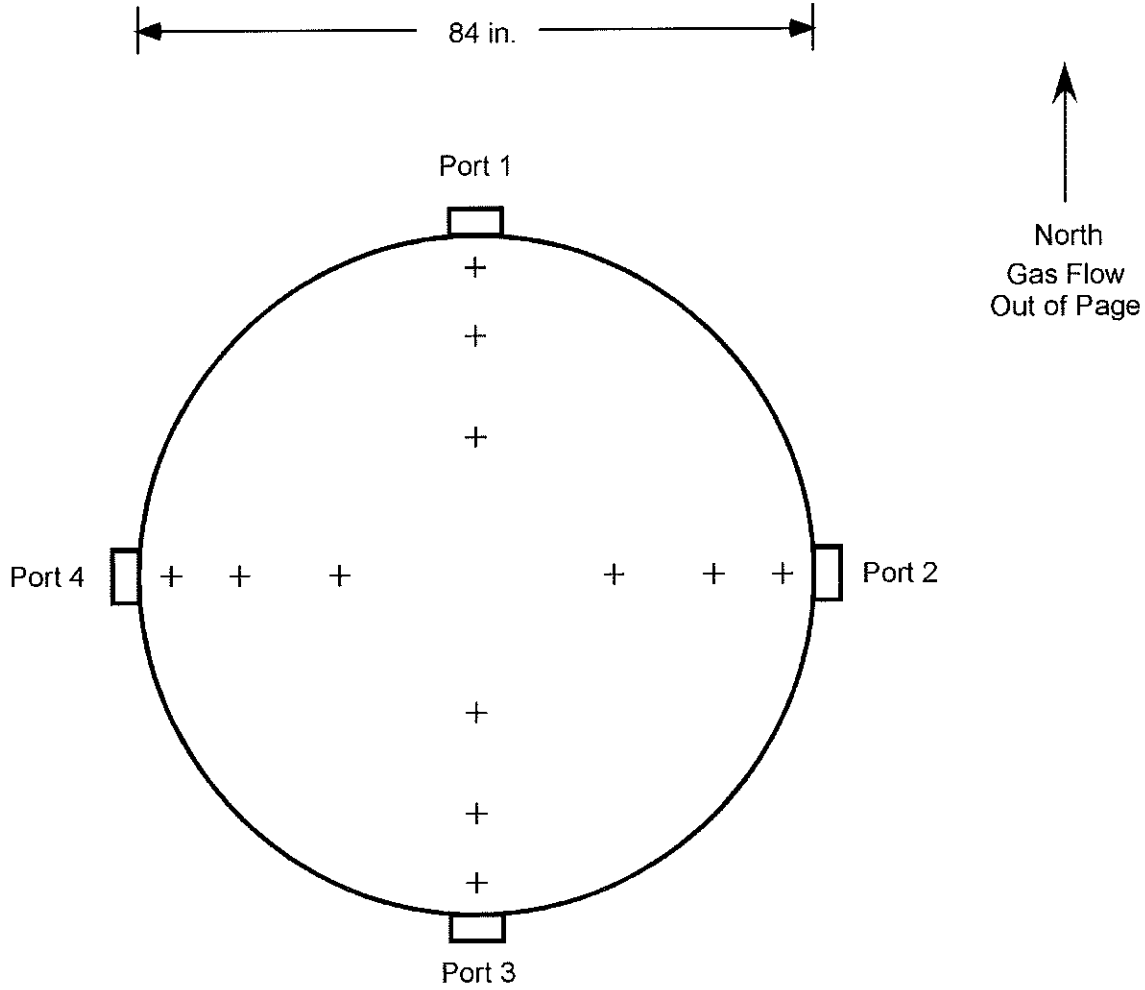
The sample point locations were determined by EPA Method 1 and PS 2 specifications. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 8 and 9 represent the layout of the test location.

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

Source	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>C2 SRU Incinerator</u>							
H ₂ SO ₄	Draft ASTM CCM	1-3	1	1	60	60	N/A ¹
Velocity & temperature	2	1-3	4	3	Varied	Varied	3-1
O ₂ / CO ₂ / SO ₂	3A / 6C	1-12	1	3	7	21	3-2

¹ Draft ASTM CCM sampling occurred at a single point near the center of the duct.

