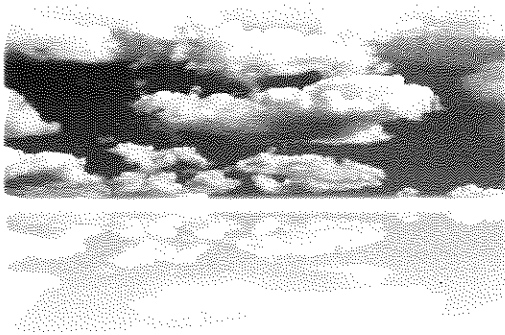




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REPORT ON A CO
COMPLIANCE AND RATA TEST
PROGRAM

Detroit Hydrogen Plant
Hydrogen Plant Heater Stack

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195
Client Reference No. 4504285902

CleanAir Project No. 13466-1
A2LA ISO 17025 Certificate No. 4342.01
A2LA / STAC Certificate No. 4342.02
Revision 0, Final Report
August 21, 2018

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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. This test program is a retest of the Hydrogen (H₂) Plant Heater Stack's carbon monoxide (CO) monitoring system. The original CO relative accuracy test audit (RATA), performed on March 6 and 7, 2018, was deemed unacceptable by the Michigan Department of Environmental Quality (MDEQ).

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 below Table 1-1.

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

Source Constituent (Units)	Reference Method (USEPA)	Relative Accuracy ¹	Units	Applicable Specification	Specification Limit
<u>H2 Plant Heater Stack</u>					
Flow rate (dscfh)	M-2	13.4	% of RM	PS6	20% of RM
O ₂ (% dv)	M-3A	0.03	%dv	PS3	± 1.0% dv
H ₂ O (% wv)	M-4	1.1	% of RM	N/A	N/A
CO (ppmdv)	M-10	0.6	ppmdv	PS4A ²	± 5 ppmdv
CO (lb/hr)	M-10	0.4	% of Std.	PS4A ²	5% of Standard ³

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 For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4ARA limit is either < 10% of RM, <5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

³ 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:

- carbon monoxide (CO)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed on July 31, 2018. The on-site schedule followed during the test program is outlined in Table 1-2.

**Table 1-2:
 Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	07:53	08:14
1	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	07:53	08:14
1	Hydrogen Heater Stack	USEPA Method 4	H ₂ O	07/31/18	07:53	09:57
2	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	08:27	08:48
2	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	08:27	08:48
3	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	09:03	09:24
3	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	09:03	09:24
4	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	09:36	09:57
4	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	09:36	09:57
5	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	10:14	10:35
5	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	10:14	10:35
2	Hydrogen Heater Stack	USEPA Method 4	H ₂ O	07/31/18	10:14	11:40
6	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	10:46	11:07
6	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	10:46	11:07
7	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	11:19	11:40
7	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	11:19	11:40
8	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	11:55	12:16
8	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	11:55	12:16
3	Hydrogen Heater Stack	USEPA Method 4	H ₂ O	07/31/18	11:55	13:58
9	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	12:30	12:51
9	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	12:30	12:51
10	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	13:04	13:25
10	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	13:04	13:25
11	Hydrogen Heater Stack	USEPA Methods 3A/10	O ₂ /CO ₂ /CO	07/31/18	13:37	13:58
11	Hydrogen Heater Stack	USEPA Method 2	Velocity & Flow Rate	07/31/18	13:37	13:58

Discussion

Project Synopsis

Eleven (11) RATA test runs were conducted with the unit operating at greater than 50% load. Run 1 was only 20 minutes in duration and is, therefore, excluded from the CO and oxygen (O₂) Relative Accuracy calculations.

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

Sample Approach

One-minute average data points for O₂, carbon dioxide (CO₂), 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 continuous emissions monitoring system (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 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 1-1 on page 1) set by PS 4A.
- CO₂ data was collected for molecular weight calculation purposes, which is used in flow rate calculations.

All RM CO concentrations measured were below the instrument reportable response (considered to be 1% of instrument span, 0.479 ppm, dv).

