

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the Coker Heater in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on July 21, 2021.

1.2 Purpose of Testing

A relative accuracy test audit (RATA) was performed on the Coker Heater stack to determine the relative accuracy of the nitrogen oxides (NO_x) and oxygen (O₂) continuous emissions monitoring system (CEMS). 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 F.

In addition, compliance testing was conducted to determine the compliance status of the units' emission for particulate matter (PM) and volatile organic compounds (VOC).

1.3 Description of Source

Marathon Petroleum Company LP operates the Coker Heater designated as EU70-COKERHTR-S1 in the refinery. This report addresses the RATA for the CEMS associated with the unit as well as the required compliance test for VOC. Table 1.1 below details the CEMS analyzer information.

Table 1.1—Marathon Coker Heater CEMS Details

Parameter	Manufacturer	Model No.	S/N	Install Date
NO _x	ABB	Limas 11	3.342678.1	2012
O ₂	ABB	Magnos 206	3.342697.1	2012

1.4 Contact Information

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2.0 SUMMARY OF RESULTS

Table 2.1—Marathon Coker Heater (EU70-COKERHTR-S1) CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO _x (0%O ₂)	Performance Spec. 2	16.1% <i>RA_{RM}</i>	<20%	Pass
NO _x (lb/MMBtu)	Performance Spec. 2	13.9% <i>RA_{RM}</i>	<20%	Pass
O ₂ (%)	Performance Spec. 3	0.52% <i>RA</i>	<1%	Pass

Table 2.2—Marathon Coker Heater (EU70-COKERHTR-S1) Compliance Results

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
VOC	EPA Method 25A	<0.0015 lb/MMBtu	0.0055 lb/MMBtu	Pass
PM	EPA Method 5	0.0013 lb/MMBtu	0.0019 lb/MMBtu	Pass
PM/PM ₁₀	EPA Method 5/202	0.0046 lb/MMBtu	0.0076 lb/MMBtu	Pass

* VOC reported as below limit of detection based on 1% of analyzer span

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 Coker unit (EU70-COKER) converts Vacuum Resid (Crude Vacuum Tower Bottoms), a product normally sold as asphalt or blended into residual fuel oil, into lighter, more valuable products. The Vacuum Resid feedstock is heated before it enters the main fractionator, where lighter material vaporizes. The fractionator bottoms are routed through a fired heater and then into a coke drum. This emission unit consists of process vessels (fractionators), coke drums, heater (EU70-COKERHTR-S1), cooling tower, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.). This emission group includes the Coke Handling System, which will collect, size, and transport the petroleum coke created during the coking process. The system consists of a coke pit, storage pad, enclosed crusher, enclosed conveyors, and surge bins. The Coker Heater is fired by refinery fuel gas. Emissions are vented to the atmosphere via the Coker Heater Stack (SV70-H1), where testing will be performed.

3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the Coker Heater (EU70-COKERHTR-S1) under EGLE Renewable Operating Permit No. MI-ROP-A9831-2012c and is required to conduct an annual RATA to demonstrate the relative accuracy of the CEMS associated with this unit and to determine the VOC and PM/PM₁₀ exhaust emissions.

3.3 Type and quantity of materials processed during tests

During the emission testing on July 21, 2021, at the Marathon Petroleum Company LP Refinery, the Coker Heater was tested while operating at the maximum achievable load condition. **NOTE:** For this testing program, the total charge was 41,500 BPD, the fuel gas flow was approximately 4,730 MSCFD, and the heater duty was 236 MMBtu/hr. 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 & O₂

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 ≤ 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 will also be 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 ≤ 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 ≤ 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.

4.2 Gaseous Emissions – VOC as THC (Method 25A)

Each VOC compliance test run was conducted during the RATA testing. The determination of the volatile organic compounds (VOC) as total hydrocarbon compounds (THC) concentration follows 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 responses 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. During this activity, the sample system response time was also recorded 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**). In addition, at the request from EGLE, the THC raw data is corrected for analyzer drift using EPA Method 7E Equation 7E-B5. The THC is measured on a wet basis and is converted to a dry basis using moisture data from a Method 4 sampling train.

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.

The figure below details the Erthwrks Gaseous Sampling System.

