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AIR EMISSIONS TESTING FOR INDUSTRY

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Emissions Compliance Test

Demonstration of Performance of the

NHT Charge Heater (EU16-NHTCHARHTR-S1)

at the

Marathon Detroit Refinery Detroit, Michigan

subject to
Permit No. MI-ROP-A9831-2012c

Test Date: May 13, 2022
Erthwrks Project No. 9049.1.B2

A9831-test_20220513

STAC STACK TESTING ACCREDITATION COUNCIL

ACCREDITED TO ASTM D7036 ONLY CERT #6147.01

Louisiana Environmental Lab Accreditation Program LELAP

CARB

Endorsement Page

This report was developed in accordance with the requirements designated in the applicable regulatory permit(s) and or regulatory rules. To the best of my knowledge the techniques, instrumentation, and calculations presented in this report will serve to accurately and efficiently detail the results of the test campaign requirements.

Erthwrks, Inc.

Name: Jason Dunn

Title: QC Specialist

Signature:

This report has been reviewed for accuracy and completeness. The actions presented in this report are, to the best of my knowledge, an accurate representation of the results and findings of the test campaign. Erthwrks, Inc. operates in conformance with the requirements on ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies and is accredited as such by the Stack Testing Accreditation Council (STAC) and the American Association for Laboratory Accreditation (A2LA).

Erthwrks, Inc.

Name: Jarrod Hoskinson, QSTI

Title: Senior Project Manager

Signature:

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ATTACHMENTS

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct the emissions performance test the NHT Charge Heater in operation at the Marathon Detroit Refinery, located in Detroit, Michigan. The performance test was conducted on May 13, 2022.

1.2 Purpose of Testing

This test program was conducted to determine the carbon monoxide (CO), sulfuric acid (H_2SO_4), and particulate matter (PM) emissions emitted from the NHT Charge Heater. All testing and audit procedures were conducted in accordance with the requirements set forth in the USEPA Title 40, Code of Federal Regulations (CFR), Part 60, Appendix B which defines the testing procedures.

1.3 Description of Source

The NHT Charge Heater (EU16-NHTCHARHTR-S1) preheats the feed to the Naphtha Hydrotreater. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the NHT Charge Heater Stack where testing was performed.

1.4 Contact Information

Marathon Petroleum Company LP
Addie Koerner
Michigan Refining Division
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419-306-5162 cell
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Erthwrks, Inc.
Jarrod Hoskinson
Senior Project Manager
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Austin, TX 78745
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jhoskinson@erthwrks.com

Facility Location:
Marathon Petroleum Company LP
Detroit Refinery
1300 South Fort Street
Detroit, MI 48217

2.0 SUMMARY OF RESULTS

Table 2.1: NHT Charge Heater Emissions Results

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
CO	EPA Method 4	0.00001 lb/MMBtu	0.02 lb/MMBtu	Pass
PM	EPA Method 5	0.0004 lb/MMBtu	0.0019 lb/MMBtu	Pass
PM_{10}	EPA Method 5/202	0.0018 lb/MMBtu	0.0076 lb/MMBtu	Pass
H_2SO_4	EPA Method CTM-013	0.23 ppm	n/a	n/a

3.0 SOURCE DESCRIPTION

3.1 Description of the process

The Naphtha Hydrotreater unit uses hydrogen to remove sulfur and nitrogen from straight-run and coker naphthas. This process, known as hydrotreating, uses a catalyst to promote the desulfurization reaction. The desulfurized or sweet naphtha is blended into gasoline or used for platformer feed. The NHT unit consists of process vessels (including exchangers, reactors, receivers, separators, and a stripper column), heaters, tanks, containers, pumps, piping, drains, and various components (pump seals, process valves, pressure relief valves, flanges, connectors, etc.).

The NHT Charge Heater preheats the feed to the reactor. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the NHT Charge Heater Stack.

3.2 Applicable permit and source designation

The Marathon Detroit Refinery operates the NHT Charge Heater under the Permit No. MI-ROP-A9831-2012c. The NHT Charge Heater is also identified as EU16- NHTCHARHTR-S1. The Marathon Detroit Refinery is required to conduct an annual compliance test to demonstrate that NOx emissions remain below the applicable limit.

