



AIR EMISSIONS TESTING FOR INDUSTRY

*Relative Accuracy Test Audit  
and Emissions Compliance Test*

**Demonstration of Performance  
of the Continuous Emission Monitoring System**

on the

**Crude/Vac Heater Stack  
Unit: SV04-H1-05-H1**

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 25-26, 2023  
Erthwrks Project No. 9284.1.B2**



## 1.0 INTRODUCTION

### 1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct a relative accuracy test audit (RATA) and emissions compliance test on a continuous emissions monitor system (CEMS) installed on the Crude/Vac Heater exhaust in operation at the Marathon Detroit Refinery in Detroit, MI. The RATA and compliance test was conducted on April 25-26, 2023.

### 1.2 Purpose of Testing

This RATA was conducted to demonstrate the accuracy and reliability of the CEMS monitors installed on the Crude/Vac Heater. The purpose of this test program was to evaluate the relative accuracy of the oxides of nitrogen (NO<sub>x</sub>), carbon monoxide (CO), and oxygen (O<sub>2</sub>) CEMS.

In addition, a compliance test was conducted to determine mass emission rates of volatile organic compounds (VOC), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), particulate matter (PM), and condensable PM. VOC was measured and recorded as total hydrocarbons (THC).

### 1.3 Contact Information

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## 2.0 SUMMARY OF RESULTS

**Table 2.1: Crude/Vac Heater CEMS RATA Results**

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO <sub>x</sub> (lb/mmBTU)	Performance Spec. 2	8.93%	<20%	Pass
CO (ppmvd)	Performance Spec. 4A	1.06 ppm	<5 ppm	Pass
O <sub>2</sub> (%vd)	Performance Spec. 3	0.06% <i>RAMD</i>	<1%	Pass

**Table 2.2: Crude/Vac Heater Emissions Compliance Results**

Pollutant Measured	Measured Result	Applicable Limit	Pass/Fail
VOC	0.0009 lb/mmBTU	0.0055 lb/mmBTU	Pass
PM	0.0003 lb/mmBTU	0.0019 lb/mmBTU	Pass
PM/PM <sub>10</sub>	0.0011 lb/mmBTU	0.0076 lb/mmBTU	Pass
H <sub>2</sub> SO <sub>4</sub>	0.0003 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 Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to the other units in the refinery for further processing. The Vacuum Unit (EI04-VACUUM) separates the reduced crude from the Crude Unit through the use of a vacuum column. The reduced crude is separated into light vacuum gas oil, medium vacuum gas oil, heavy vacuum gas oil and a bottoms product called flux. The various fractions are sent to the other units in the refinery for further processing.

The Vacuum Heater (EU04-VACHTR-S1) and the Crude Heater (EU05-CRUDEHTR-S1) is fired by refinery fuel gas and the emissions are vented to the atmosphere via a common stack known as the Crude/Vac Heater Stack (SV04-H1-05-H1), where testing was performed.

Table 3.1 below details the CEMS analyzer information.

**Table 3.1: Crude/Vac Heater CEMS Description**

Pollutant Measured	Analyzer Manufacturer	Analyzer Model	Serial Number
NO <sub>x</sub>	ABB	Limas 11	3.242485.4
CO	ABB	Uras 26	3.242473.4
O <sub>2</sub>	ABB	Magnos 106	3.242483.4

### 3.2 Applicable permit and source designation

During the emission testing on April 25-26, 2023 at the Marathon Petroleum Company LP Refinery, the Crude/Vac Heater was tested while operating at the maximum achievable load condition. NOTE: For this testing program, the average Crude Charge was approximately 149,000 BPD with a Vac Heater firing rate of ~122 mmBTU/hr and a Crude Heater firing rate of ~186 mmBTU/hr. This operational data was provided by MPC and is located in Attachment G of this report.

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

During the emission testing on April 25-26, 2023, at the Marathon Petroleum Company LP refinery, the Crude/Vac 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 Sampling – NO<sub>x</sub>, CO & O<sub>2</sub>, and CO<sub>2</sub>

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

- EPA Method 3A for the determination of O<sub>2</sub> and CO<sub>2</sub> concentration
- EPA Method 7E for the determination of NO<sub>x</sub> 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.