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

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 was used to convert flow rate from wet basis to dry basis and was obtained from concurrently operated Method 4 test runs. The dry volumetric flows were then used to calculate the CO emission rates in pounds per hour.

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 per Method 2 specifications concurrently with each test run.

General Considerations

All run times listed throughout this report correspond to actual time. The Air Products CEMS and data acquisition systems plant time is 60 minutes earlier than actual Eastern Daylight Savings Time.

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

Table 2-1:
Dry Standard Flow Rate RATA (EPA Method 2 / PS 6)

Run No.	Start Time	Date (2018)	RM Data (DSCFH)	CEMS Data (DSCFH)	Difference 0	Difference Percent
1	07:53	Jul 31	5,300,179	4,944,761	355,418	6.7%
2	08:27	Jul 31	5,471,494	5,117,283	354,211	6.5%
3	09:03	Jul 31	5,439,877	5,146,510	293,367	5.4%
4	09:36	Jul 31	5,450,074	4,930,176	519,898	9.5%
5 *	10:14	Jul 31	5,341,995	4,418,076	923,919	17.3%
6	10:46	Jul 31	5,091,952	4,267,121	824,831	16.2%
7 *	11:19	Jul 31	4,969,144	4,104,280	864,864	17.4%
8	11:55	Jul 31	4,778,686	4,175,566	603,120	12.6%
9	12:30	Jul 31	4,791,668	4,275,078	516,590	10.8%
10	13:04	Jul 31	4,877,953	4,180,484	697,469	14.3%
11	13:37	Jul 31	4,866,386	4,151,588	714,798	14.7%
Average			5,118,697	4,576,507	542,189	10.6%

Relative Accuracy Test Audit Results

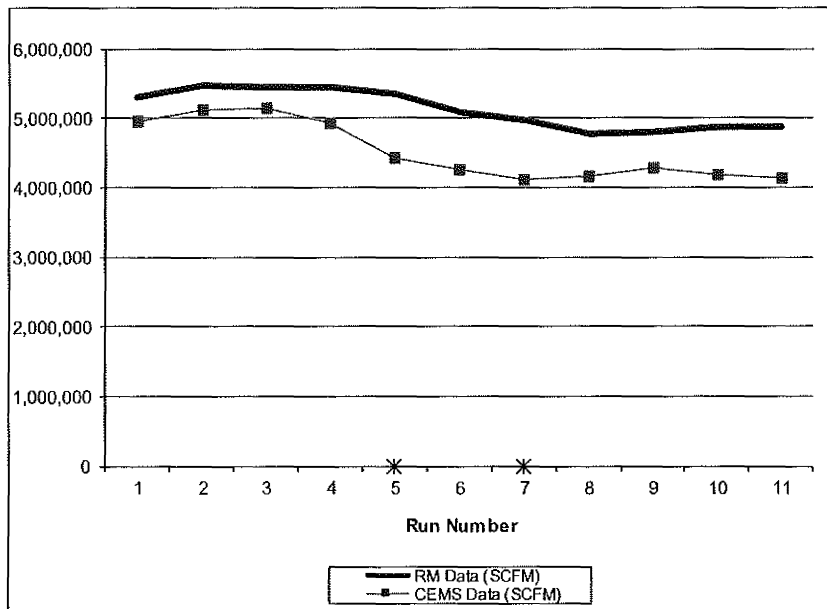
Standard Deviation of Differences	183979.80	
Confidence Coefficient (CC)	141419.14	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	13.4%	20.0%

RM = Reference Method (CleanAir Data)

0820 8 142609

CEMS = Continuous Emissions Monitoring System (Air Products Data)

RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.