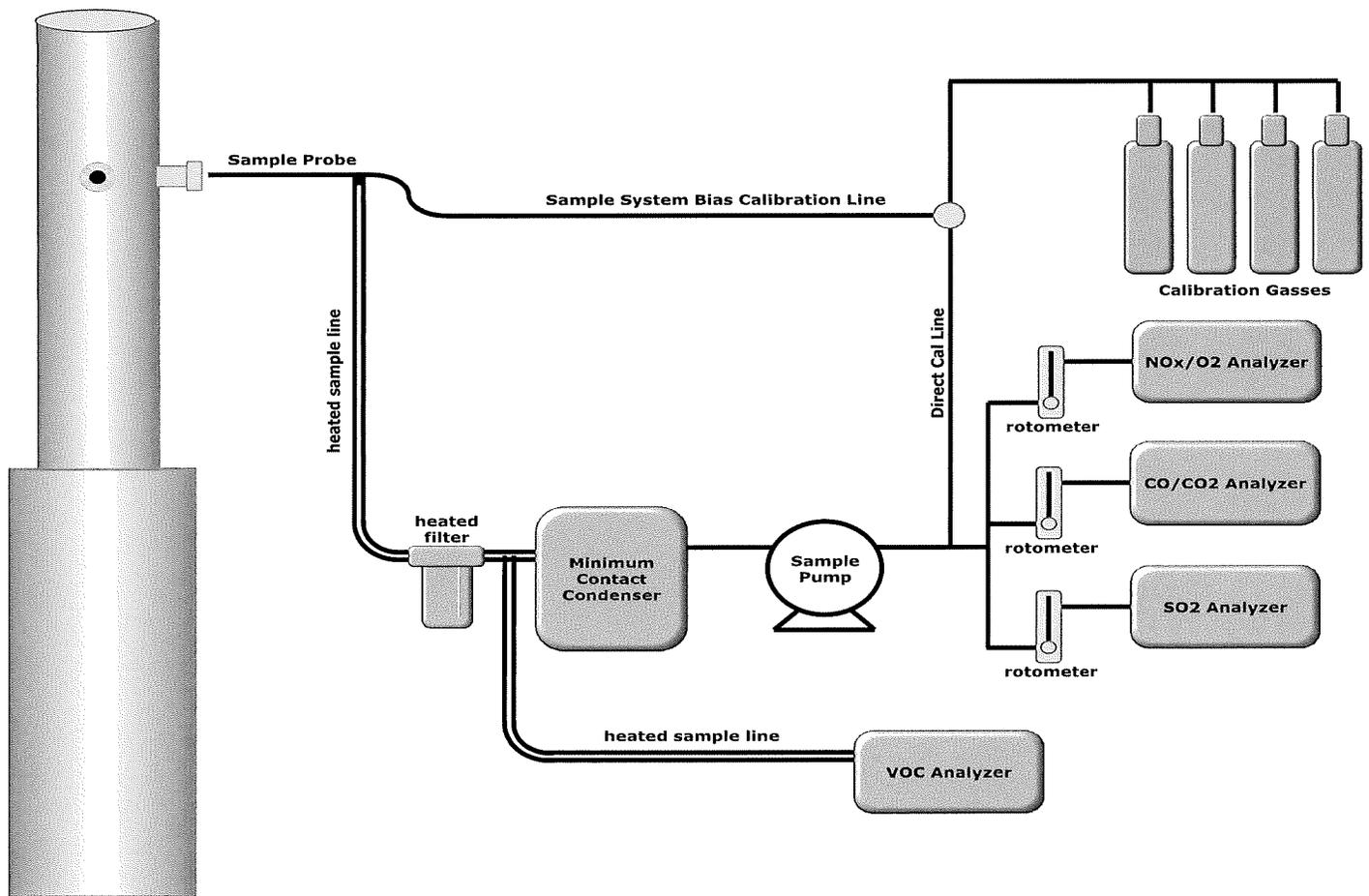
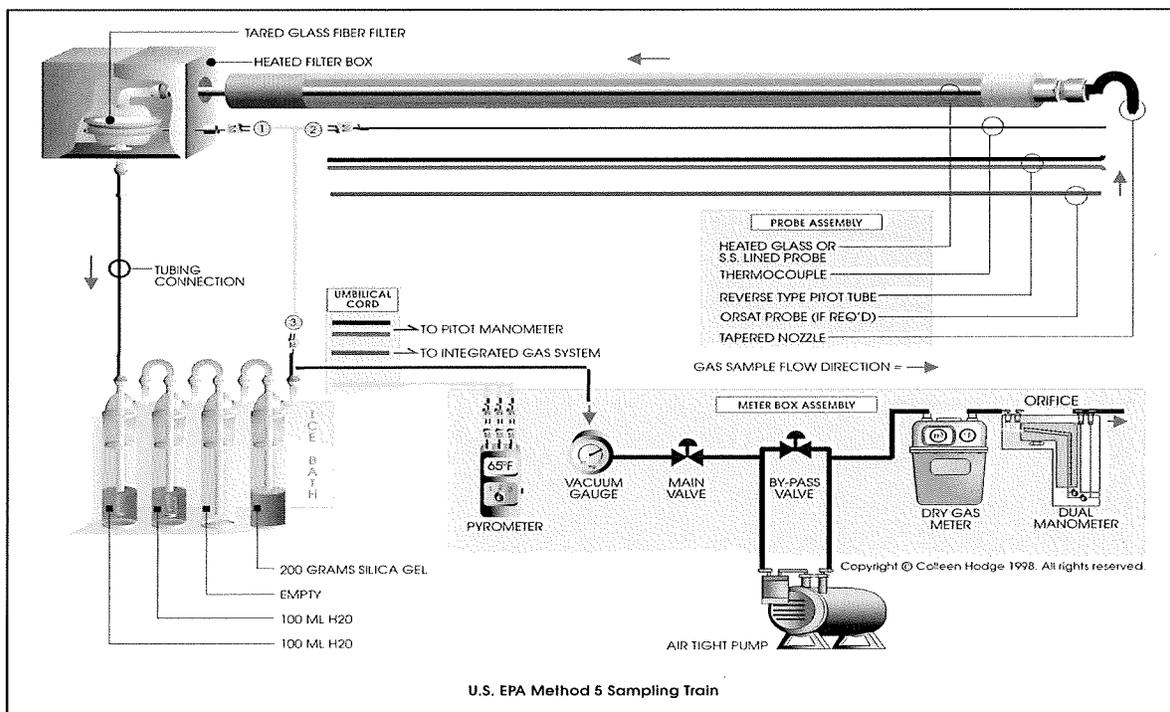