The nitrogen dioxide (NO<sub>2</sub>) to nitric oxide (NO) conversion efficiency test was conducted prior to each field test in accordance with EPA Method 7E §8.2.4.1. This was conducted by introducing the converter efficiency gas (~50 ppm NO<sub>2</sub>) directly to the NO<sub>x</sub> analyzer and recording the NO value. The NO<sub>2</sub>-NO Conversion Efficiency test was within acceptable limits.

All gaseous sampling was done utilizing three appropriate traverse points. The three traverse points were selected to ensure acquisition of a representative sample over the stack cross section as required by 40 CFR Part 60, Appendix B, Performance Specification 2 §8.1.3.2.

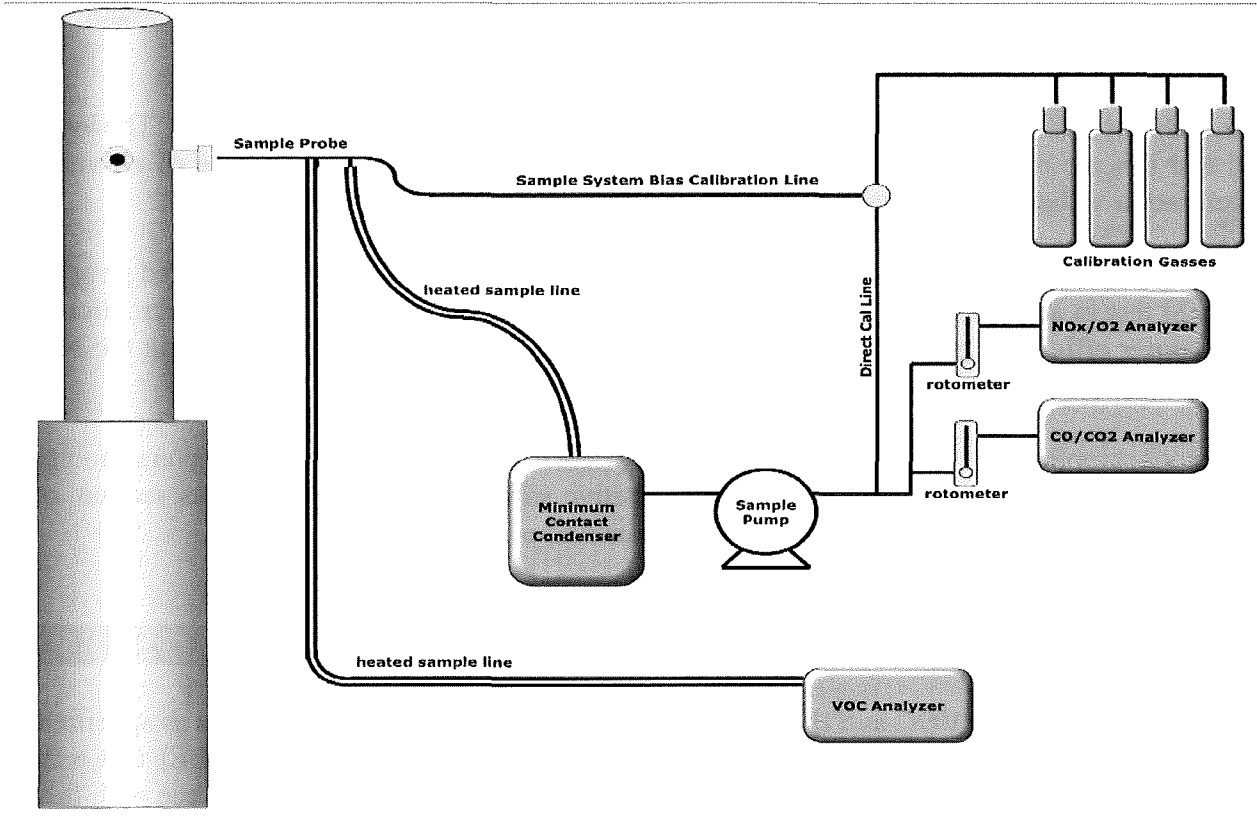
## 4.2 Gaseous Sampling – VOC (measured as THC)

The determination of the VOC as THC concentration followed all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A. 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 was recorded. The results of the CE test are acceptable if the results for the low and mid-level calibration gasses are within ±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 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 ±3.0% of the span value (EPA Method 25A §13.1.2). The THC is measured on a wet basis and will be converted to a dry basis using moisture data from Method 5.

Because the THC concentration was found to be below the permitted limit for VOC, the test results are reported as VOC (as THC) and therefore no Method 18 analysis was required to subtract methane and ethane from the THC results.

