

1. PROJECT OVERVIEW

TEST PROGRAM SUMMARY

Air Products and Chemicals, Inc. (Air Products) contracted CleanAir Engineering (CleanAir) to successfully complete emissions compliance measurements at the Detroit Hydrogen Plant, located in Detroit, Michigan. The testing was performed at the Hydrogen (H₂) Plant Heater Stack. The test program included the following objectives:

- To perform a relative accuracy test audit (RATA) on the continuous emission monitoring system (CEMS);
- To determine compliance for particulate matter (PM) and particulate matter less than 10 microns in diameter (PM₁₀);
- To determine emissions of sulfuric acid mist (H₂SO₄); and
- To determine compliance for volatile organic compounds (VOCs).

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 Emissions Compliance Test Results**

Source	Constituent (Units)	Sampling Method	Average Emission	Permit Limit ¹
H ₂ Plant Heater Stack				
	PM (lb/MMBtu)	USEPA M-5	0.00042	0.0034
	PM (Ton/yr)	USEPA M-5	1.14	6.86
	PM ₁₀ (lb/MMBtu)	USEPA M-5/202	0.0033	0.010
	H ₂ SO ₄ (lb/MMBtu)	Modified CTM-013	0.00011	N/A
	VOC (lb/MMBtu)	USEPA M-25A	<0.00068	0.0055
	NO _x (lb/MMBtu)	USEPA M-7E	0.0056	0.013
	NO _x (ppmdv @ 0% O ₂)	USEPA M-7E	5.3	60
	CO (Ton/yr)	USEPA M-10	< 1.0	13

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

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

Source Constituent (Units)	Reference Method (USEPA)	Relative Accuracy ¹	Units	Applicable Specification	Specification Limit ²
H ₂ Plant Heater Stack					
Flow rate (dscfh)	M-2	14.5%	% of RM	PS6	20% of RM
O ₂ (% dv)	M-3A	0.16	%dv	PS3	± 1.0% dv
H ₂ O (% wv)	M-4	10.4%	% of RM	N/A	N/A
NOx (ppmdv)	M-7E	6.9%	% of RM	PS2	20% of RM
NOx (lb/MMBtu)	M-7E	12.3%	% of RM	PS2	20% of RM
NOx (ppmdv @ 0%O ₂)	M-7E	5.7%	% of RM	PS2	20% of RM
CO (ppmdv)	M-10	0.4	ppmdv	PS4A ³	± 5 ppmdv
CO (lb/hr)	M-10	0.4%	% of Std.	PS4A ³	5% of Standard ⁴

¹ Relative Accuracy is expressed in terms of comparison to the reference method (% RM) or applicable emission standard (% Std.), equivalent to the permit limit in Table 1-2. The specific expression used depends on the specification limit.

² Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications, unless otherwise noted.

³ For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4A RA limit is either < 10% of RM, <5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

⁴ CO Standard = 13 Ton/yr = 56.9 lb/hr (assuming 8,760 operating hours/year)

TEST PROGRAM DETAILS

PARAMETERS

The test program included the following measurements:

- PM assumed equivalent to filterable particulate matter (FPM)
- condensable particulate matter (CPM)
- PM₁₀ assumed to be the sum of:
 - FPM
 - CPM
- sulfuric acid mist/vapor (H₂SO₄)
- VOCs assumed equivalent to total hydrocarbons (THCs) minus:
 - methane (CH₄)
 - ethane (C₂H₆)
- nitrogen oxide (NO_x)
- carbon monoxide (CO)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

SCHEDULE

Testing was performed on September 8-9, 2021. The on-site schedule followed during the test program is outlined in Table 1-3. All times are Eastern Daylight Time (EDT).

**Table 1-3:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	H ₂ Heater Stack	USEPA Method 5/202	FPM/CPM	09/08/21	08:18	10:28
1	H ₂ Heater Stack	USEPA Method 3A, 25A	O ₂ /CO ₂ , VOC	09/08/21	08:35	09:35
2	H ₂ Heater Stack	USEPA Method 3A, 25A	O ₂ /CO ₂ , VOC	09/08/21	09:45	10:45
2	H ₂ Heater Stack	USEPA Method 5/202	FPM/CPM	09/08/21	11:10	13:15
3	H ₂ Heater Stack	USEPA Method 3A, 25A	O ₂ /CO ₂ , VOC	09/08/21	12:45	13:45
3	H ₂ Heater Stack	USEPA Method 5/202	FPM/CPM	09/08/21	13:42	15:47
1	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	08:58	09:19
1	H ₂ Heater Stack	Modified CTM-013	H ₂ SO ₄ / Moisture	09/09/21	09:00	10:00
1	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	09:08	09:14
2	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	09:19	09:40
2	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	09:24	09:30
3	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	09:41	10:02
3	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	09:43	09:49
2	H ₂ Heater Stack	Modified CTM-013	H ₂ SO ₄ / Moisture	09/09/21	10:30	11:30
4	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	10:30	10:51
4	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	10:36	10:42
5	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	10:52	11:13
5	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	10:53	10:59
6	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	11:13	11:34
6	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	11:15	11:21
7	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	12:02	12:23
7	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	12:03	12:09
3	H ₂ Heater Stack	Modified CTM-013	H ₂ SO ₄ / Moisture	09/09/21	12:12	13:12
8	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	12:23	12:44
8	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	12:25	12:31
9	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	12:48	12:56
9	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	12:50	13:11
10	H ₂ Heater Stack	USEPA Method 3A, 7E, 10	O ₂ /CO ₂ , NO _x , CO	09/09/21	13:11	13:32
10	H ₂ Heater Stack	USEPA Method 2	Velocity & Flow Rate	09/09/21	13:13	13:19

DISCUSSION

Project Synopsis

CleanAir conducted the sample program over a two-day span. During the first test day, three (3) EPA Method 5/202 test runs were conducted along with three (3) EPA Method 25A test runs.

The RATA was conducted during the second test day, along with EPA Method 2 traverses for flow measurements and three (3) modified Conditional Test Method 013 (CTM-013) test runs for H₂SO₄ mist. The CTM-013 test runs were used for moisture determination for the coinciding flow measurement calculations. The average of the CTM-013 moisture determinations was used for the RATA Run 10 moisture.

A cyclonic flow check, per EPA Method 1, Section 11.4, was performed during every CleanAir-performed test program from 2013 to 2018. The sampling location met method criteria during all previous cyclonic flow checks and no modifications had been made to the test location. Due to this fact, no cyclonic flow check was performed during this mobilization.

USEPA Method 5/202

For this test program, the PM emission rate is assumed equivalent to the FPM emission rate. The PM₁₀ emission rate is assumed equivalent to the sum of FPM and CPM emission rates (units of lb/hr, Ton/yr, or lb/MMBtu for all constituents).

The analytical procedures in 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 H₂SO₄) that may be present in the sample. This step speeds up the sample desiccation process and allows the samples to come to 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 determined that only samples with an initial pH less than 4.5 require a significant amount of ammonium neutralization, resulting in a correction in excess of 0.5 mg. Based on this observation, the laboratory altered its procedures to read that a sample must have a pH lower than 4.5 in order to be titrated. All samples collected had pH's over 4.5 and therefore did not require neutralization.

The final results for each parameter were expressed as the average of three runs and were below the permit limits for both PM and PM₁₀.

An integrated gas sample (IGS) was collected during Run 1 and analyzed for O₂ and CO₂ by the RATA analyzers. Run 2 utilized the O₂ and CO₂ concentrations from the Method 25A Run 2 and Run 3 used Method 25A Run 3 for molecular weight calculation purposes.

Modified Conditional Test Method 13

Three (3) test runs were performed on November 9. The result is expressed as the average of three valid runs (Runs 1, 2, and 3).

USEPA Method 25A

Three (3) valid EPA Method 25A test runs for THC's were performed concurrently with the first two (2) Method 5/202 test runs on November 8. The final results for each parameter are expressed as the average of three (3) valid runs (Runs 1, 2, and 3).

Method 25A states that the mid-range calibration gas should be used for the drift checks between runs. Because the flue gas contained very low levels of hydrocarbons, the operator used the low-level calibration gas for the drift checks.