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

Run No.	Start Time	Date (2018)	RM Data (Percent)	CEMS Data (Percent)	Difference	Difference Percent
1 *	07:53	Jul 31	15.9	16.0	-0.10	-0.6%
2	08:27	Jul 31	15.9	16.0	-0.10	-0.6%
3	09:03	Jul 31	15.9	16.0	-0.10	-0.6%
4	09:36	Jul 31	15.9	16.0	-0.10	-0.6%
5	10:14	Jul 31	16.1	16.0	0.10	0.6%
6	10:46	Jul 31	16.1	16.0	0.10	0.6%
7	11:19	Jul 31	16.1	16.0	0.10	0.6%
8	11:55	Jul 31	16.5	16.0	0.50	3.0%
9	12:30	Jul 31	16.5	16.0	0.50	3.0%
10	13:04	Jul 31	16.5	16.0	0.50	3.0%
11	13:37	Jul 31	16.5	16.0	0.50	3.0%
Average			16.2	16.0	0.20	1.2%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.270801	
Confidence Coefficient (CC)	0.193706	
t-Value for 10 Data Sets	2.262	
Relative Accuracy (as % of RM)	2.4%	Limit NA

RM = Reference Method (CleanAir Data)

061318 093223

CEMS = Continuous Emissions Monitoring System (Air Products Data)

RATA calculations are based on 10 of 11 runs. * indicates the excluded run.

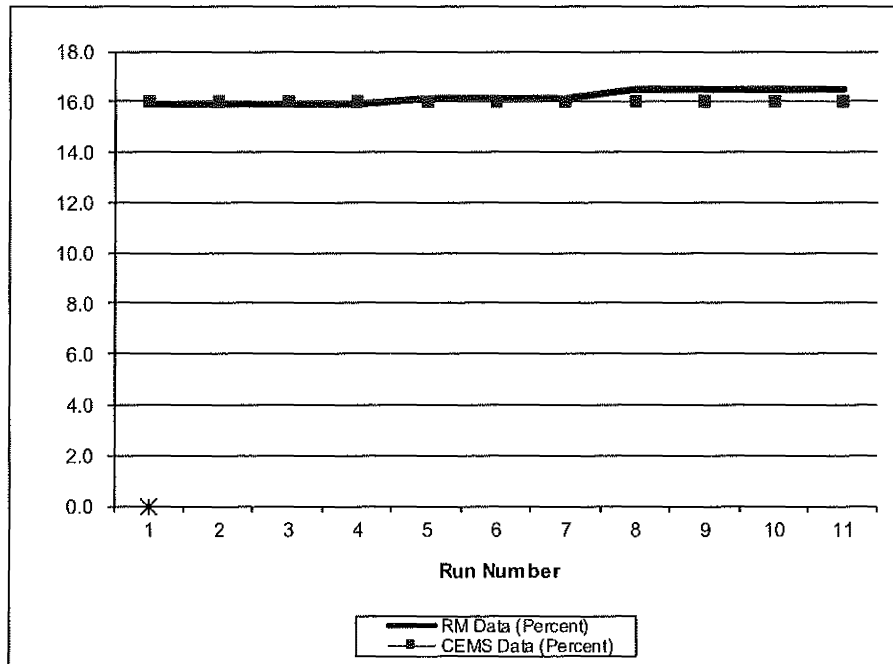


Table 2-3:
O₂ (%dv) RATA (EPA Method 3A / PS 3)

Run No.	Start Time	Date (2018)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1 *	07:53	Jul 31	3.21	3.20	0.01	0.3%
2	08:27	Jul 31	3.20	3.20	0.00	0.0%
3	09:03	Jul 31	3.36	3.40	-0.04	-1.2%
4	09:36	Jul 31	3.74	3.80	-0.06	-1.6%
5	10:14	Jul 31	3.72	3.70	0.02	0.5%
6	10:46	Jul 31	3.60	3.60	0.00	0.0%
7	11:19	Jul 31	3.45	3.50	-0.05	-1.4%
8	11:55	Jul 31	3.45	3.40	0.05	1.4%
9	12:30	Jul 31	3.20	3.20	0.00	0.0%
10	13:04	Jul 31	3.28	3.30	-0.02	-0.6%
11	13:37	Jul 31	3.38	3.40	-0.02	-0.6%
Average			3.44	3.45	-0.01	-0.3%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0333	
Confidence Coefficient (CC)	0.0238	
t-Value for 10 Data Sets	2.262	
Avg. Abs. Diff. (%dv)	0.026	Limit 1.0

RM = Reference Method (CleanAir Data)

081318 093307

CEMS = Continuous Emissions Monitoring System (Air Products Data)

RATA calculations are based on 10 of 11 runs. * indicates the excluded run.

