



AIR EMISSIONS TESTING FOR INDUSTRY

***Emissions Compliance Test Report
and Relative Accuracy Test Audit***

for the
**GOHT Heater 2
EU08-GOHTCHARHTR2-S1**

at the
Marathon Detroit Refinery

in
Detroit, MI

subject to
**Permit No. MI-ROP-A9831-2012c
Title 40 CFR Part 60, Appendix F**

prepared for



**Marathon
Petroleum Company LP**

**Test Date: April 10, 2024
Erthwrks Project No. 9565.1.B2**



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: QAQC Manager

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: John Wood

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Signature: 

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ATTACHMENTS

- A. Detailed Results of Emissions Test
- B. Quality Control Documentation
- C. Example Calculations
- D. Field Sampling Worksheets
- E. Raw Datalog Records
- F. Calibrations and Certifications
- G. CEMS/Process Logs
- H. Laboratory Analysis Report

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the GOHT Heater 2 in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on April 10, 2024.

1.2 Purpose of Testing

This test was conducted to determine the GOHT Heater 2 mass emission rates of volatile organic compounds (VOCs), sulfuric acid (H_2SO_4), and particulate matter (PM). In addition, a relative accuracy test audit (RATA) was conducted to demonstrate the accuracy and reliability of the Marathon Petroleum Company LP nitrogen oxides (NO_x), carbon monoxide (CO) and oxygen (O_2) continuous emissions monitoring system (CEMS) in operation on the GOHT Heater 2.

Moisture content and stack volumetric flow rate were also measured to calculate mass emission rates in pounds per hour (lb/hr) and pounds per million British Thermal Units (lb/mmBTU).

1.3 Contact Information

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2.0 SUMMARY OF RESULTS

Table 2.1: GOHT Heater 2 CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO _x (lb/mmBTU)	Performance Spec. 2	7.70% R _{ARM}	<20%	Pass
CO (ppmvd)	Performance Spec. 4A	0.45 ppm	<5 ppm	Pass
O ₂ (%vd)	Performance Spec. 3	0.77% R _{AMD}	<1%	Pass

Table 2.2: GOHT Heater 2 Emissions Compliance Results

Pollutant Measured	Measured Result	Applicable Limit	Pass/Fail
VOC	0.0005 lb/mmBTU	0.0055 lb/mmBTU	Pass
PM	0.0012 lb/mmBTU	0.0019 lb/mmBTU	Pass
PM/PM ₁₀	0.0021 lb/mmBTU	0.0076 lb/mmBTU	Pass
H ₂ SO ₄	0.00003 lb/mmBTU	n/a	n/a

3.0 SOURCE DESCRIPTION

3.1 Description of the process

Marathon Petroleum Company LP produces refined petroleum products from crude oil and is required to demonstrate that select process emission sources are operating in compliance with permitted emissions limits.

The Gas Oil Hydrotreater Unit (EU08-GOHT-S1) reacts sour gas oil streams with hydrogen over a catalyst bed to remove sulfur. The GOHT unit consists of process vessels (reactors, distillation tower, absorbing towers, stripper tower), two charge heaters (EU08-GOHTCHARHTR-S1 and EU08-GOHTCHARHTR2-S1), cooling tower, flare, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The GOHT # 2 Heater (EU08-GOHTCHARHTR2-S1) is fired by refinery fuel gas. Emissions are vented to the atmosphere via the GOHT #2 Heater Stack (SV08-H2), where testing will be performed.

Table 3.1: GOHT Heater 2 CEMS Description

Pollutant Measured	Analyzer Manufacturer	Analyzer Model	Serial Number
NO _x	ABB	Limas 11	3.362955.7
CO	ABB	Uras 26	3.365875.7
O ₂	ABB	Magnos 206	3.365877.7

3.2 Applicable permit and source designation

The GOHT Heater 2 is identified as EU08-GOHTCHARHTR2-S1 and is operated under Permit No. MI-ROP-A9831-2012c.

3.3 Type and quantity of materials processed during tests

During the emission testing on April 10, 2024, at the Marathon Petroleum Company LP refinery, the GOHT Heater 2 was tested while operating at the maximum achievable load condition. This operational data was provided by MPC and is located in Attachment G of this report.