VOC emission rate is normally equivalent to THC emission rate, minus CH₄ and C₂H₆ emission rate (units of lb/hr, Ton/yr or lb/MMBtu for all constituents). For all runs, the THC concentration was below the reportable instrument response (considered to be 1% of instrument span, 0.451 ppm, wv); therefore, no EPA Method 18 sample bags were collected, and no CH₄ and C₂H₆ corrections were made.

USEPA Methods 2, 3A, 4, 7E, and 10 – Performance Specifications 2, 3, 4A, and 6

Sample Approach

One-minute average data points for O₂, CO₂, NO_x, and CO (dry basis) were collected over a period of 21 minutes for each RATA reference method (RM) run.

The average result for each RM run was calculated and compared to the average result from the facility CEMS over identical time intervals in order to calculate relative accuracy (RA):

- For O₂ (%dv), RA is expressed as the average absolute difference between the RM and facility CEMS runs. The final result was below the limit of $\pm 1.0\%$ dv set by Performance Specification (PS) 3.
- For NO_x (ppmdv) concentration, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For NO_x (lb/MMBtu) emission rate, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For NO_x (ppmdv @ 0% O₂) concentration, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For CO (ppmdv) concentration, the RA limit is expressed as the average absolute difference between the RM and facility CEMS runs, plus 2.5 times the confidence coefficient. The final result was below the limit of ± 5 ppmdv set by PS 4A, which is applicable to sources that emit less than 200 ppmv of CO.
- For CO (lb/hr) diluent, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 5% of the standard (permit limit listed in Table 1-2 on page 2) set by PS 4A.
- CO₂ data was collected only as supplemental information.
- The flow rate, RA, is expressed as the percent difference between RM and facility CEMS data. The final results were below the limit of 20% of the RM set by PS 6.
- Moisture data presented in Table 2-6 on page 13 is for comparison purposes only.

All CO concentrations measured were below the instrument reportable response (considered to be 1% of instrument span, 0.452 ppm, dv). For RATA calculations the CO was considered zero and for CO compliance it was considered less than the detection limit (DL).

Facility flow rate CEMS were evaluated using EPA Method 2 as the RM. A complete flow and temperature traverse were performed during each 21-minute RATA run, converted to units of dry standard cubic feet per hour (dscfh), and then compared to the facility CEMS results over the corresponding 21-minute intervals.

Moisture data was used to convert flow rate from wet basis to dry basis and was obtained from concurrently operated CTM-013 test runs:

- For RATA Runs 1 and 2, H₂O data was obtained from CTM-013 Run 1.
- For RATA Runs 3, 4, and 5, H₂O data was obtained from CTM-013 Run 2.
- For RATA Runs 6, 7, 8 and 9, H₂O data was obtained from CTM-013 Run 3.
- For RATA Run 10, H₂O data was and average of CTM-013 Runs 1-3.

NO_x and CO results from the RATA were converted from units of dry volume-based concentration (ppmdv) to mass-based emission rate units (lb/hr, Ton/yr, and lb/MMBtu) to demonstrate compliance with permit limits. The final results for each parameter were expressed as the average of ten (10) RATA runs. The final results were below the permit limits.

Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted to units of lb/MMBtu using the F_d factor method. Fuel F_d factors were provided by Air Products. Flow rates used in calculating lb/hr emissions were obtained in the following manner:

- For Method 5/202, flow rate measurements were incorporated into the sampling procedures.
- For Method 25A, flow rate measurements from the most nearly concurrent Method 5/202 test runs were used.
- For Method 7E/10, a flow rate measurement, per Method 2 specifications, was performed concurrently with each test run.
- For CTM-013, the flow rate measurements made concurrently with the Method 7E/10 run that most closely corresponded were used.

General Considerations

All run times listed throughout this report correspond to the plant time utilized by Air Products was Eastern Standard Time (EST). Plant time is the time of the Air Products CEMS and data acquisition system.

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2. RESULTS

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

**Table 2-1:
H₂SO₄ Emissions**

Run No.	1	2	3	Average
Date (2021)	Sep 9	Sep 9	Sep 9	
Start Time (approx.)	09:00	10:30	12:12	
Stop Time (approx.)	10:00	11:30	13:12	
Process Conditions				
R _P Hydrogen production rate (Mscf/hr)	55.9	55.9	55.9	55.9
P ₁ Aqueous NH ₃ feed rate (lb/hr)	36.0	37.3	38.5	37.3
P ₂ SCR inlet temperature (°F)	633	634	634	634
F _d Oxygen-based F-factor (dscf/MMBtu)	9,007	9,006	9,004	9,005
H _i Actual heat input (MMBtu/hr)	536	530	526	531
Cap Capacity factor (hours/year)	8,760	8,760	8,760	8,760
Gas Conditions				
O ₂ Oxygen (dry volume %)	4.0	4.1	4.0	4.0
CO ₂ Carbon dioxide (dry volume %)	18.6	18.6	18.6	18.6
T _s Stack temperature (°F)	335	335	334	335
B _w Actual water vapor in gas (% by volume)	14.15	14.90	14.98	14.68
Gas Flow Rate				
Q _a Volumetric flow rate, actual (acfm)	210,000	213,000	212,000	212,000
Q _s Volumetric flow rate, standard (scfm)	136,000	138,000	137,000	137,000
Q _{std} Volumetric flow rate, dry standard (dscfm)	117,000	119,000	118,000	118,000
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	24.56	24.59	24.66	24.60
Laboratory Data (Ion Chromatography)				
m _n Total H ₂ SO ₄ collected (mg)	0.1102	0.1031	0.1243	
Sulfuric Acid Vapor (H₂SO₄) Results				
C _{sd} H ₂ SO ₄ Concentration (lb/dscf)	9.89E-09	9.24E-09	1.11E-08	1.01E-08
C _{sd} H ₂ SO ₄ Concentration (ppmdv)	0.0389	0.0363	0.0437	0.0396
E _{lb/hr} H ₂ SO ₄ Rate (lb/hr)	0.0692	0.0657	0.0785	0.0711
E _{T/yr} H ₂ SO ₄ Rate (Ton/yr)	0.303	0.288	0.344	0.312
E _{Fd} H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	0.000110	0.000103	0.000124	0.000113

**Table 2-2:
FPM, CPM and Total PM₁₀ Emissions (EPA Method 5/202)**

Run No.	1	2	3	Average
Date (2021)	Sep 8	Sep 8	Sep 8	
Start Time (approx.)	08:18	11:10	13:42	
Stop Time (approx.)	10:28	13:15	15:47	
Process Conditions				
R _P Hydrogen production rate (Mscf/hr)	55.9	55.9	55.9	55.9
P ₁ Aqueous NH ₃ feed rate (lb/hr)	36.1	38.3	39.4	37.9
P ₂ SCR inlet temperature (°F)	634	634	634	634
F _d Oxygen-based F-factor (dscf/MMBtu)	9,006	9,005	9,008	9,006
Cap Capacity factor (hours/year)	8,760	8,760	8,760	8,760
Gas Conditions				
O ₂ Oxygen (dry volume %)	4.7	4.0	4.0	4.3
CO ₂ Carbon dioxide (dry volume %)	16.9	18.1	18.1	17.7
T _s Stack temperature (°F)	329	328	328	328
B _w Actual water vapor in gas (% by volume)	15.2	14.9	15.0	15.0
Gas Flow Rate				
Q _a Volumetric flow rate, actual (acfm)	209,000	210,000	212,000	210,000
Q _s Volumetric flow rate, standard (scfm)	135,000	136,000	137,000	136,000
Q _{std} Volumetric flow rate, dry standard (dscfm)	115,000	116,000	117,000	116,000
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	78.40	78.85	78.26	78.51
%I Isokinetic sampling (%)	108.7	108.0	106.3	107.6
Laboratory Data				
m _n Total FPM (g)	0.00189	0.00130	0.00124	
m _{CPM} Total CPM (g)	0.00962	0.00889	0.00817	
m _{Part} Total particulate matter (g)	0.01151	0.01019	0.00941	
FPM Results				
C _{sd} Particulate Concentration (lb/dscf)	5.32E-08	3.64E-08	3.49E-08	4.15E-08
E _{lb/hr} Particulate Rate (lb/hr)	0.365	0.253	0.245	0.288
E _{T/yr} Particulate Rate (Ton/yr)	1.60	1.11	1.07	1.26
E _{Fd} Particulate Rate - F _d -based (lb/MMBtu)	0.000619	0.000405	0.000390	0.000471
CPM Results				
C _{sd} Particulate Concentration (lb/dscf)	2.71E-07	2.49E-07	2.30E-07	2.50E-07
E _{lb/hr} Particulate Rate (lb/hr)	1.86	1.73	1.61	1.73
E _{T/yr} Particulate Rate (Ton/yr)	8.15	7.58	7.07	7.60
E _{Fd} Particulate Rate - F _d -based (lb/MMBtu)	0.00315	0.00277	0.00257	0.00283
Total Particulate Matter Results				
C _{sd} Particulate Concentration (lb/dscf)	3.24E-07	2.85E-07	2.65E-07	2.91E-07
E _{lb/hr} Particulate Rate (lb/hr)	2.23	1.98	1.86	2.02
E _{T/yr} Particulate Rate (Ton/yr)	9.75	8.68	8.14	8.86
E _{Fd} Particulate Rate - F _d -based (lb/MMBtu)	0.00377	0.00317	0.00296	0.00330