3.3 Type and quantity of materials processed during tests

During the emission testing on May 13, 2022 at the Marathon Petroleum Company LP Refinery, the NHT Charge Heater was tested while operating at the maximum achievable load condition. NOTE: For this testing program, the average NHT Charge Rate was approximately 36,000 BPD with a Vac Heater firing rate of ~60 MMBtu/hr and a Fuel Gas rate of ~1383 MSCFD. This operational data was provided by MPC and is located in Attachment F of this report.

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 Gaseous Sampling – CO, O_2, and CO_2

For the gaseous sampling, Erthwrks utilized a stainless-steel probe, of sufficient length to reach all sampling points, inserted into a sampling port that is located on the stack in accordance with EPA Method 1. The sample is extracted through the probe, a heated Teflon sampling line, to a heating filter. The sample then enters a minimum contact sample conditioner that cools and removes moisture from the gas matrix prior to entering the Erthwrks sampling manifold.

Erthwrks followed all quality assurance and quality control procedures as defined in US EPA 40 CFR 60 Appendix A. The Calibration Error (CE) Test was conducted as specified in EPA Method 7E §8.2.3. In accordance with this requirement, a three-point analyzer calibration error test was conducted prior to sampling. The CE test was conducted by introducing the low, mid, and high-level calibration gasses (as defined in EPA Method 7E §3.3.1-3) sequentially and the response was recorded. The results of the CE test are acceptable if the calculated calibration error is within ±2.0% of calibration span (or ≤ 0.5 ppmv).

The Initial System Bias and System Calibration Error Check was conducted in accordance with EPA Method 7E §8.2.5. The upscale calibration gas was introduced at the probe upstream of all sample system components and the response recorded. The procedure will was repeated with the low-level gas and the response recorded. During this activity, the sample system response time was also be recorded. This specification is acceptable if the calculated values of the system calibration error check are within ±5.0% of the calibration span value (or ≤0.5 ppmv).

After each test run, the sample system bias check is conducted to validate the run data. The low-level and upscale drift are calculated using Equation 7E-4. The run data is valid if the calculated drift is within ±3.0% of the calibration span value (or ≤0.5 ppmv).

After each test run, the corrected effluent gas concentration was calculated as specified in EPA Method 7E §12.6. The arithmetic average of all valid concentration values are adjusted for bias using equation 7E-5B.