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 Gaseous Sampling – NO_x, CO, O₂ and CO₂

The following EPA reference methods were utilized to complete this testing program:

- EPA Method 3A for the determination of O₂ and CO₂ concentration
- EPA Method 7E for the determination of NO_x concentration
- EPA Method 10 for the determination of CO concentration

A calibration error (CE) test was conducted as specified in US EPA Method 7E §8.2.3. In accordance with this requirement, a three-point analyzer calibration error test was conducted prior to exhaust sampling. The CE test was conducted by introducing the low, mid, and high-level calibration gasses (as defined by EPA Method 7E §3.3.1-3) sequentially and the response was recorded.

The initial system bias and system calibration error check were 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 was recorded. The procedure was repeated with the low-level gas concentration and response recorded.

After each test run, the sample system bias check was conducted to validate the run data. The low-level and upscale drift was calculated using equation 7E-4. The arithmetic average of all valid concentration values was adjusted for bias using equation 7E-5B.

A stratification test was conducted in accordance with EPA Method 7E §8.1.2 at the beginning of Run 1. The results were determined to be unstratified and single-point sampling was utilized throughout the remainder of the test. The results of the stratification test is included in Attachment B of this report.

See Figure 1 below for a sample system diagram.

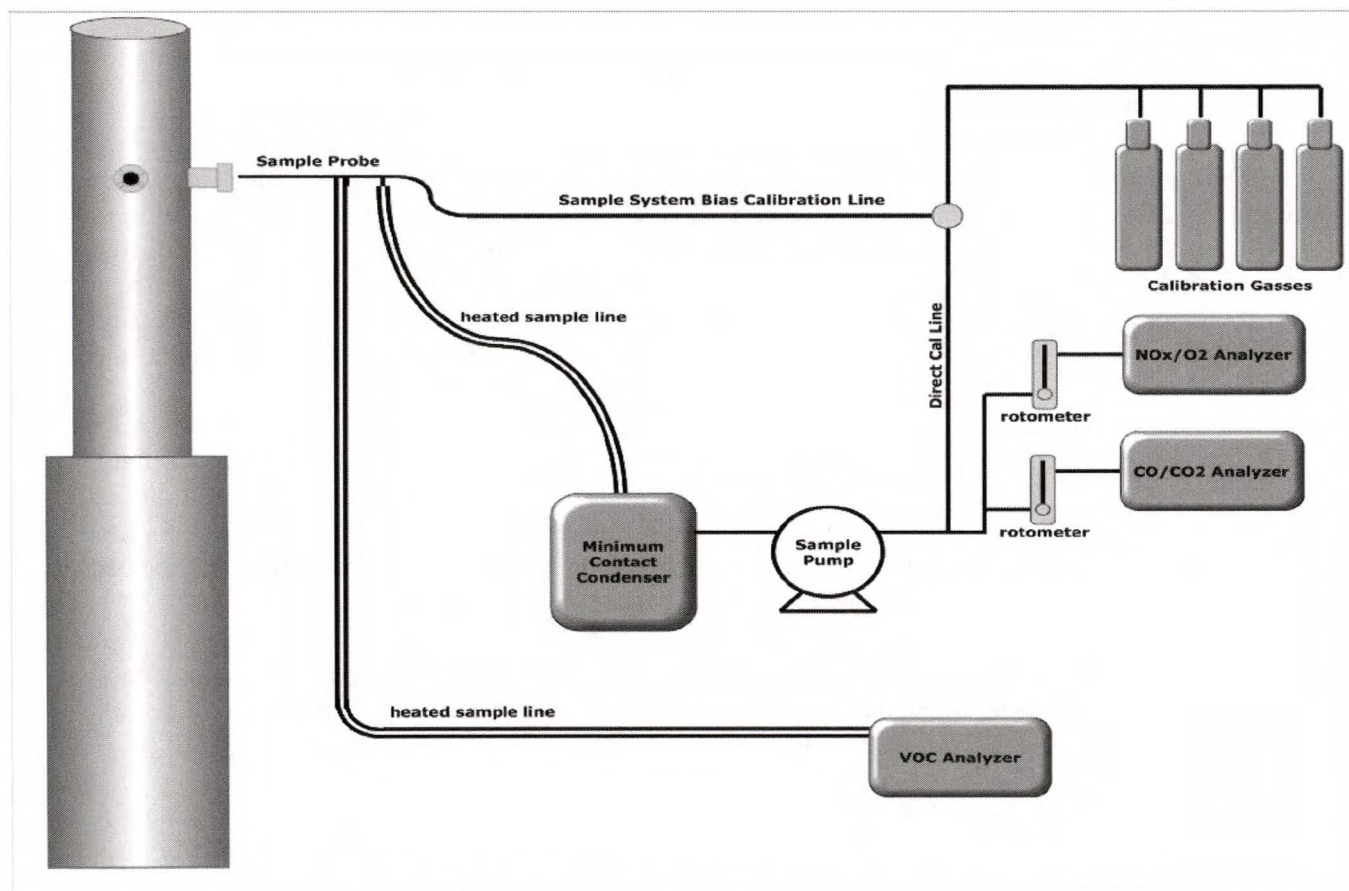


Figure 1: Example Erthwrks Gaseous Sampling System Diagram

4.2 RATA Procedures

The RATA testing for CO and O₂ was conducted following the sampling and measurement procedures found in the EPA Part 60, Appendix B, Performance Specifications which requires that EPA Reference Methods, from EPA Part 60, Appendix A, be utilized to conduct independent stack emissions measurements for comparison with installed CEMS readings. The following performance specifications was used during this testing program.

- EPA Performance Specification 2 for NO_x relative accuracy
- EPA Performance Specification 3 for O₂ relative accuracy
- EPA Performance Specification 4A for CO relative accuracy

As required by these specifications, the use EPA Protocol 1 gases are mandatory and were used for this portion of the project.

A minimum of nine (9) RATA test runs were conducted at each exhaust stack for a minimum duration of twenty-one (21) minutes for each run. A 3-point traverse located at 16.7%, 50.0%, and 83.3% of the way across the stack (or 0.4, 1.2, and 2.0 meters from the stack wall) was conducted during each RATA test run (7 minutes per point). A maximum of twelve (12) RATA test runs was conducted and up to three test runs was discarded and not used to determine relative accuracy. The results of the reference method tests were compared to CEMS measurement data from the same time periods to determine the relative accuracy of the CEMS.