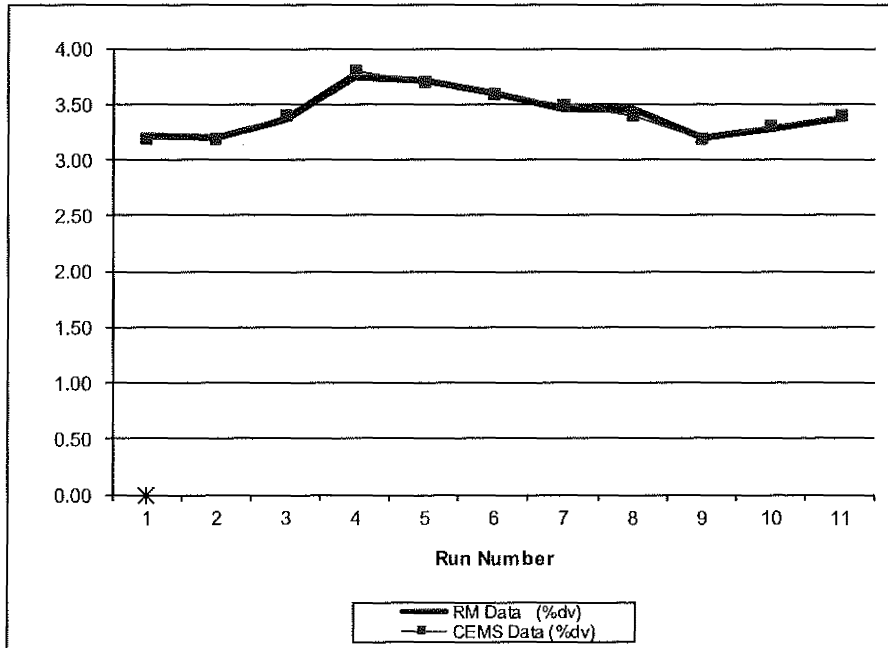


Table 2-4:
CO (ppmdv) Concentration RATA (EPA Method 10 / PS 4A)

Run No.	Start Time	Date (2018)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1 *	07:53	Jul 31	0.0	0.6	-0.6	N/A
2	08:27	Jul 31	0.0	0.6	-0.6	N/A
3	09:03	Jul 31	0.0	0.6	-0.6	N/A
4	09:36	Jul 31	0.0	0.6	-0.6	N/A
5	10:14	Jul 31	0.0	0.6	-0.6	N/A
6	10:46	Jul 31	0.0	0.6	-0.6	N/A
7	11:19	Jul 31	0.0	0.6	-0.6	N/A
8	11:55	Jul 31	0.0	0.6	-0.6	N/A
9	12:30	Jul 31	0.0	0.6	-0.6	N/A
10	13:04	Jul 31	0.0	0.6	-0.6	N/A
11	13:37	Jul 31	0.0	0.6	-0.6	N/A
Average			0.0	0.6	-0.6	NA