**Table 2-3:
VOC Emissions (EPA Method 25A)**

Run No.	1	2	3	Average
Date (2021)	Sep 8	Sep 8	Sep 8	
Start Time (approx.)	11:16	12:31	14:03	
Stop Time (approx.)	12:16	13:31	15:03	
Process Conditions				
P ₁ Hydrogen Production (Mscf/day)	55.9	56.0	55.9	55.9
P ₂ Aqueous NH ₃ feed to SCR (lb/hr)	38.2	38.5	39.4	38.7
P ₃ SCR Inlet Temperature	606	608	616	610
F _d Oxygen-based F-factor (dscf/MMBtu)	9,005	9,004	9,008	9,004
H _i Actual heat input (MMBtu/hr)	536	526	526	529
Cap Capacity factor (hours/year)	8,760	8,760	8,760	8,760
Gas Conditions				
O ₂ Oxygen (dry volume %)	4.0	4.0	4.0	4.0
CO ₂ Carbon dioxide (dry volume %)	18.2	18.1	18.1	18.1
B _w Actual water vapor in gas (% by volume) ¹	15.2	14.9	15.0	15.1
Gas Flow Rate²				
Q _a Volumetric flow rate, actual (acfm)	191,167	191,167	192,376	210,000
Q _s Volumetric flow rate, standard (scfm)	126,553	126,553	126,849	136,000
Q _{std} Volumetric flow rate, dry standard (dscfm)	106,047	106,047	106,683	116,000
THC Results (as Propane)³				
C _{sd} Concentration (ppm dv)	<0.53	<0.53	<0.53	<0.53
C _{sd} Concentration (lb/dscf)	<6.1E-08	<6.1E-08	<6.1E-08	<6.1E-08
E _{lb/hr} Emission Rate (lb/hr)	<0.42	<0.42	<0.43	<0.42
E _{T/yr} Emission Rate (Ton/yr)	<1.8	<1.8	<1.9	<1.8
E _{Fd} Emission Rate - F _d -based (lb/MMBtu)	<0.00068	<0.00067	<0.00068	<0.00068
E _{Hi} Emission Rate - Heat input-based (lb/MMBtu)	<0.00079	<0.00080	<0.00081	<0.00080

¹ Moisture data used for ppmwv to ppm dv correction obtained from nearly-concurrent M-5/202 runs.² Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 5/202 runs .

**Table 2-4:
NO_x and CO Emissions (EPA Method 7E/10)**

Run No.	1	2	3	4	5	6
Date (2021)	Sep 9					
Start Time (approx.)	08:58	09:19	09:41	10:30	10:52	11:13
Stop Time (approx.)	09:19	09:40	10:02	10:51	11:13	11:34
Process Conditions						
R _P Hydrogen Production (Mscf/day)	56.0	56.3	56.2	55.9	55.8	55.9
P ₁ Aqueous NH ₃ feed to SCR (lb/hr)	38.3	38.4	38.5	38.0	38.0	37.8
P ₂ SCR Inlet Temperature	639	640	640	639	639	639
F _d Oxygen-based F-factor (dscf/MMBtu)	9,003	9,002	9,004	9,004	9,005	9,005
H _i Actual heat input (MMBtu/hr)	542	542	541	536	536	538
Cap Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760	8,760
Gas Conditions						
O ₂ Oxygen (dry volume %)	4.0	4.0	4.0	4.1	4.1	4.0
CO ₂ Carbon dioxide (dry volume %)	18.6	18.5	18.6	18.5	18.6	18.6
B _w Actual water vapor in gas (% by volume) ¹	14.1	14.1	14.1	14.9	14.9	14.9
Gas Flow Rate²						
Q _a Volumetric flow rate, actual (acfm)	210,000	213,000	212,000	213,000	211,000	216,000
Q _s Volumetric flow rate, standard (scfm)	136,000	138,000	137,000	138,000	137,000	140,000
Q _{std} Volumetric flow rate, dry standard (dscfm)	117,000	119,000	118,000	117,000	116,000	119,000
Nitrogen Oxides Results						
C _{sd} Concentration (ppmdv)	4.2	4.3	4.1	4.3	4.2	4.1
C _{sd-x} Concentration @ 0% O ₂ (ppmdv)	5.2	5.4	5.1	5.3	5.3	5.1
C _{sd} Concentration (lb/dscf)	5.0E-07	5.2E-07	4.9E-07	5.1E-07	5.1E-07	5.0E-07
E _{lb/hr} Emission Rate (lb/hr)	3.5	3.7	3.5	3.6	3.5	3.5
E _{T/yr} Emission Rate (Ton/yr)	15	16	15	16	15	16
E _{Fd} Emission Rate - F _d -based (lb/MMBtu)	0.0056	0.0058	0.0055	0.0057	0.0057	0.0055
Carbon Monoxide Results³						
C _{sd} Concentration (ppmdv)	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
C _{sd-x} Concentration @ 0% O ₂ (ppmdv)	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56
C _{sd} Concentration (lb/dscf)	<3.3E-08	<3.3E-08	<3.3E-08	<3.3E-08	<3.3E-08	<3.3E-08
E _{lb/hr} Emission Rate (lb/hr)	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23
E _{T/yr} Emission Rate (Ton/yr)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
E _{Fd} Emission Rate - F _d -based (lb/MMBtu)	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04

¹ Moisture data obtained from nearly-concurrent Draft ASTM CCM runs.² Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 2 runs.³ For CO, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

**Table 2-4 (Continued):
NO_x and CO Emissions (EPA Method 7E/10)**

Run No.		7	8	9	10	Average
Date (2021)		Sep 9	Sep 9	Sep 9	Sep 9	
Start Time (approx.)		12:02	12:23	12:50	13:11	
Stop Time (approx.)		12:23	12:44	13:11	13:32	
Process Conditions						
R _P	Hydrogen Production (Mscf/day)	55.8	55.8	55.9	55.9	56.0
P ₁	Aqueous NH ₃ feed to SCR (lb/hr)	37.4	37.3	37.4	37.4	37.8
P ₂	SCR Inlet Temperature	639	639	639	638	639
F _d	Oxygen-based F-factor (dscf/MMBtu)	9,009	9,008	9,008	9,008	9,006
H _i	Actual heat input (MMBtu/hr)	535	534	524	535	536
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760
Gas Conditions						
O ₂	Oxygen (dry volume %)	4.0	4.0	4.0	4.0	4.0
CO ₂	Carbon dioxide (dry volume %)	18.6	18.6	18.6	18.6	18.6
B _w	Actual water vapor in gas (% by volume) ¹	15.0	15.0	15.0	14.7	14.7
Gas Flow Rate²						
Q _a	Volumetric flow rate, actual (acfm)	210,000	213,000	212,000	213,000	212,300
Q _s	Volumetric flow rate, standard (scfm)	136,000	138,000	137,000	138,000	137,500
Q _{std}	Volumetric flow rate, dry standard (dscfm)	117,000	119,000	118,000	117,000	117,700
Nitrogen Oxides Results						
C _{sd}	Concentration (ppmdv)	4.2	4.3	4.3	4.2	4.2
C _{sd-x}	Concentration @ 0% O ₂ (ppmdv)	5.2	5.4	5.3	5.2	5.3
C _{sd}	Concentration (lb/dscf)	5.0E-07	5.2E-07	5.1E-07	5.0E-07	5.1E-07
E _{lb/hr}	Emission Rate (lb/hr)	3.5	3.7	3.6	3.5	3.6
E _{T/yr}	Emission Rate (Ton/yr)	15	16	16	16	16
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0056	0.0058	0.0057	0.0056	0.0056
Carbon Monoxide Results³						
C _{sd}	Concentration (ppmdv)	<0.45	<0.45	<0.45	<0.45	<0.45
C _{sd-x}	Concentration @ 0% O ₂ (ppmdv)	<0.56	<0.56	<0.56	<0.56	<0.56
C _{sd}	Concentration (lb/dscf)	<3.3E-08	<3.3E-08	<3.3E-08	<3.3E-08	<3.3E-08
E _{lb/hr}	Emission Rate (lb/hr)	<0.23	<0.23	<0.23	<0.23	<0.23
E _{T/yr}	Emission Rate (Ton/yr)	<1.0	<1.0	<1.0	<1.0	<1.0
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04

¹ Moisture data obtained from nearly-concurrent CTM-013 runs. Run 10 is an average of all three CTM-013 Runs.

² Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 2 runs.

³ For CO, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

**Table 2-5:
 Dry Standard Flow Rate RATA (EPA Method 2 / PS 6)**

Run No.	Start Time	Date (2021)	RM Data (DSCFH)	CEMS Data (DSCFH)	Difference	Difference Percent
1	08:58	Sep 9	6,993,836	6,107,067	886,768	12.7%
2	09:19	Sep 9	7,111,392	6,092,254	1,019,137	14.3%
3	09:41	Sep 9	7,058,780	6,081,815	976,965	13.8%
4	10:30	Sep 9	7,024,805	6,045,198	979,608	13.9%
5	10:52	Sep 9	6,983,649	6,059,231	924,418	13.2%
6 *	11:13	Sep 9	7,145,713	6,062,193	1,083,520	15.2%
7	12:02	Sep 9	6,964,825	6,022,610	942,214	13.5%
8	12:23	Sep 9	7,077,509	6,029,282	1,048,226	14.8%
9	12:50	Sep 9	7,044,556	6,029,506	1,015,050	14.4%
10	13:11	Sep 9	7,058,118	6,026,029	1,032,089	14.6%
Average			7,035,274	6,054,777	980,497	13.9%

Relative Accuracy Test Audit Results

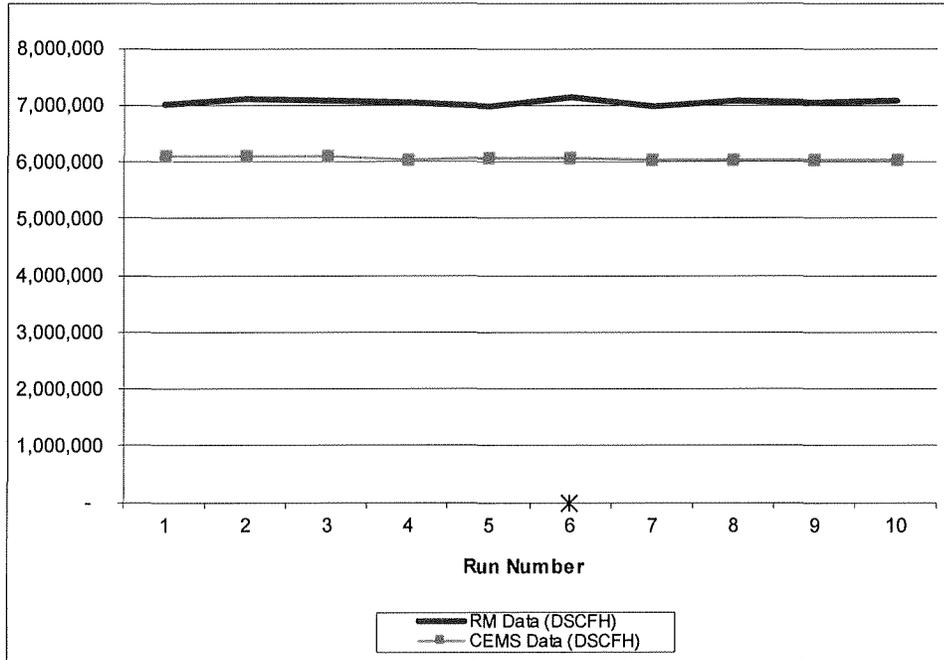
Standard Deviation of Differences	54,019	
Confidence Coefficient (CC)	41,523	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	14.5%	Limit 20.0%

RM = Reference Method (CleanAir Data)

092221 080545

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



**Table 2-6:
 H₂O Concentration RATA (EPA Method 4)**

Run No.	Start Time	Date (2021)	CEMS Data		Difference (%wv)	Difference Percent
			RM Data (%wv)	(%wv)		
1	08:58	Sep 9	14.1	16.0	-1.9	-13.1%
2	09:19	Sep 9	14.1	16.0	-1.9	-13.1%
3 *	09:41	Sep 9	14.1	16.0	-1.9	-13.1%
4	10:30	Sep 9	14.9	16.0	-1.1	-7.4%
5	10:52	Sep 9	14.9	16.0	-1.1	-7.4%
6	11:13	Sep 9	14.9	16.0	-1.1	-7.4%
7	12:02	Sep 9	15.0	16.0	-1.0	-6.8%
8	12:23	Sep 9	15.0	16.0	-1.0	-6.8%
9	12:50	Sep 9	15.0	16.0	-1.0	-6.8%
10	13:11	Sep 9	14.7	16.0	-1.3	-9.0%
Average			14.7	16.0	-1.3	-8.6%

Relative Accuracy Test Audit Results

Standard Deviation of Differences 0.3453
 Confidence Coefficient (CC) 0.2654
 t-Value for 9 Data Sets 2.306

Relative Accuracy (as % of RM) **10.4%** **Limit 20.0%**

RM = Reference Method (CleanAir Data) 092221 080545
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)
 RATA calculations are based on 9 of 10 runs. * indicates the excluded run.

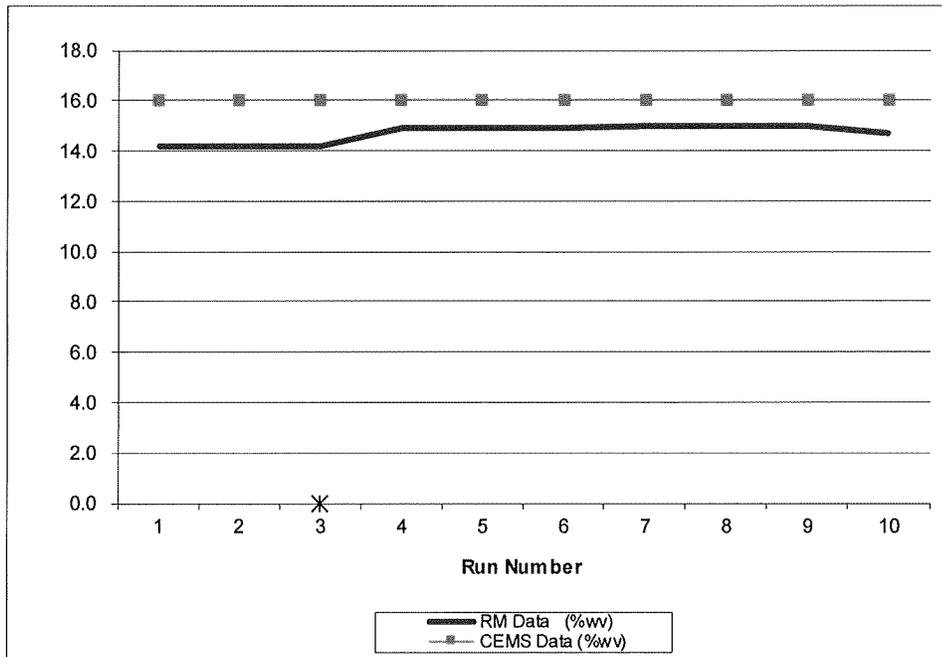


Table 2-7:
O₂ (%dv) RATA (EPA Method 3A / PS 3)