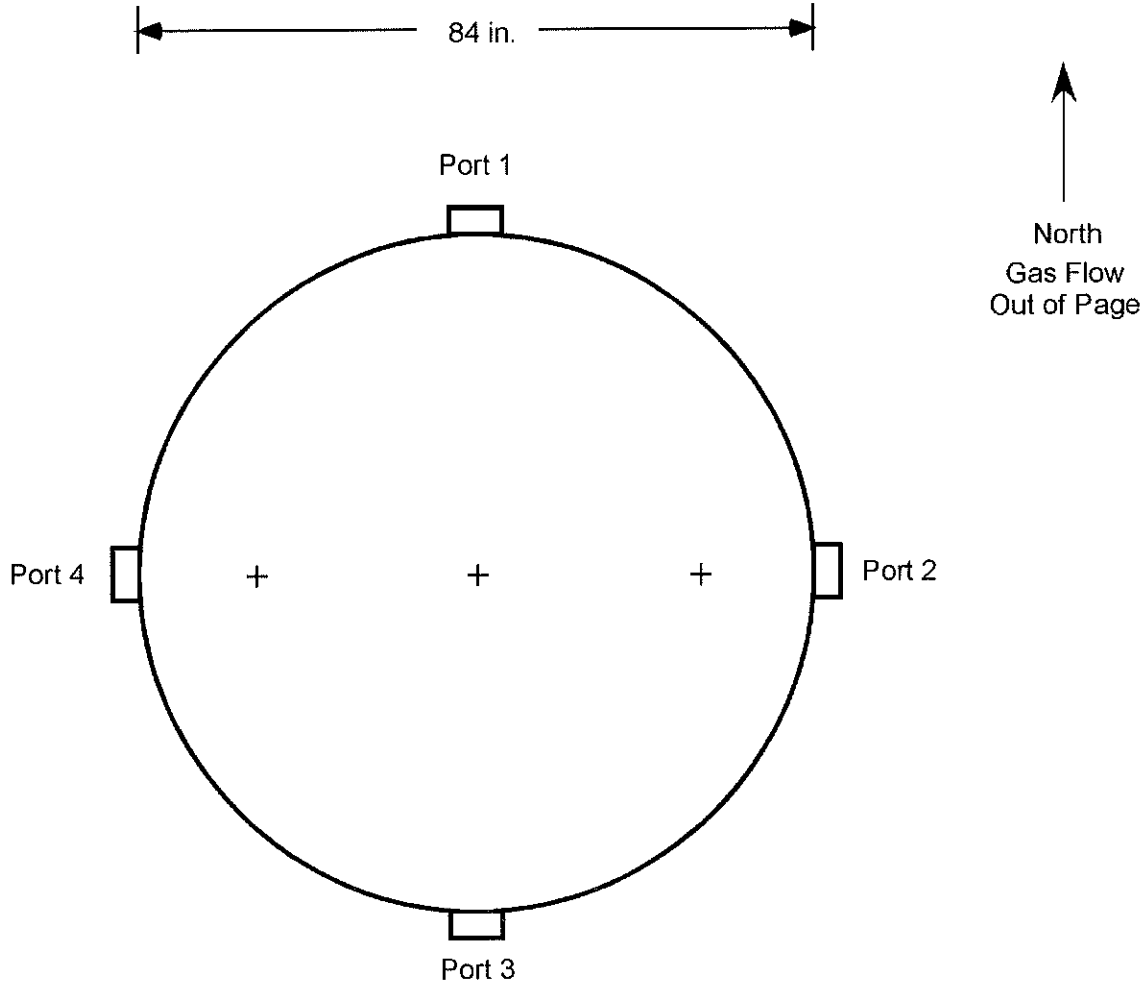
**Figure 3-1:
 Velocity and Temperature Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	29.6	24.9
2	14.6	12.3
3	4.4	3.7

Duct diameters upstream from flow disturbance (A): 20 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 15 Limit: 2.0

**Figure 3-2:
 O₂, CO₂ and SO₂ Sample Point Layout (EPA Method 6C)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	70.0
2	50.0	42.0
3	16.7	14.0

Duct diameters upstream from flow disturbance (A): 20 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 15 Limit: 2.0

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (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. 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 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 6C	"Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"

Title 40 CFR Part 60, Appendix B Performance Specifications

PS 2	"Specifications and Test Procedures for SO ₂ and NO _x Continuous Emission Monitoring Systems in Stationary Sources"
PS 3	"Specifications and Test Procedures for O ₂ and CO ₂ Continuous Emission Monitoring Systems in 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

O₂, CO₂ & SO₂ Testing – USEPA Methods 3A and 6C

Reference method O₂ and CO₂ emissions were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. Reference method SO₂ emissions were determined using an ultraviolet - photometric analyzer per EPA Method 6C.

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

Calibration error checks were performed by introducing zero nitrogen (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 EPA Methods 3A and 6C, the average results for each run were drift-corrected.

H₂SO₄ Testing – Draft ASTM CCM

H₂SO₄ emissions were determined referencing the Draft ASTM 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°F ± 25°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°F ± 9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved SO₂ into the H₂SO₄-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 was maintained below 68°F. Moisture content of the sample gas was determined from condensate collected from the knock-out jars. 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.

Prior to the first official test run, a 60-minute sample conditioning run 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.

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

Velocity and Temperature Testing – USEPA Method 2

Velocity and temperature of the sample gas were determined utilizing EPA Method 2. Velocity and temperature traverses were utilized to determine volumetric flow to convert H₂SO₄ concentrations to mass emission rates. CleanAir utilized an S-type pitot tube with an adjoined type K thermocouple connected to a manometer to determine velocity pressure and temperature of the flue gas.

End of Section