Relative Accuracy Test Audit Results

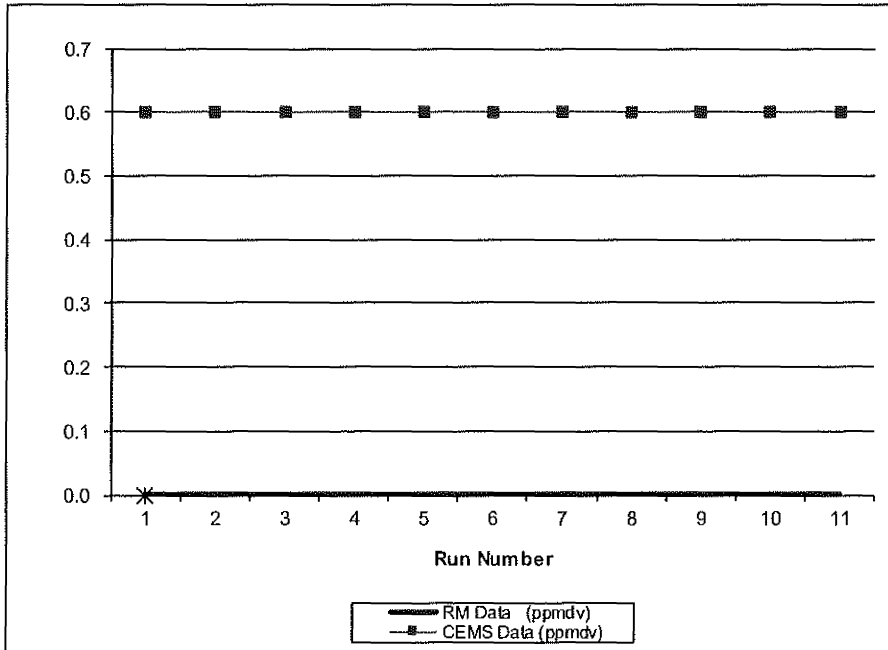
Standard Deviation of Differences	0.0000	
Confidence Coefficient (CC)	0.0000	
t-Value for 10 Data Sets	2.262	
Avg. Abs. Diff. + CC (ppmdv)	0.60	Limit 5.0

RM = Reference Method (CleanAir Data)

081318 093454

CEMS = Continuous Emissions Monitoring System (Air Products Data)

RATA calculations are based on 10 of 11 runs. * indicates the excluded run.



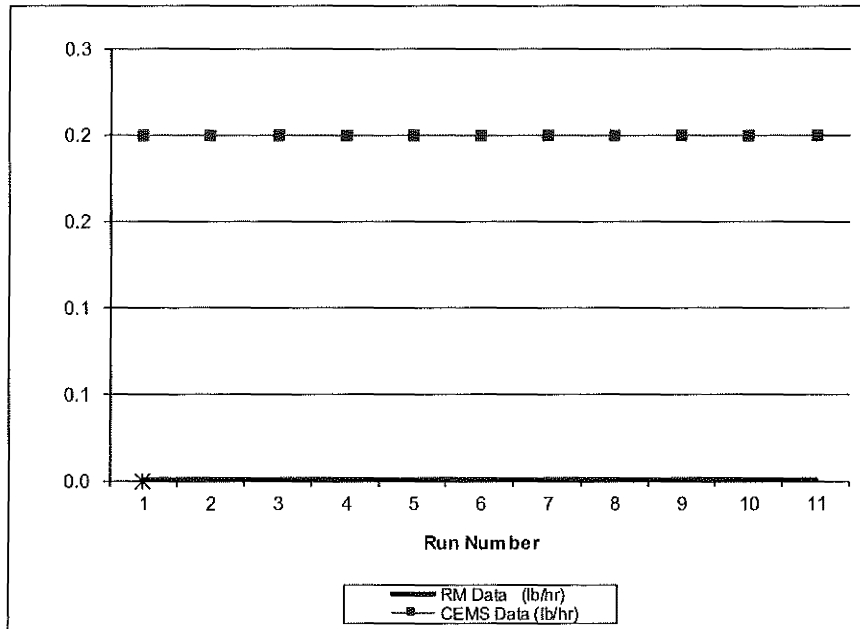
**Table 2-5:
 CO (lb/hr) Emission Rate RATA (EPA Method 10 / PS 4A)**

Run No.	Start Time	Date (2018)	RM Data (lb/hr)	CEMS Data (lb/hr)	Difference (lb/hr)	Difference Percent
1 *	07:53	Jul 31	0.0	0.2	-0.2	N/A
2	08:27	Jul 31	0.0	0.2	-0.2	N/A
3	09:03	Jul 31	0.0	0.2	-0.2	N/A
4	09:36	Jul 31	0.0	0.2	-0.2	N/A
5	10:14	Jul 31	0.0	0.2	-0.2	N/A
6	10:46	Jul 31	0.0	0.2	-0.2	N/A
7	11:19	Jul 31	0.0	0.2	-0.2	N/A
8	11:55	Jul 31	0.0	0.2	-0.2	N/A
9	12:30	Jul 31	0.0	0.2	-0.2	N/A
10	13:04	Jul 31	0.0	0.2	-0.2	N/A
11	13:37	Jul 31	0.0	0.2	-0.2	N/A
Average			0.0	0.2	-0.2	