Run No.	Start Time	Date (2021)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	08:58	Sep 9	4.04	4.20	-0.16	-4.0%
2	09:19	Sep 9	4.03	4.20	-0.17	-4.2%
3 *	09:41	Sep 9	4.00	4.20	-0.20	-5.0%
4	10:30	Sep 9	4.06	4.20	-0.14	-3.5%
5	10:52	Sep 9	4.06	4.20	-0.14	-3.5%
6	11:13	Sep 9	4.05	4.20	-0.15	-3.7%
7	12:02	Sep 9	4.03	4.20	-0.17	-4.2%
8	12:23	Sep 9	4.03	4.20	-0.17	-4.2%
9	12:50	Sep 9	4.03	4.20	-0.17	-4.1%
10	13:11	Sep 9	4.00	4.20	-0.20	-5.0%
Average			4.04	4.20	-0.16	-4.0%

Relative Accuracy Test Audit Results

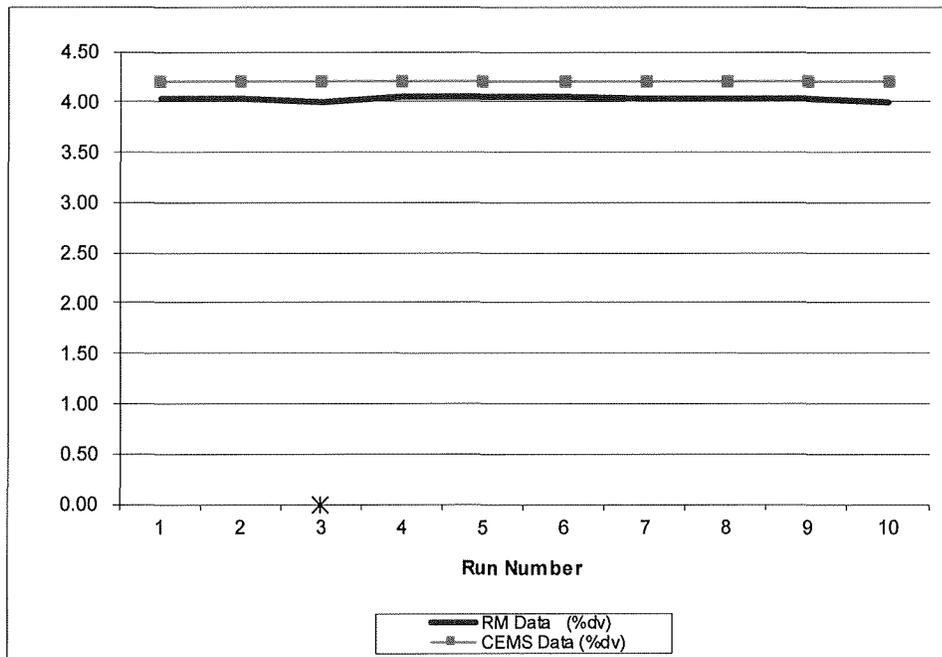
Standard Deviation of Differences	0.0173	
Confidence Coefficient (CC)	0.0133	
t-Value for 9 Data Sets	2.306	
Avg. Abs. Diff. (%dv)	0.16	Limit 1.0

RM = Reference Method (CleanAir Data)

092221 080545

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



**Table 2-8:
 NO_x (ppmdv) Concentration RATA (EPA Method 7E / PS 2)**

Run No.	Start Time	Date (2021)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	08:58	Sep 9	4.21	3.90	0.31	7.4%
2	09:19	Sep 9	4.34	4.10	0.24	5.6%
3	09:41	Sep 9	4.15	4.00	0.15	3.5%
4	10:30	Sep 9	4.27	4.00	0.27	6.3%
5	10:52	Sep 9	4.24	4.00	0.24	5.7%
6	11:13	Sep 9	4.15	3.90	0.25	6.0%
7	12:02	Sep 9	4.23	4.00	0.23	5.4%
8	12:23	Sep 9	4.33	4.00	0.33	7.5%
9	12:50	Sep 9	4.26	4.00	0.26	6.1%
10	13:11	Sep 9	4.20	3.90	0.30	7.1%
Average			4.24	3.98	0.26	6.1%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.050954	
Confidence Coefficient (CC)	0.036448	
t-Value for 10 Data Sets	2.262	
Relative Accuracy (as % of RM)	6.9%	Limit 20.0%

RM = Reference Method (CleanAir Data)

092221 080545

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on all 10 runs.

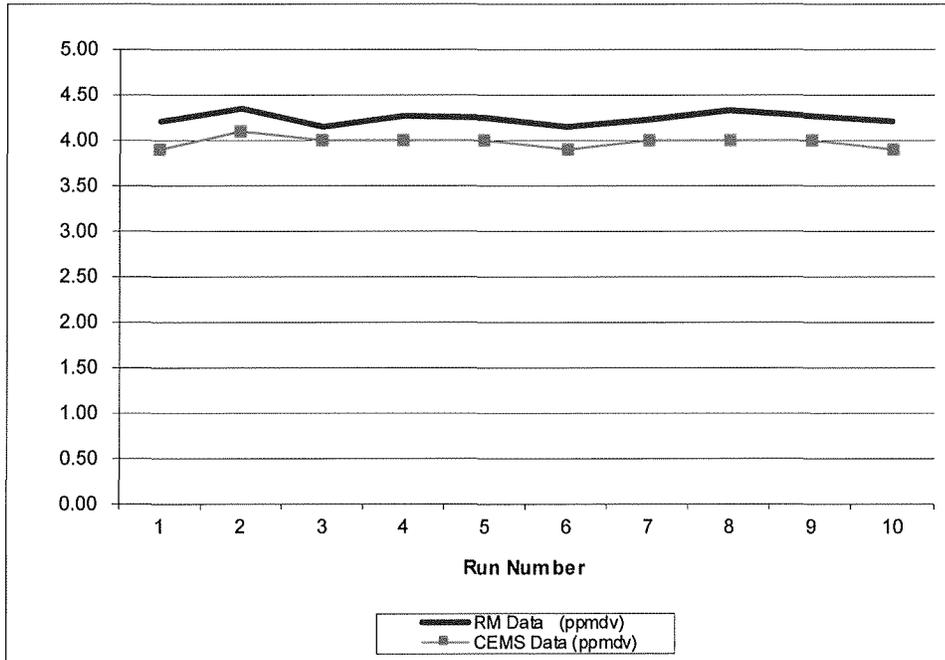


Table 2-9:
NO_x (ppmdv @ 0% O₂) Concentration RATA (EPA Method 7E / PS 2)

Run No.	Start Time	Date (2021)	RM Data (ppm@0%O ₂)	CEMS Data (ppm@0%O ₂)	Difference (ppm@0%O ₂)	Difference Percent
1	08:58	Sep 9	5.22	4.90	0.32	6.1%
2	09:19	Sep 9	5.38	5.10	0.28	5.2%
3	09:41	Sep 9	5.13	5.00	0.13	2.5%
4	10:30	Sep 9	5.30	5.00	0.30	5.6%
5	10:52	Sep 9	5.26	5.00	0.26	5.0%
6	11:13	Sep 9	5.14	4.90	0.24	4.8%
7 *	12:02	Sep 9	5.24	5.00	0.24	4.5%
8	12:23	Sep 9	5.36	5.10	0.26	4.8%
9	12:50	Sep 9	5.28	5.10	0.18	3.4%
10	13:11	Sep 9	5.19	4.90	0.29	5.7%
Average			5.25	5.00	0.25	4.8%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0615	
Confidence Coefficient (CC)	0.0472	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	5.7%	20.0%
Relative Accuracy (as % of Appl. Std.)	0.5%	10.0%
Appl. Std. = 60 ppm@0%O ₂		

RM = Reference Method (CleanAir Data)

092221 080545

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. * indicates the excluded run.