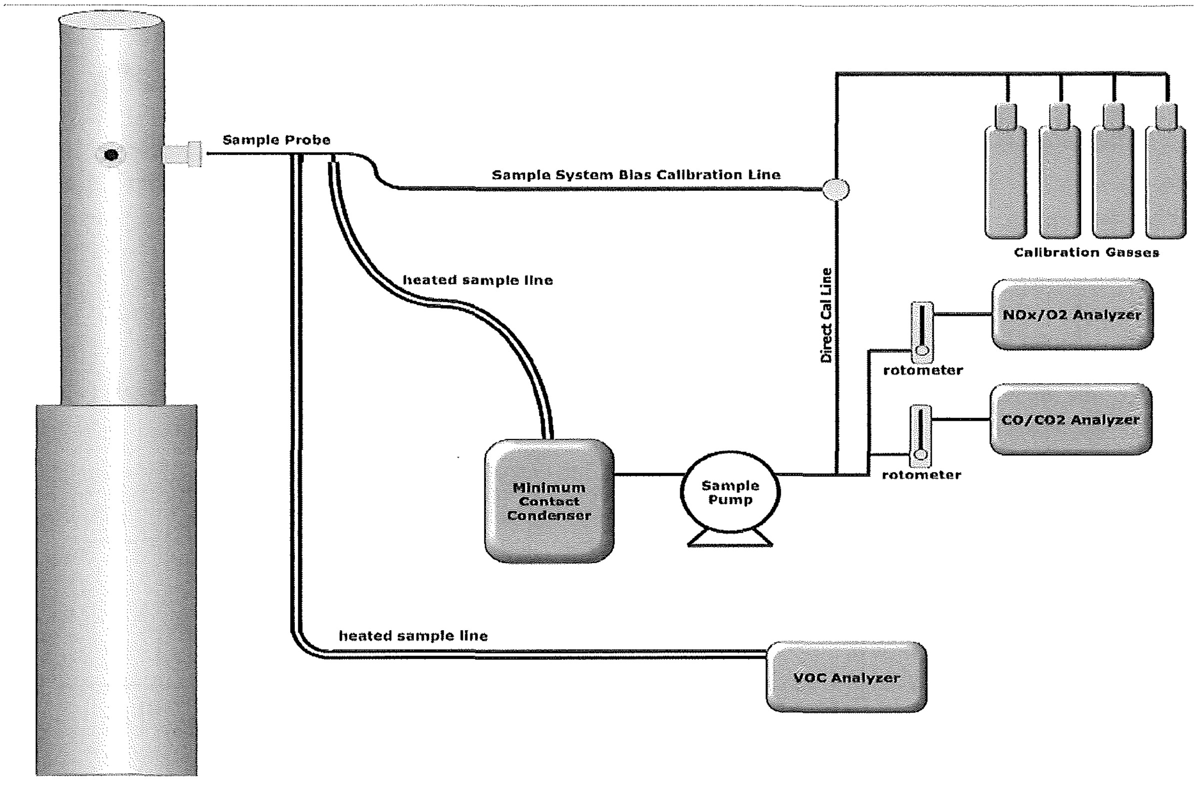

Figure 1: Example Erthwrks Gaseous Sampling System Diagram

4.2 Filterable Particulate Matter Sampling – EPA Method 5

EPA Test Method 1 will be used for the selection of sampling points. Stack dimensions, number of sample ports and sample port locations were confirmed prior to testing to determine the appropriate number of traverse points for the test.

EPA Test Method 5 was used to determine filterable particulate matter emission rates. Method 5 is the method at which particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter and on the lining of the isokinetic probe maintained at a temperature of 120 ± 14°C. Upon completion of each test run, the nozzle and probe liner were rinsed and brushed with acetone. The acetone rinse catch will be collected and combined with the filter holder rinse and labeled as "front half rinse". The total PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically. Filterable PM will be calculated by combining the net gravimetric gain of the filter and the net gravimetric gain of the evaporated front half rinse. Figure 2 below shows the Method 5 sampling system components.

