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AIR EMISSIONS TESTING FOR INDUSTRY

*Emissions Performance Testing*

*for*

**Marathon Petroleum Company LP**

*at the*

**Marathon Detroit Refinery in Detroit, MI**

*on the*

**KHT Charge Heater**

**Unit: EU19-KHTCHARHTR-S1**

**Permit No. MI-ROP-A9831-2012c**

*Prepared for:*



**Marathon  
Petroleum Company LP**

**Test Date: April 27, 2022**

**Erthwrks Project No. 9049.1.B1**

*A9831 test 20220427*



## 1.0 INTRODUCTION

### 1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the KHT Charge Heater in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on April 27, 2022.

### 1.2 Purpose of Testing

This test program was conducted to determine the oxides of nitrogen (NO<sub>x</sub>), carbon monoxide (CO), particulate matter (PM) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) emissions emitted from the NHT Stripper. The testing was conducted in accordance with the requirements in the Marathon Permit No. MI-ROP-A9831-2012c and the Title 40 CFR Part 60, Appendix B.

### 1.3 Description of Source

The KHT Charge Heater (EU19-KHTCHARHTR-S1) is fired by refinery fuel gas. Emissions are vented to the atmosphere via the KHT Charge Heater Stack where testing was performed.

## 1.4 Contact Information

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### **Facility Location:**

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



## 2.0 SUMMARY OF RESULTS

**Table 2.1—Marathon KHT Charge Heater (EU19-KHTCHARHTR-S1) Compliance Results**

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
CO	EPA Method 10	<0.0005 lb/MMBtu	0.02 lb/MMBtu	<i>Pass</i>
NO <sub>x</sub>	EPA Method 7E	0.139 lb/MMBtu	0.20 lb/MMBtu	<i>Pass</i>
H <sub>2</sub> SO <sub>4</sub>	EPA Method CTM-013	0.000345 lb/MMBtu	n/a	<i>n/a</i>
PM	EPA Method 5	0.0002 lb/MMBtu	0.0019 lb/MMBtu	<i>Pass</i>
PM/PM <sub>10</sub>	EPA Method 5/202	0.0048 lb/MMBtu	0.0076 lb/MMBtu	<i>Pass</i>

**NOTE:** Four (4) test runs were conducted for PM/PM<sub>10</sub> because Run 1 was stopped short due to a glass nozzle breaking, and potentially exposed sample to pieces of glass. Runs 2, 3 and 4 were used to apply for compliance.

## 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 Kerosene Hydrotreater unit uses hydrogen to remove sulfur and nitrogen from kerosene (and occasionally Naphtha). This process, known as hydrotreating, uses a catalyst with hydrogen and temperature to promote the desulfurization reaction. The KHT unit consists of process vessels (including exchangers, a reactor, a receiver, separators and a stripper column), a heater, tanks, containers, pumps, compressors, piping, drains and various components (pump and compressors, seals, process valves, pressure relief valves, flanges, connectors, etc.).

The KHT Heater (EU19-KHTCHARHTR-S1) preheats the feed to the reactor. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the KHT Charge Heater Stack (SV19-H2) where testing will be performed.

### 3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the KHT Charge Heater (EU19-KHTCHARHTR-S1) under EGLE Renewable Operating Permit No. MI-ROP-A9831-2012c.

### 3.3 Type and quantity of materials processed during tests

During the emission testing on April 27, 2022, at the Marathon Petroleum Company LP Refinery, the KHT Charge Heater 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 Emissions – NOX, CO, O<sub>2</sub>, and CO<sub>2</sub>

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  $\pm 2.0\%$  of calibration span (or  $\leq 0.5$  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 be repeated with the low-level gas and the response recorded. During this activity, the sample system response time was also recorded. This specification is acceptable if the calculated values of the system calibration error check are within  $\pm 5.0\%$  of the calibration span value (or  $\leq 0.5$  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  $\pm 3.0\%$  of the calibration span value (or  $\leq 0.5$  ppmv).