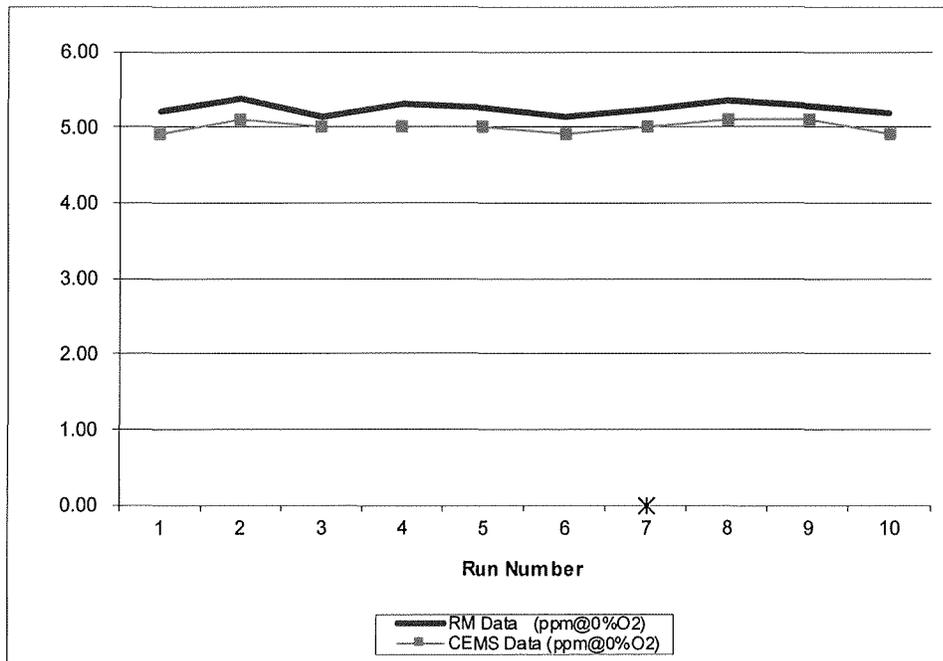


Table 2-10:
NO_x (lb/MMBtu) Emission Rate RATA (EPA Method 7E / PS 2)

Run No.	Start Time	Date (2021)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	08:58	Sep 9	0.0056	0.0050	0.0006	10.9%
2 *	09:19	Sep 9	0.0058	0.0050	0.0008	13.6%
3	09:41	Sep 9	0.0055	0.0050	0.0005	9.3%
4	10:30	Sep 9	0.0057	0.0050	0.0007	12.2%
5	10:52	Sep 9	0.0057	0.0050	0.0007	11.6%
6	11:13	Sep 9	0.0055	0.0050	0.0005	9.6%
7	12:02	Sep 9	0.0056	0.0050	0.0006	11.2%
8	12:23	Sep 9	0.0058	0.0050	0.0008	13.3%
9	12:50	Sep 9	0.0057	0.0050	0.0007	12.0%
10	13:11	Sep 9	0.0056	0.0050	0.0006	10.5%
Average			0.0056	0.0050	0.0006	11.2%

Relative Accuracy Test Audit Results

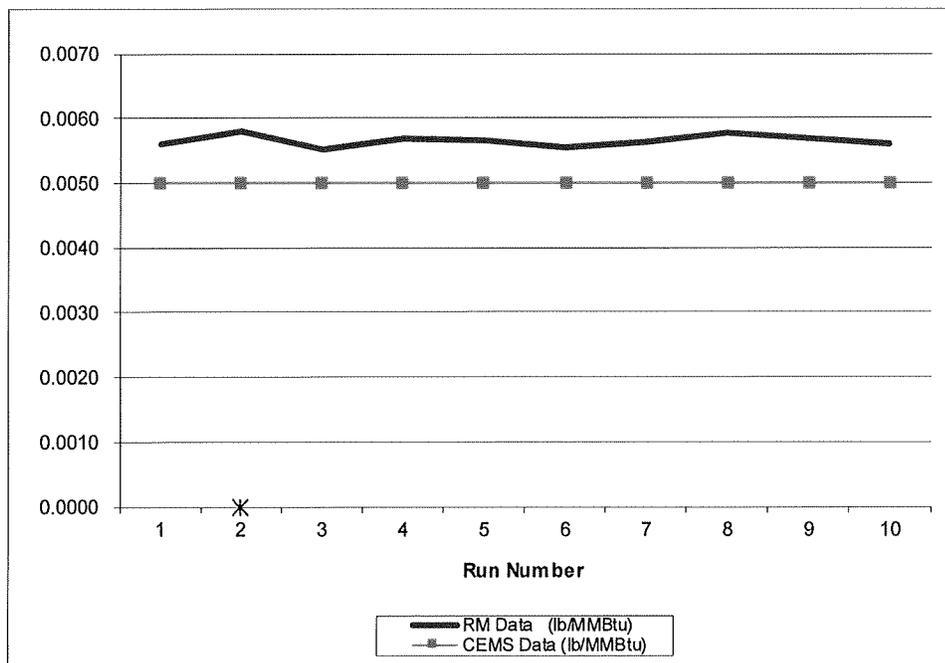
Standard Deviation of Differences	0.000080	
Confidence Coefficient (CC)	0.000062	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	12.3%	20.0%
Relative Accuracy (as % of Appl. Std.)	5.3%	10.0%
Appl. Std. = 0.013 lb/MMBtu		

RM = Reference Method (CleanAir Data)

092221 080545

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



**Table 2-11:
 CO (ppmdv) Concentration RATA (EPA Method 10 / PS 4A)**

Run No.	Start Time	Date (2021)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	08:58	Sep 9	0.00	0.40	-0.40	N/A
2	09:19	Sep 9	0.00	0.50	-0.50	N/A
3	09:41	Sep 9	0.00	0.40	-0.40	N/A
4	10:30	Sep 9	0.00	0.50	-0.50	N/A
5	10:52	Sep 9	0.00	0.40	-0.40	N/A
6	11:13	Sep 9	0.00	0.40	-0.40	N/A
7	12:02	Sep 9	0.00	0.40	-0.40	N/A
8	12:23	Sep 9	0.00	0.40	-0.40	N/A
9	12:50	Sep 9	0.00	0.40	-0.40	N/A
10	13:11	Sep 9	0.00	0.40	-0.40	N/A
Average			0.00	0.42	-0.42	NA

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0422	
Confidence Coefficient (CC)	0.0302	
t-Value for 10 Data Sets	2.262	
Avg. Abs. Diff. (ppmdv)	0.420	Limit 5.0

RM = Reference Method (CleanAir Data) 092221 080545
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)
 RATA calculations are based on all 10 runs.