See Figure 1 below for a sample system diagram.



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

### 4.3 RATA Procedures

The RATA testing 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 were used during this testing program.

- EPA Performance Specification 2 for NO<sub>x</sub> relative accuracy
- EPA Performance Specification 3 for O<sub>2</sub> relative accuracy
- EPA Performance Specification 4A for CO relative accuracy

As required by these methods, 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 were conducted and up to three test runs may be 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<sub>x</sub>, 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 O<sub>2</sub>, 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.

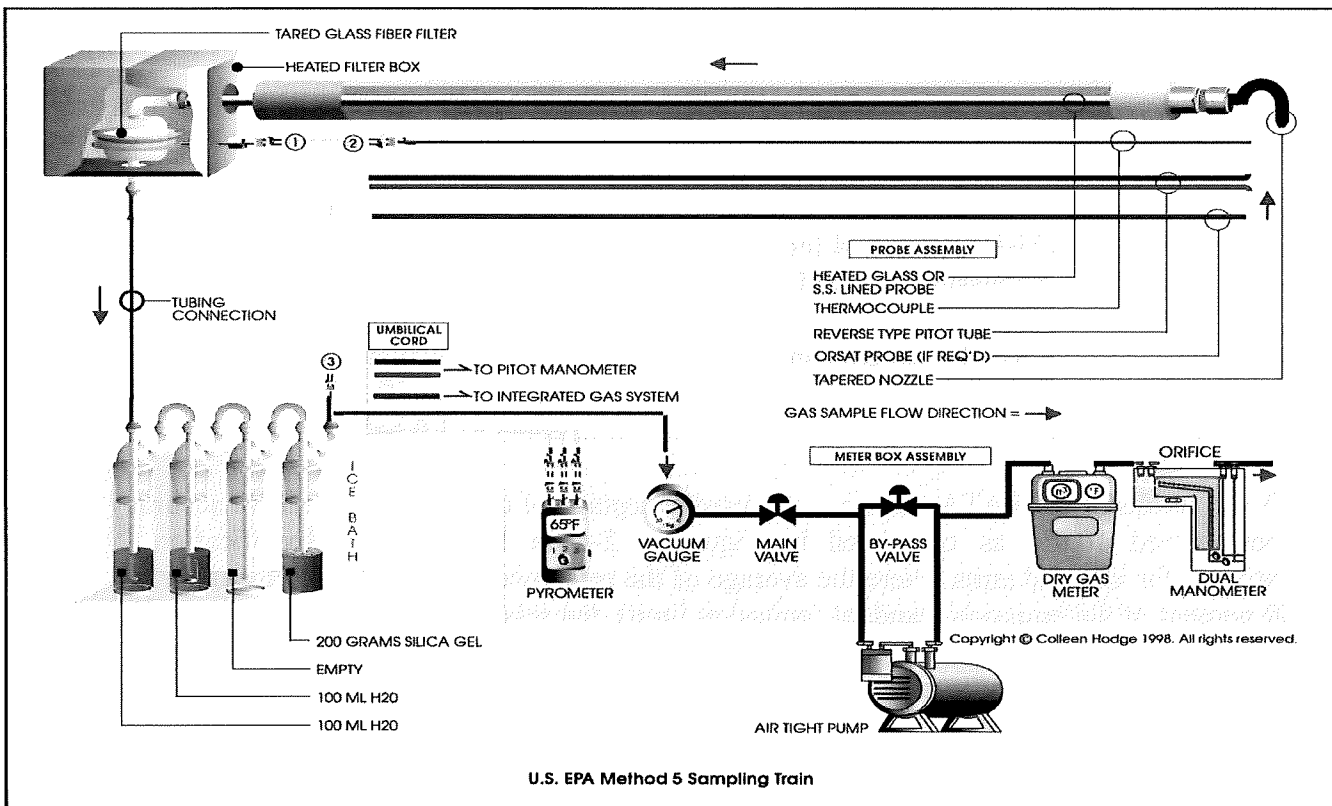
The reference method sampling locations are defined in the Erthwrks QA/QC worksheet located in Attachment B. Three sampling points were used in accordance with the EPA Performance Specification 2, §8.1.3.2, located at 16.7, 50.0 and 83.3 percent of the stack inner diameter from

the port location. Erthwrks sampled at each traverse point individually for 7-minutes per point for each 21-minute test run.

#### 4.4 Filterable Particulate Matter Sampling – EPA Method 5

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.