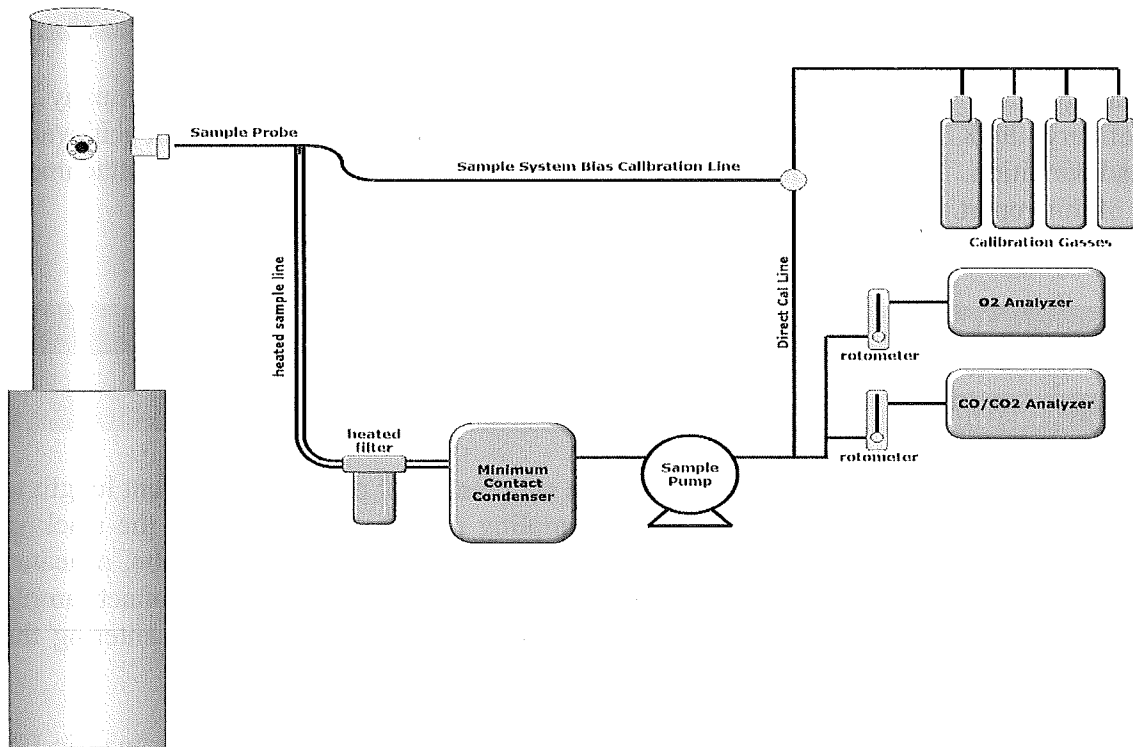
After each test run, the corrected effluent gas concentration was calculated as specified in EPA Method 7E §12.6. The arithmetic average of all valid concentration values are adjusted for bias using equation 7E-5B.

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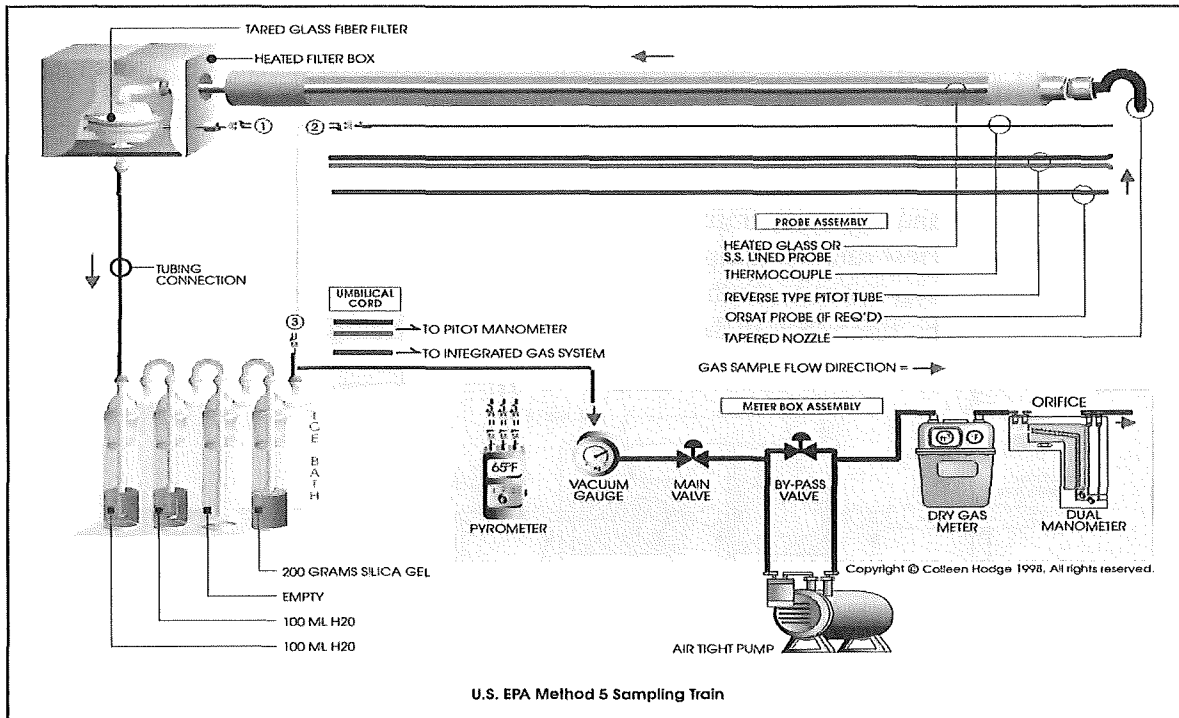