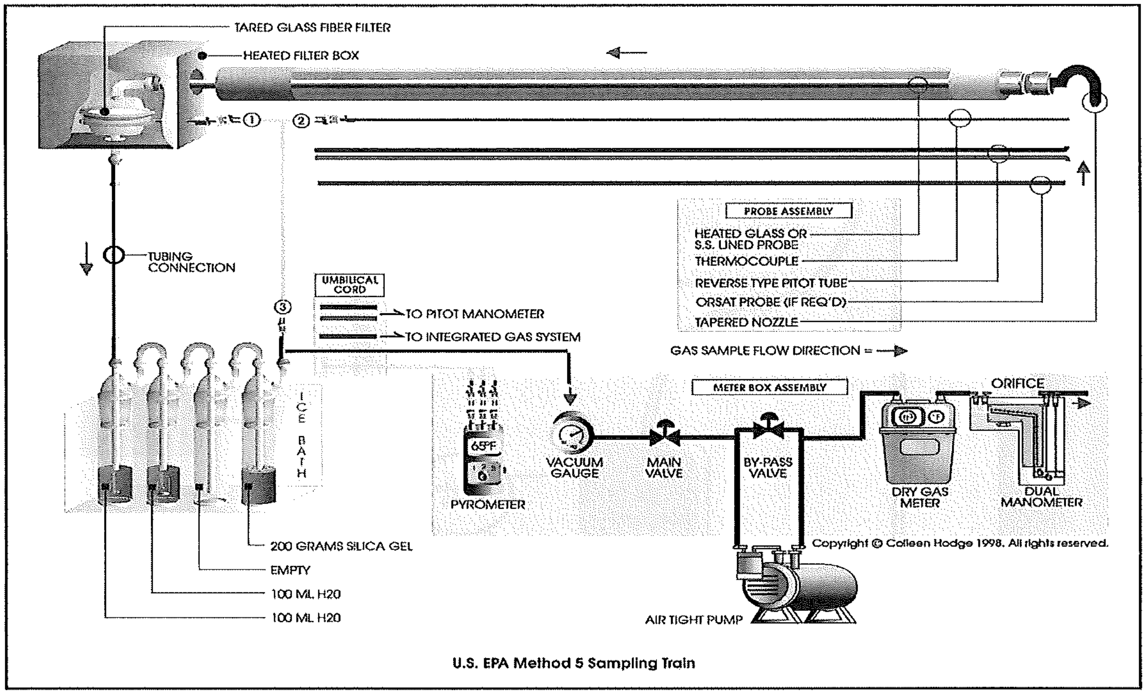

Figure 2: Example Erthwrks Particulate Matter Sampling System Diagram

4.3 EPA Method CTM-013 (ALT-133 Analysis) H_2SO_4 Determination

The H_2SO_4 emissions were determined utilizing the conditional test method 13 (CTM-013). The sample was extracted at a constant rate through a quartz lined heated probe (>350 ˚F), A heated quartz filter holder and filter (>500 ˚F), and through a Modified Grahm condenser (H_2SO_4 Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing condenser coil. The H_2SO_4 condenser is maintained between 167 to 185 ˚F. Because SO_2 was not to be determined via this method, the sample was then passed through four impingers with the specifications delineated in EPA Method 4.

The sampling was conducted at a single point at a constant rate of about 10 L/min and the DGM readings and all temperatures were recorded every five minutes. After the completion of the test run, the samples were recovered in accordance with the test method and the samples were sent to Enthalpy Analytical for analysis via Ion Chromatography (ALT-133).

See the figure below that details the CTM-013 Sampling Train.

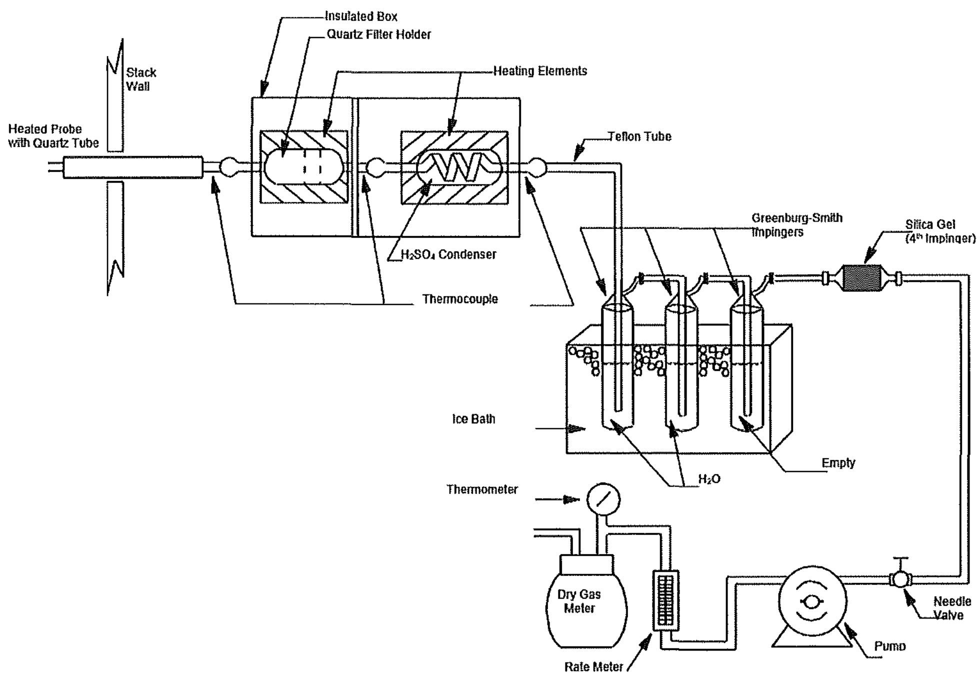

Figure 3: Example Erthwrks H_2SO_4 System Diagram

4.4 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted the emissions testing with no sampling or procedural variances.