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0000	
Confidence Coefficient (CC)	0.0000	
t-Value for 10 Data Sets	2.262	
		Limit
Relative Accuracy (as % of Appl. Std.)	0.4%	5.0%
Appl. Std. = 56.9 lb/hr		

RM = Reference Method (CleanAir Data) 081318 093454
 CEMS = Continuous Emissions Monitoring System (Air Products Data)
 RATA calculations are based on 10 of 11 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 hydrogen (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 stream are converted into 99.9% pure H₂ and high-pressure steam through the use of 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 specifications determined the sample point location. Table 3-1 presents the sampling information for the test location. The figures shown on pages 10 and 11 represent the layout of the test location.

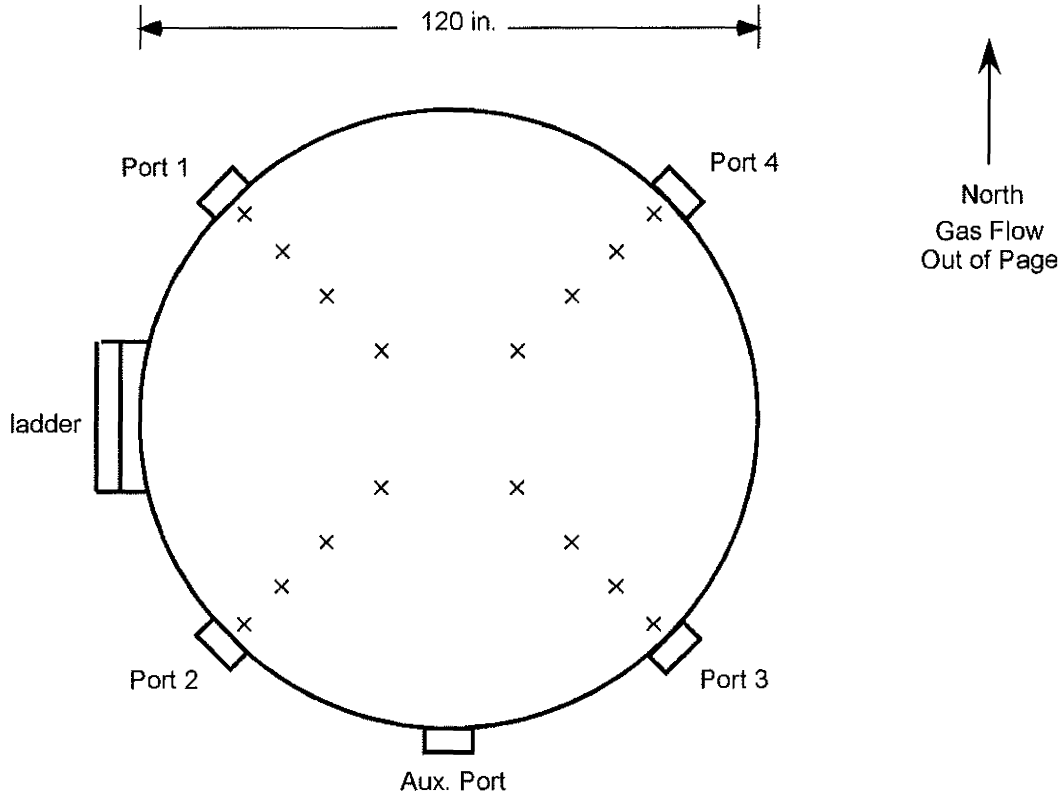
**Table 3-1:
 Sampling Information**

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	1-11	4	6	varied	varied	3-1
Moisture	M-4	1-3	1	1	63 or 84	63 or 84	NA ¹
O ₂ / CO (RATAs)	M-3A+PS3 / M-10+PS4A	1-11	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.