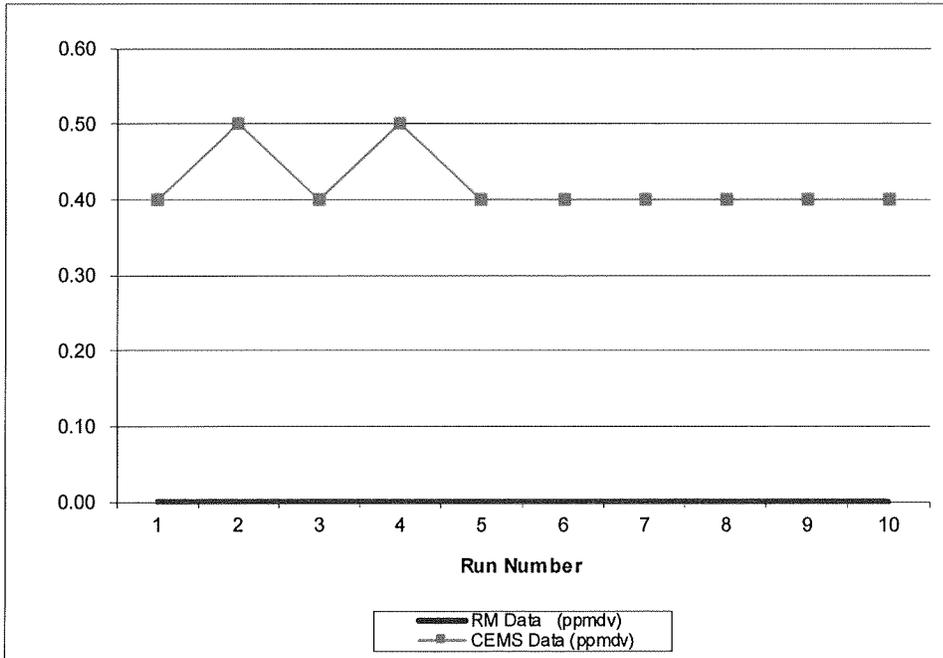


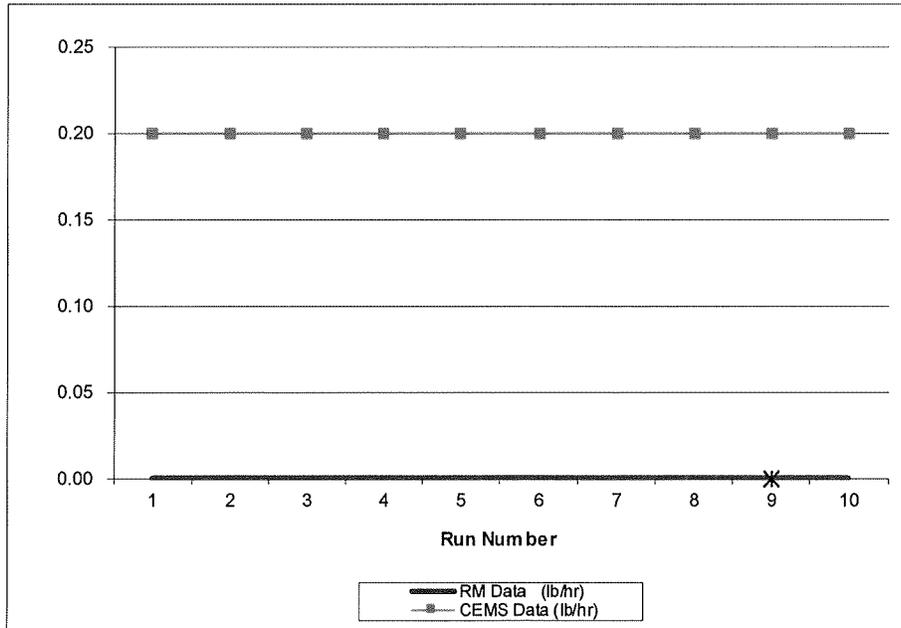
Table 2-12:
CO (lb/hr) Emission Rate RATA (EPA Method 10 / PS 4A)

Run No.	Start Time	Date (2021)	CEMS Data		Difference	
			RM Data (lb/hr)	(lb/hr)	Difference (lb/hr)	Percent
1	08:58	Sep 9	0.00	0.20	-0.20	N/A
2	09:19	Sep 9	0.00	0.20	-0.20	N/A
3	09:41	Sep 9	0.00	0.20	-0.20	N/A
4	10:30	Sep 9	0.00	0.20	-0.20	N/A
5	10:52	Sep 9	0.00	0.20	-0.20	N/A
6	11:13	Sep 9	0.00	0.20	-0.20	N/A
7	12:02	Sep 9	0.00	0.20	-0.20	N/A
8	12:23	Sep 9	0.00	0.20	-0.20	N/A
9 *	12:50	Sep 9	0.00	0.20	-0.20	N/A
10	13:11	Sep 9	0.00	0.20	-0.20	N/A
Average			0.00	0.20	-0.20	NA

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0000	
Confidence Coefficient (CC)	0.0000	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of Appl. Std.)	0.35%	Limit 5.0%
Appl. Std. = 56.9 lb/hr		

RM = Reference Method (CleanAir Data) 092221 080545
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)
 RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



3. DESCRIPTION OF INSTALLATION

PROCESS DESCRIPTION

Air Products owns and operates the Detroit Hydrogen Plant located within the Marathon Petroleum Company Detroit Refinery. The Hydrogen Plant supplies H₂ to the Detroit Refinery, which is utilized in the petroleum refining process. Natural gas, refinery fuel gas and/or a high-pentane (C₅H₁₂) refinery streams are converted into 99.9% pure H₂ and high-pressure steam using steam/methane reforming technology. The unit consists of process vessels, a heater, compressors, pumps, piping, drains, and other various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Hydrogen Plant Heater (EG71-H2HTR) is fired by a combination of refinery gas, pressure swing absorption gas, syngas and/or natural gas. The heater is equipped with a selective catalytic reduction (SCR) system to control emissions, which are vented to the atmosphere via the Hydrogen Plant Heater Stack (SV71-H1).

The testing described in this document was performed at the Hydrogen Plant Heater Stack.

TEST LOCATION

EPA Method 1 and PS 2 determined the sample point location. Table 3-1 presents the sampling information for the test location. The figures shown on pages 21 and 22 represent the layout of the test location.

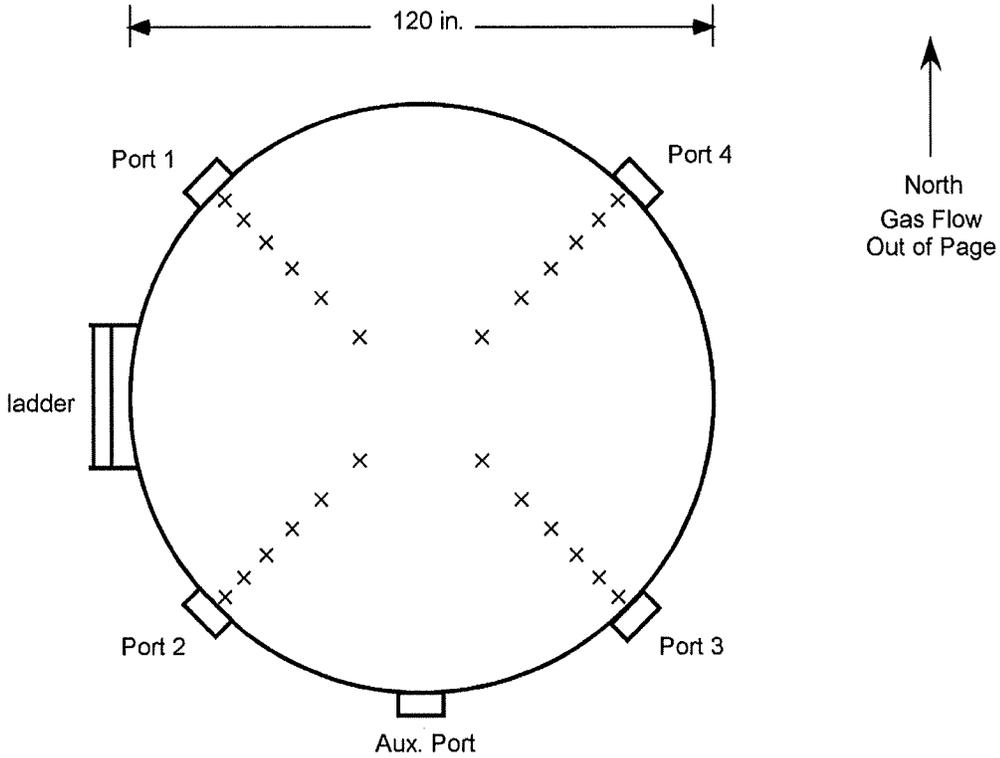
**Table 3-1:
Sampling Information**

Source Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>H₂ Plant Heater Stack</u>							
Velocity & Flow Rate	M-2	1-10	4	6	varied	varied	3-1
FPM/CPM	M-5/202	1-3	4	6	5	120	3-1
H ₂ SO ₄	Mod. CTM-013	1-3	1	1	60	60	N/A ¹
Moisture	M-4	1	1	1	60	60	N/A ¹
O ₂ / CO ₂ / THC	M-3A / 25A	1-3	1	1	60	60	N/A ²
O ₂ / NO _x / CO (RATAs)	M-3A+PS3 / 7E+PS2 / 10+PS4A	1-10	1	3	7	21	3-2

¹ Sampling occurred at a single point at least 3.3 feet from the duct wall in a port on a lower test plane.

² Sampling occurred at a single point at least 3.3 feet from the duct wall.