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Attachment A
Detailed Results of Emission Test

Summary of Results - CO Compliance Test

Date: 5/13/2022
Client: Marathon
Facility: Detroit
Unit ID: 16H4
Erthwrks Tech: JHM, AL, AM, JT

Run Information				
Run Number	**Run 1**	**Run 2**	**Run 3**	
Date	5/13/2022	5/13/2022	5/13/2022	
Run Start Time	8:31	10:47	12:40	
Run End Time	10:04	12:20	14:13	
Unit Fuel Flow Data				Average
Fuel F Factor (F_d) (scf/MMBtu)	8614.7	8614.7	8614.7	8614.7
Emission Concentrations				
CO (ppmvd)	0.01	0.01	0.02	0.01
O_2 (%vd)	5.46	5.46	5.51	5.48
Emission Rates (lb/scf)				
CO (lb/scf)	7.27E-10	7.27E-10	1.45E-09	9.692E-10
Emission Rates (lb/MMBtu)				
CO (lb/MMBtu)	0.00001	0.00001	0.00002	0.00001

Erthwrks Particulate Matter Summary of Results

Project:	Marathon
Facility:	Detroit Refinery
Location:	Detroit, MI
Unit ID:	NHT Charge Heater (16H4)

Run Designation						
Run Number		1	2	3	Average	
Date		5/13/2022	5/13/2022	5/13/2022		mm:dd:yyyy
Run Start Time		8:31	10:46	12:40		hh:mm
Run End Time		10:07	12:22	14:15		hh:mm
Operating Conditions						
Firing Rates (MMBTU/hr)		59.68	60.07	59.98	59.91	MMBtu/hr
Stack Gas Composition						
Oxygen Concentration	($\%O_2$)	5.50	5.50	5.50	5.50	%
Carbon Dioxide Concentration	($\%CO_2$)	9.00	9.10	9.10	9.07	%
Stack Moisture Content	(B_{ws})	14.50	14.58	13.13	14.07	%
Stack Dry Molecular Weight	(M_d)	29.66	29.68	29.68	29.67	lb/lb-mole
Stack Wet Molecular Weight	(M_s)	27.97	27.97	28.14	28.03	lb/lb-mole
Stack Gas Volumetric Flow Calculations						
Absolute Stack Pressure	(P_s)	30.16	30.16	30.16	30.16	in Hg
Average Stack Temperature	($(t_s)_{avg}$)	1371.2	1366.3	1365.7	1367.8	°R
Average Square Root of ΔP's	($(\Delta p^{1/2})_{avg}$)	0.4345	0.4328	0.4466	0.4380	%
Average Stack Gas Velocity	(v_s)	2387.00	2373.31	2440.96	2400.42	ft/min
Average Stack Gas Flow	(Q_{aw})	4.01E+04	3.99E+04	4.10E+04	4.03E+04	acfm
Wet Standard Stack Flow Rate	(Q_{sw})	9.34E+05	9.32E+05	9.59E+05	9.42E+05	wscfh
Dry Standard Stack Flow Rate	(Q_{sd})	7.99E+05	7.96E+05	8.33E+05	8.09E+05	dscfh
Particulate Matter Emission Rate Calculations						
Mass of Filterable PM (M.5)	mg	1.59	0.6	0.98	1.06	mg
Mass of Condensible PM (M.202)	mg	3.83	3.58	3.44	3.62	mg
Total Mass of Particulates	mg	5.42	4.18	4.42	4.67	mg
Filterable PM Mass Concentration	lb/dscf	4.69E-08	1.78E-08	2.79E-08	3.09E-08	lb/dscf
Total PM Mass Concentration	lb/dscf	1.60E-07	1.24E-07	1.26E-07	1.37E-07	lb/dscf
Filterable PM Mass Emission Rate	lb/hr	0.04	0.01	0.02	0.02	lb/hr
Total PM Mass Emission Rate	lb/hr	0.13	0.10	0.10	0.11	lb/hr
Filterable PM Mass Emission Rate	lb/day	0.90	0.34	0.56	0.60	lb/day
Total PM Mass Emission Rate	lb/day	3.07	2.36	2.51	2.65	lb/day
Filterable PM Mass Emission Rate	lb/MMBtu	0.0006	0.0002	0.0004	0.0004	lb/MMBtu
Total PM Mass Emission Rate	lb/MMBtu	0.0021	0.0016	0.0017	0.0018	lb/MMBtu