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**Figure 3-1:
 H₂ Plant Heater Stack Volumetric Flow Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	32.3	38.8
2	19.4	23.3
3	10.5	12.6
4	3.2	3.8

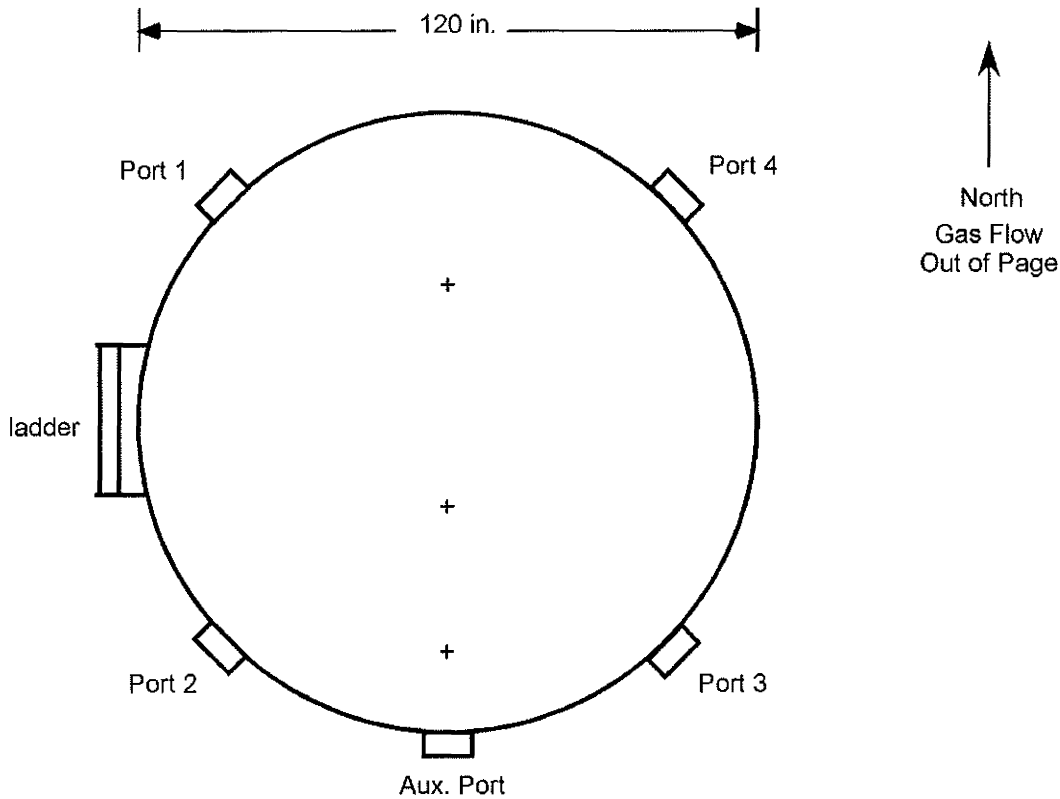
Duct diameters upstream from flow disturbance (A): 1.9

Limit: 0.5

Duct diameters downstream from flow disturbance (B): 5.93

Limit: 2.0

**Figure 3-2:
 H₂ Plant Heater Stack RATA Sample Point Layout (EPA 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): 5.93 Limit: 2.0

End of Section

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 Michigan DEQ. These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. 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 10	"Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"

Title 40 CFR Part 60, Appendix B Performance Specifications

PS 3	"Specifications and Test Procedures for O ₂ and CO ₂ 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"

Methodology Discussion

Flow Rate, Moisture, O₂, CO₂, and CO – USEPA Methods 1, 2, 3A, 4, and 10; Performance Specifications 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 CO emissions and RA were determined using an infrared analyzer per EPA Method 10 and PS 4 and/or 4A.

The Method 3A/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 and 10, the average results for each run were drift-corrected.

General Considerations

A verification of the absence of cyclonic flow was performed at the Hydrogen Plant Heater Stack on March 6, following Method 1 specifications. Documentation is included in CleanAir Report No. 13466.

End of Section