For NO_x, the results of the RATA test are considered acceptable if the calculated relative accuracy does not exceed 20.0% as calculated by Equation 2-6 in Performance Specification 2. Alternatively, for affected units where the average of the reference method measurements is less than 50 percent of the emission standard (emission limit), the relative accuracy must not exceed 10% when the applicable emission standard is used in the denominator of Eq. 2-6.

For O₂, the results of the RATA test are considered acceptable if the calculated relative accuracy does not exceed 20.0% as calculated by Equation 3.1 in Performance Specification 3. The results are also acceptable if the result of Equation 3-2 is less than or equal to 1.0 percent.

For CO, the results of the RATA test are considered acceptable if the calculated relative accuracy does not exceed 10.0% as calculated by Equation 2-6 in Performance Specification 2. Alternatively, for affected units where the average of the reference method measurements is less than 50 percent of the emission standard (emission limit), the relative accuracy must not exceed 5% when the applicable emission standard is used in the denominator of Eq. 2-6. Performance Specification 4A criteria may be used to determine relative accuracy for CEMS with low emission standards (less than 200 ppmv). In these cases, the results of the RATA test are considered acceptable if the absolute average difference between the RM and CEMS is within 5 ppmv.

4.3 Gaseous Sampling – VOC as THC (Method 25A)

The determination of the VOC concentration was determined by measuring total hydrocarbon compound (THC) and followed all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A with the exception of the EGLE requirement to adjust the final results for drift using Equation 7E-5B. The calibration error (CE) test was conducted following the procedures specified in EPA Method 25A §8.4. In accordance with this requirement, a four-point analyzer calibration error test was conducted prior to exhaust sampling. This CE test was conducted by introducing the zero, low, mid, and high-level calibration gases (as defined by EPA Method 25A §7.1.2-5) and the response recorded. The results of the CE test are acceptable if the results for the low and mid-level calibration gasses are within $\pm 5.0\%$ of the predicted responses as defined by the linear curve from the zero and high-level results. The sample system response time was also recorded at this time in accordance with EPA Method 25A §8.5.

Immediately following the completion of each test run, the drift determination was conducted to validate the test data in accordance with EPA Method 25A §8.6.2. The test data is valid if the calculated drift is within $\pm 3.0\%$ of the span value (EPA Method 25A §13.1.2). The THC was measured on a wet basis and was converted to a dry basis using moisture data from the concurrently run Method 5 sampling train.

4.4 Particulate Matter Sampling – EPA Method 5 and 202

EPA Test Method 1 was 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 $120 \pm 14^{\circ}\text{C}$. Upon completion of each test run, the nozzle and probe liner were rinsed and brushed with acetone. The acetone rinse catch was 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 was 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.

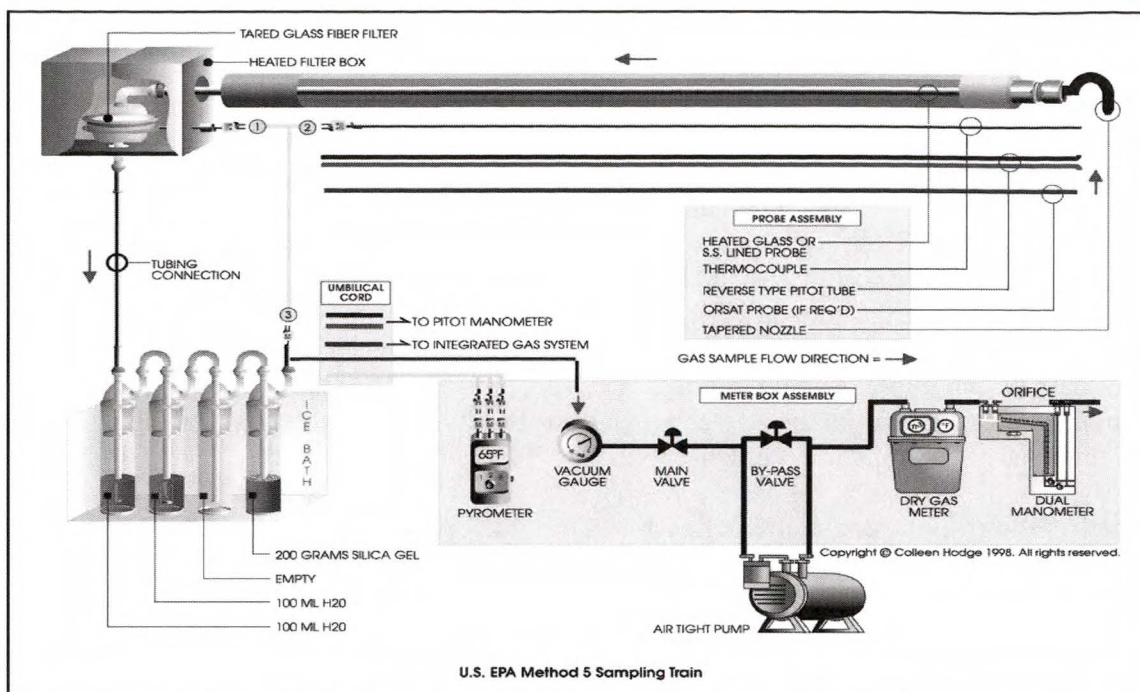


Figure 2: Example PM Sampling System Diagram

For the determination of PM/PM₁₀, the CPM was measured via EPA Method 202. The Method 202 components begin at the back half of the Method 5 filter housing. The filterable particulate matter is removed in these “front half” components. The condensable particulate matter is then collected by drawing the filtered gas through a water jacketed, spiral condenser maintained at 65° – 85° F. The cooled effluent gas is then passed through two empty impingers and finally through a hexane extracted Teflon filter. Upon completion of each test run, the moisture collected in this portion of the sampling train is purged with ultra-high purity (UHP) nitrogen gas for one hour to remove any dissolved sulfur dioxide. The moisture is collected in a container and combined with the deionized water used to rinse all Method 202 sampling glassware two times.

The glassware is next rinsed with hexane and acetone. These rinses are collected and combined in an additional container. The Teflon filter is removed from the filter housing, labeled, and collected. Gravimetric analysis is then conducted on the extracted, evaporated samples for each run.

4.5 Stack Gas Velocity and Moisture Determination

The moisture concentration of the gas sample was determined by the US EPA 40 CFR 60 Appendix A, Method 4. The method was modified by acquiring the Method 4 sample from a slip stream off the heated sampling line at the same sampling point of the Method 25A sampling location. The moisture concentration was determined using equations found in EPA Method 4 §12.1.

At each of the Method 2 exhaust sampling locations, stack gas velocity, and volumetric flow rate was measured in accordance with EPA Method 1 and EPA Method 2.

Each sampling period consisted of conducting a differential pressure and temperature traverse of the stack using an S-type pitot tube for exhaust stacks greater than 12" inside diameter or a standard pitot tube for exhaust stacks less than 12" and K-type thermocouple. Appendix B contains a schematic of the EPA Method 2.

The above data was combined with concurrently collected diluent data (see Appendix A) to calculate the stack gas velocity and volumetric flow rate in units of actual cubic feet per minute (acfm), dry standard (1 atmosphere and 68 degrees Fahrenheit) cubic feet per hour (dscfh), and pounds per hour (lb/hr).

4.6 EPA Method CTM-013 (ALT-133 Analysis) H₂SO₄ Determination

The H₂SO₄ 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 Graham condenser (H₂SO₄ Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing condenser coil. The H₂SO₄ condenser is maintained between 167 to 185 °F. Because SO₂ 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.

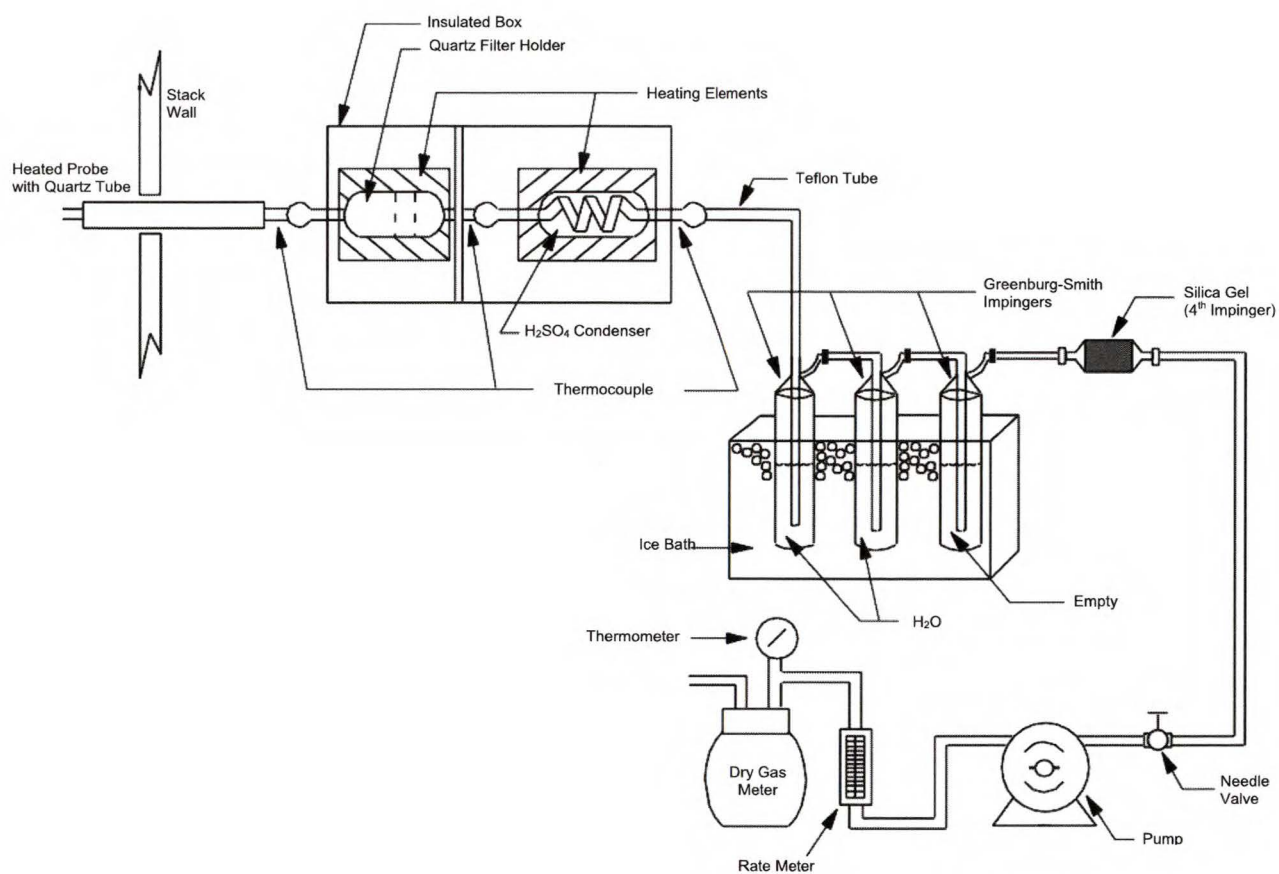


Figure 3: Example Erthwrks CTM-013 Sample System Diagram

4.7 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted the emissions testing with no sampling or procedural variances. The GOHT Heater 2 was tested and operated with no variances.