Detailed Summary of Results

Client:	Marathon
Facility:	Detroit Refinery
Unit ID:	16H4
Erthwrks Tech:	JK, AL, JH, AM

Run Information				
Run Number	**Run 1**	**Run 2**	**Run 3**	
Date	5/10/2022	5/10/2022	5/10/2022	
Run Start Time	8:44	11:49	13:44	
Run End Time	9:44	12:49	14:44	
Unit Fuel Flow Data				**Averages**
Fuel F Factor (F_d) (scf/MMBtu)	8614.7	8614.7	8614.7	8614.7
Emission Concentrations				
H_2SO_4 (ug)	475	621	496	530.67
Train volume (scf)	20.53	20.42	20.30	20.42
H2SO4 (lb/scf)	5.10E-08	6.70E-08	5.39E-08	5.73E-08
H_2SO_4 (ppm)	**0.20**	**0.26**	**0.21**	**0.23**

Attachment B
Quality Control Documentation

Erthwrks Method 1 Traverse Point Location Worksheet

Client: Marathon
Project #: 9049.1.B2
Facility: Detroit
Unit ID: 16H4
Technician: JHM, AL, AM, JT

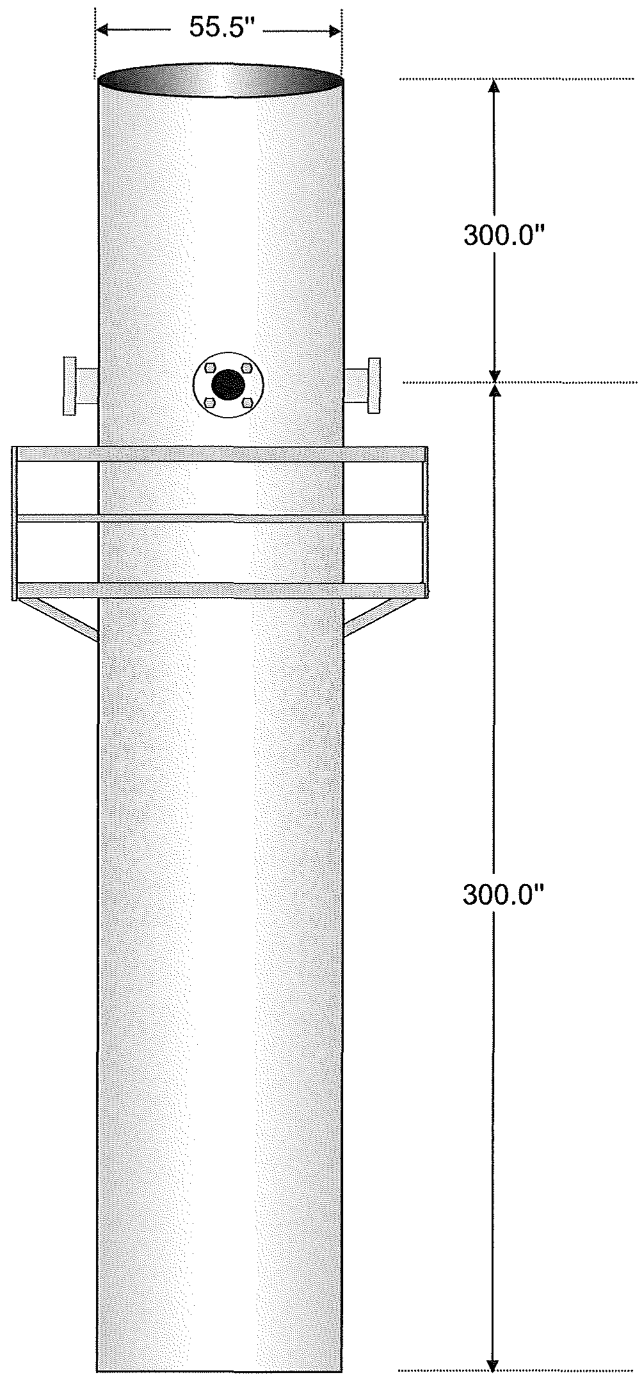
Stack ID Measurements

Stack ID + Port (inches):	64
Port Extension (inches):	8.5
Stack Diameter (inches):	55.5

Port Location Measurements

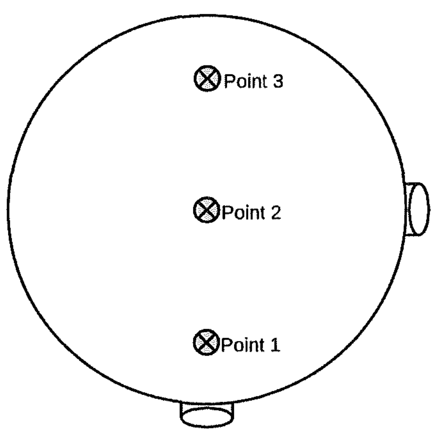
Distance Upstream (A) (inches):	300
Distance Downstream (B) (inches):	300
Stack Diameters Upstream (A):	5.4
Stack Diameters Downstream (B):	5.4

Total Traverse Points to be used:	3
Traverse Points per Diameter:	3



Traverse Point Locations[(1)(2)]	
Point 1:	9.27"
Point 2:	27.75"
Point 3:	46.23"

Stack Cross Section View



[(1)]For stack diameter >4.0" and <2.4 meters, stratification is measured at 16.7%, 50.0%, and 83.3" of stack diameter (M7E, §8.1.2).