#### 4.5 EPA Method 202 – Condensable Particulate Matter

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.

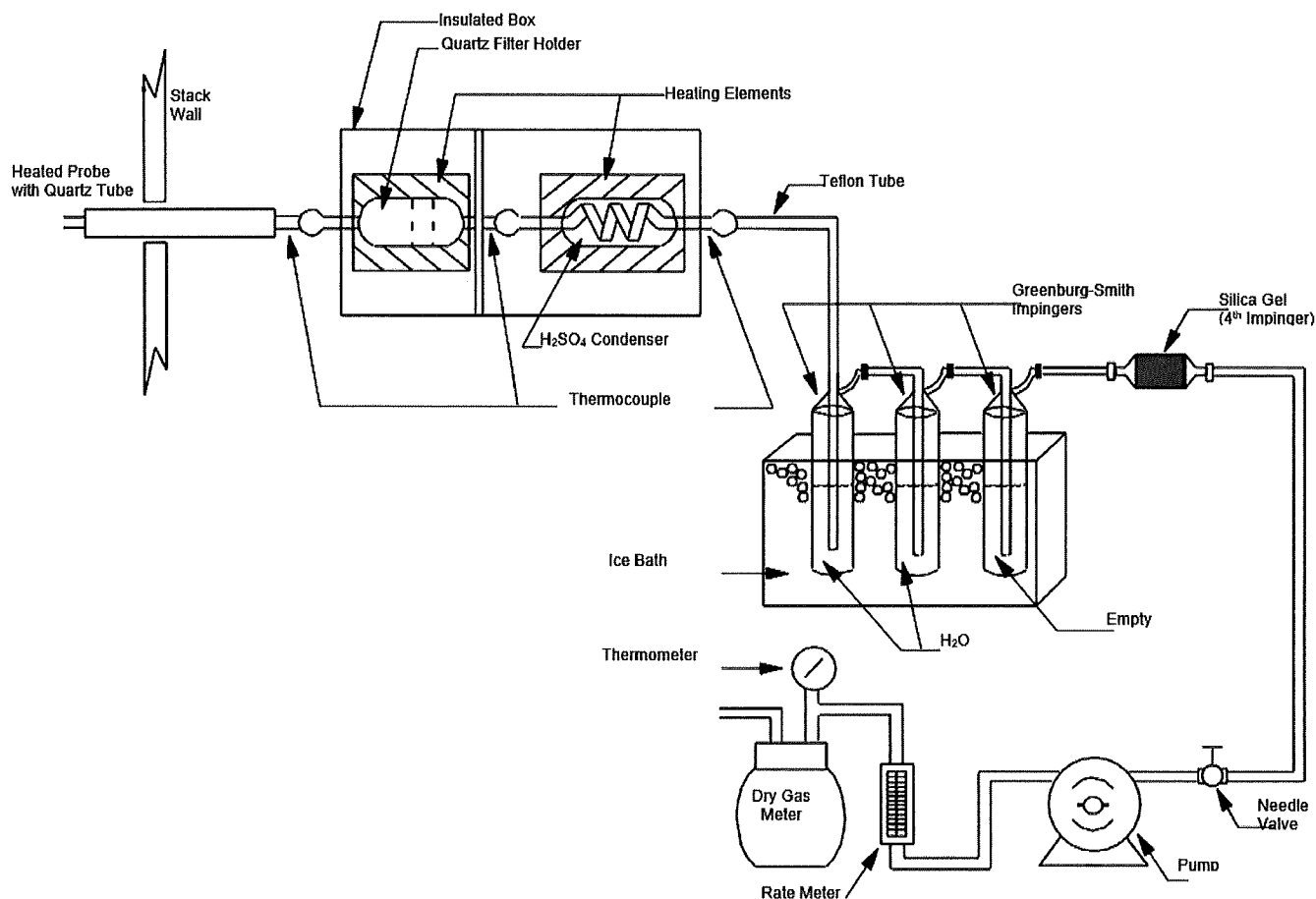
The glassware is next rinsed with Hexane and acetone. These rinses are collected and combined in an additional container. The Teflon filter is removed from the filter housing, labeled, and collected. Gravimetric analysis is then conducted on the extracted, evaporated samples for each run.

#### 4.6 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 EPA 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 (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**

#### 4.7 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted the emission testing with no sampling or procedural variances. The process unit tested and operated with no operational variances.