Figure 3-1:
H₂ Plant Heater Stack, EPA Method 5/202 Sample Point Layout (EPA Method 1)



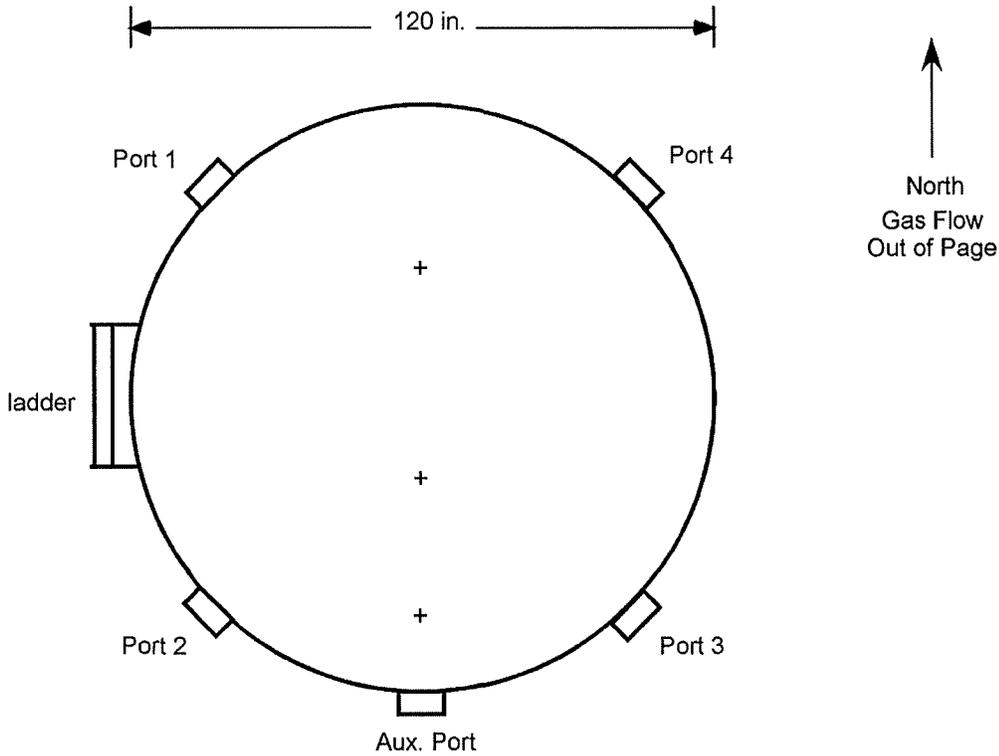
Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	42.7
2	25.0	30.0
3	17.7	21.2
4	11.8	14.2
5	6.7	8.0
6	2.1	2.5

Duct diameters upstream from flow disturbance (A): 1.9
 Duct diameters downstream from flow disturbance (B): 5.9

Limit: 0.5

Limit: 2.0

**Figure 3-2:
 H₂ Plant Heater Stack, RATA Sample Point Layout (PS 2)**



Sampling Point	% of Stack Diameter	Port to Point Distance (Inches)
1	13.1	15.7
2	39.3	47.2
3	65.6	78.7

Duct diameters upstream from flow disturbance (A): 1.9

Limit: 0.5

Duct diameters downstream from flow disturbance (B): 5.9

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 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 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 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"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"

TITLE 40 CFR PART 60, APPENDIX B PERFORMANCE SPECIFICATIONS

- PS 2 "Specifications and Test Procedures for SO₂ and NO_x Continuous Emission Monitoring Systems in Stationary Sources"
- PS 3 "Specifications and Test Procedures for O₂ and CO₂ Continuous Emission Monitoring Systems in Stationary Sources"
- PS 4A "Specifications and Test Procedures for Carbon Monoxide Continuous Emission Monitoring Systems in Stationary Sources"
- PS 6 "Specifications and Test Procedures for Continuous Emission Rate Monitoring Systems in Stationary Sources"

TITLE 40 CFR PART 51, APPENDIX M

- Method 202 "Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources"

CTM-013 (MODIFIED)

"Determination of Sulfuric Acid Vapor or Mist and Sulfur Dioxide Emissions from Kraft Recovery Furnaces"

METHODOLOGY DISCUSSION

PM AND PM₁₀ TESTING – USEPA METHOD 5/202

PM and PM₁₀ emissions were determined using EPA Method 5/202. For this test program, PM is assumed equivalent to FPM. PM₁₀ is 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. Where appropriate, the total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of total PM₁₀ emissions since Method 5 will collect all FPM present in the flue gas (regardless of particle size). Since the Hydrogen Plant Heater is fired by a combination of refinery gas, pressure swing absorption gas, syngas and/or natural gas, the worst-case assumption can safely be made that any FPM in the flue gas exists as FPM₁₀ and can be collected using standard front-half filtration methods without additional 10 µm speciation.

The front-half (Method 5) of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 250°F, and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

The back-half (Method 202) of the sampling train is designed to mimic ambient conditions and collect only the particles that would truly form CPM in the atmosphere. It minimizes the sulfur dioxide (SO₂) and 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 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 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 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 N₂ at a rate of 14 liters per minute (lpm) for one 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.

H₂SO₄ TESTING – MODIFIED CONDITIONAL TEST METHOD 013 (EPA METHOD 8A)

H₂SO₄ emissions were determined referencing CTM-013.

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of greater than 350°F and a quartz fiber filter maintained at a temperature of greater than 500°F to remove PM.

The sample passed through an H₂SO₄ condenser, which consisted of a Modified Graham condenser with a sulfuric acid mist (SAM) filter, for collection of H₂SO₄ vapor and/or mist. The condenser temperature was modified to be 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 condenser, 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 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.

Three (3) official 60-minute Modified CTM-013 test runs were performed. H₂SO₄ emission results have been calculated in units of lb/MMBtu. The final result presented in Table 1-1 is expressed as the average of three (3) valid runs.

Reagent blanks were collected and analyzed to quantify background contamination.

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

O₂, CO₂, AND VOC TESTING – USEPA METHODS 3A AND 25A

O₂ and CO₂ concentrations were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. VOC emissions were determined using EPA Method 25A to quantify THC emissions.

The Method 3A/18/25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate and delivered at 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}).
- No Method 18 gas sample was collected due to the THC concentrations for all three runs being below the analyzer's detection limit of 1% of scale.

The 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 range, and mid-range calibration gases to the inlet of each analyzer. 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.

FLOW RATE, MOISTURE, O₂, CO₂, CO, AND NO_x – USEPA METHODS 2, 3A, 4, 7E, AND 10; PS 2, 3, 4A, AND 6

RM flow rate measurements and RA were determined from Type-S Pitot tube traverses per EPA Method 2 and PS 6. RM O₂ and CO₂ emissions and RA were determined using a paramagnetic/NDIR analyzer per EPA Method 3A and PS 3. RM NO_x emissions and RA were determined using a chemiluminescent analyzer per EPA Method 7E and PS 2. RM CO emissions and RA were determined using an infrared analyzer per EPA Method 10 and PS 4 and/or PS 4A.

The Method 3A/7E/10 sampling system consisted of a heated probe, heated filter, and heated sample line. Flue gas was extracted at a constant rate at the points specified by the performance specification and delivered at 250°F to a gas conditioner which removed moisture. The flue gas was then delivered via a flow panel to an analyzer bank. Each analyzer 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. 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, 7E, and 10, the average results for each run were drift corrected. Documentation of interference checks and NO₂ converter efficiency checks are included in Appendix D of this report.

GENERAL CONSIDERATIONS

O₂ and CO₂ data for the non-instrumental (wet) sampling methods (used in molecular weight calculations and calculation of F_d-based emissions) were obtained using concurrently operated Method 3A sampling with the exception of the 5/202 Run 1.

H₂O data used for moisture correction of concentration data was obtained (when required) in the following manner during the test program:

- For Method 5/202, Method 4 measurements are incorporated into the sampling and recovery procedures.
- For Modified CTM-013, a modified Method 4 measurement is incorporated into the sampling and recovery procedures.
 - Sample gas was extracted through a heated probe at a single point at least one meter from the stack wall. Moisture stratification is not expected at test locations without free water droplets present in the flue gas.
 - Sample gas was extracted at a constant rate no greater than 0.75 cfm and at least 21 scf of flue gas was sampled.
 - After passing through the sulfuric acid mist (SAM) condenser and filter, the sample gas was drawn through gum rubber tubing and into four iced knock-out jars for moisture collection and measurement. The knock-out jars were arranged in a series and contained identical contents as the impinger train, as prescribed by Method 4 but with gum rubber connections and stainless-steel internal components.
- For Method 25A, H₂O data was obtained from concurrently operated Method 5/202 trains.
- For RATA testing, H₂O data was obtained from concurrently operated CTM-013 trains, as outlined above, and one EPA Method 4 train which was used for Runs 9 and 10.

End of Section