[(2)] For stack diameter >2.4 meters, stratification is measured at 0.4, 1.2, and 2.0 meters from stack wall (M7E, §8.1.2).

Erthwrks Gaseous Sample Collection and Quality Assurance Worksheet

Date: 5/13/2022
Client: Marathon
Facility: Detroit
Project No: 9049.1.B2
Unit ID: 16H4
Erthwrks Tech: JHM, AL, AM, JT

Calibration Gas Verification

Pollutant	Low-Level Gas Conc. (C_v)	Cylinder Serial #	Mid-Level Gas Conc. (C_v)	Cylinder Serial #	High-Level Gas Conc. (C_v/CS)	Cylinder Serial #	Dilutor Root Gas
CO	NA	NA	50.83	CC339873	93.52	SG9170693BAL	NA
O_2	NA	NA	10.00	CC287657	19.92	ALM038955	NA
CO_2	NA	NA	10.13	CC287657	19.69	ALM038955	NA

Reference Method Analyzer Info

Make	Model	Serial No.
Teledyne	T300M	734
Teledyne	T200H	802
Teledyne	T300M	734

Direct Calibration Error Test

Pollutant	Zero Gas Response (C_{Dir})	Calibration Error (ACE)*	Low-Level Response (C_{Dir})	Calibration Error (ACE)*	Mid-Level Response (C_{Dir})	Calibration Error (ACE)*	High-Level Response (C_{Dir})	Calibration Error (ACE)*
CO	0.23	0.24%	n/a	n/a	50.82	-0.01%	93.58	0.07%
O_2	-0.01	-0.04%	n/a	n/a	9.94	-0.33%	19.92	-0.03%
CO_2	0.00	0.01%	n/a	n/a	10.08	-0.27%	19.82	0.67%

*Unless otherwise noted in protocol or report, THC's calibration error test is conducted using the entire sample system and must be less than 5% of applicable calibration gas
** ACE must either be within ± 2.0% or ≤ 0.5 ppmv absolute difference*