Figure 1: Example Erthwrks Gaseous Sampling System Diagram

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.



For the determination of PM/PM₁₀, 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 $65^\circ - 85^\circ\text{F}$. 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 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 will be used during this testing program.

- EPA Performance Specification 2 for NO_x relative accuracy
- EPA Performance Specification 3 for O₂ relative accuracy

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

The RATA test is a direct comparison of the CEMS monitoring data with that data collected from an independently operated EPA Reference Method tests for each pollutant, following all the quality assurance and quality control procedures as required in the reference method. The following EPA reference methods were utilized to complete this testing program:

- EPA Method 3A for the determination of O₂ concentration
- EPA Method 7E for the determination of NO_x concentration

For this testing program, Erthwrks utilized a calibration gas dilution system, operated in accordance with EPA Method 205, for the generation of the calibration gases used to calibrate the reference method analyzers. This gas dilution system is calibration annual in accordance with section 2.1.1 of this method. This documentation is located in Attachment F. In addition, the gas diluter accuracy was verified on the day of the test in accordance with the Field Evaluation procedure defined in Section 3.2 of the method. This activity is documented in Attachment B and the raw data logs are located in Attachment E.

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 will be 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

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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.

4.4 Discussion of sampling procedure or operational variances

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

During the particulate matter sample recovery, it was noticed that filter material was separating from the filter and adhering to the filter housing and filter holder gasket. The decision was made to wash this filter material into the front half rinse container in order to include this weight into the front half PM analysis. Erthwrks believes this action could bias the front half PM result high due to the fact that much of the filter holder gasket lies behind the filter and would be considered part of the “back half.” The sum of the front half rinse and filter weight gain constitutes the filterable PM analysis. Because filter material was washed into the acetone wash, two of the filters lost weight. The laboratory report provided did not sum the filter weight with the acetone wash due to the negative weight gain on two of the filters. Because of the recovery procedures conducted in the field, Erthwrks summed the filter and acetone wash, as appropriate and consistent with the test method, to calculate the filter particulate matter emissions.

The average results of the three test runs show the unit was operating under the permitted limit, but the results are inconsistent. Run 1 resulted in a negative weight gain, while Run 3 resulted in unusually high weight gain. After further discussion with the field-testing team, and with Erthwrks quality assurance manager, Erthwrks believes other variables may have affected the results. These may include inconsistent analytical sample recovery procedures and the fact that longer test run times will yield more consistent results from low emitting sources.