**Figure 1: Example Erthwrks Gaseous Sampling System Diagram**

#### 4.2 Particulate Matter Sampling – EPA Method 5/202

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  $120 \pm 14^{\circ}\text{C}$ . Upon completion of each test run, the nozzle and probe liner were rinsed and brushed with acetone. The acetone rinse catch 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 PM System Diagram**

For the determination of PM/PM<sub>10</sub>, condensable particulate matter (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.

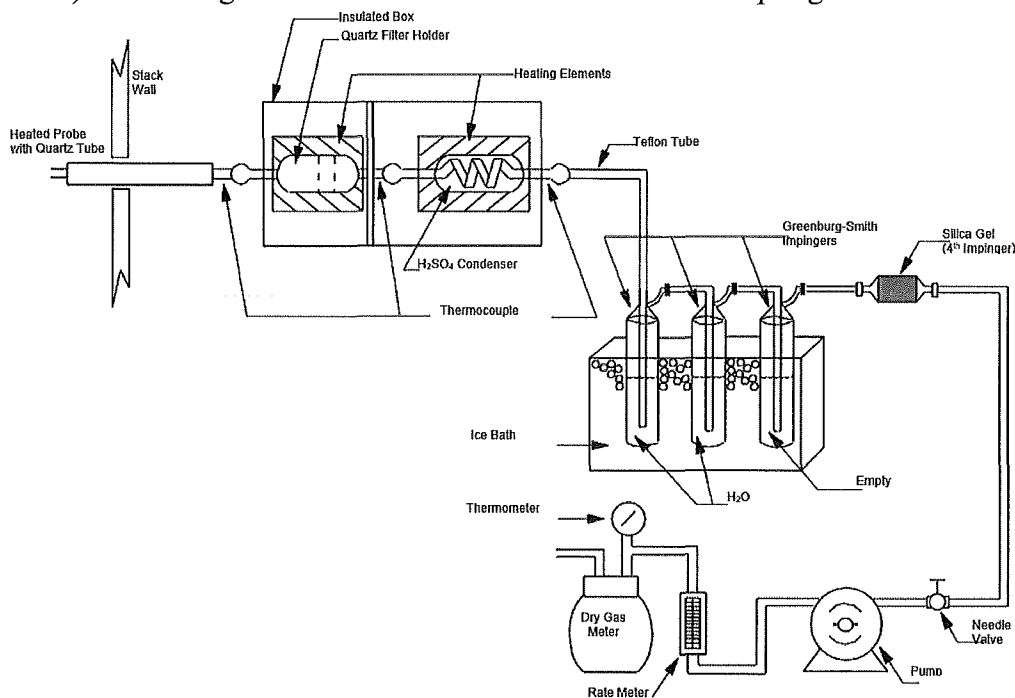
The glassware is next rinsed with hexane and acetone. These rinses are collected and combined in an additional container. The Teflon filter is removed from the filter housing, labeled, and collected. Gravimetric analysis is then conducted on the extracted, evaporated samples for each run.

#### 4.3 EPA Method CTM-013 (ALT-133 Analysis) H<sub>2</sub>SO<sub>4</sub> Determination

The H<sub>2</sub>SO<sub>4</sub> 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 Gramh condenser (H<sub>2</sub>SO<sub>4</sub> Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing

condenser coil. The H<sub>2</sub>SO<sub>4</sub> condenser is maintained between 167 to 185 °F. Because SO<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub> System Diagram**

**4.4 Discussion of sampling procedure or operational variances**

Run 1 for Method 5 PM testing was discarded because the probe’s glass liner broke during the run, causing excess glass to entire the sampling system and collect on the Method 5 filter.