Initial Sample System Bias and Response Time

Pollutant	Upscale Gas Cert. Conc. (C_{vs})	Upscale Gas Direct (C_{Dir})	Upscale Response (C_s)	Sample System Bias (SB)*	Response Time (sec)	Downscale Response (C_s)	Sample System Bias (SB)*	Response Time (sec)
CO	50.83	50.82	48.77	-2.19%	50	0.42	0.20%	50
O_2	10.00	9.94	9.95	0.07%	35	0.18	0.94%	35
CO_2	10.13	10.08	9.92	-0.82%	50	0.00	0.01%	50

** SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference*

Sample Collection Raw Data--Pre and Post Sample System Calibration (SSC) and Raw Run Results

Run #: Run 1
Start Time: 8:31
End Time: 10:04

Pollutant	Initial Zero SSC (C_s)	Initial Upscale SSC (C_s)	Raw Results (C_{Avg})	Final Zero SSC (C_s)	Final Upscale SSC (C_s)
CO	0.42	48.77	-0.42	-0.49	47.66
O_2	0.18	9.95	5.51	0.19	9.92
CO_2	0.00	9.92	9.28	0.00	9.87

Run #: Run 2
Start Time: 10:47
End Time: 12:20

Pollutant	Initial Zero SSC (C_s)	Initial Upscale SSC (C_s)	Raw Results (C_{Avg})	Final Zero SSC (C_s)	Final Upscale SSC (C_s)
CO	-0.49	47.66	-0.86	-0.10	47.48
O_2	0.19	9.92	5.50	0.20	9.93
CO_2	0.00	9.87	9.26	0.02	9.91

Sample Collection Raw Data--Pre and Post Sample System Calibration (SSC) and Raw Run Results

Run #: Run 3
Start Time: 12:40
End Time: 14:13

Pollutant	Initial Zero SSC (C_s)	Initial Upscale SSC (C_s)	Raw Results (C_{Avg})	Final Zero SSC (C_s)	Final Upscale SSC (C_s)
CO	-0.10	47.48	-0.10	-0.13	47.42
O_2	0.20	9.93	5.55	0.20	9.88
CO_2	0.02	9.91	9.20	0.00	9.89

Run 1 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C_o)	Avg. Upscale Sys. Bias (C_M)	Zero Drift Assessment (D)†	Upscale Drift Assessment (D)†	Corrected Results (C_{Gas})	
CO	0.20%	-2.19%	-0.77%	-3.37%	-0.04	48.22	0.97%	1.19%	-0.40	< 0.01 MDL applied
O_2	0.94%	0.07%	0.97%	-0.06%	0.18	9.94	0.03%	0.13%	5.46	
CO_2	0.01%	-0.82%	0.00%	-1.03%	0.00	9.90	0.01%	0.21%	9.50	

** SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference*
† D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference

Run 2 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C_o)	Avg. Upscale Sys. Bias (C_M)	Zero Drift Assessment (D)†	Upscale Drift Assessment (D)†	Corrected Results (C_{Gas})	
CO	-0.77%	-3.37%	-0.36%	-3.57%	-0.30	47.57	0.41%	0.20%	-0.60	< 0.01 MDL applied
O_2	0.97%	-0.06%	1.03%	-0.04%	0.19	9.93	0.06%	0.02%	5.46	
CO_2	0.00%	-1.03%	0.09%	-0.85%	0.01	9.89	0.09%	0.18%	9.48	

** SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference*
† D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference

Run 3 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C_o)	Avg. Upscale Sys. Bias (C_M)	Zero Drift Assessment (D)†	Upscale Drift Assessment (D)†	Corrected Results (C_{Gas})
CO	-0.36%	-3.57%	-0.38%	-3.63%	-0.12	47.45	0.03%	0.06%	0.02
O_2	1.03%	-0.04%	1.04%	-0.29%	0.20	9.90	0.02%	0.25%	5.51
CO_2	0.09%	-0.85%	0.01%	-0.93%	0.01	9.90	0.08%	0.09%	9.41

** SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference*
† D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference