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AIR EMISSIONS TESTING FOR INDUSTRY

Relative Accuracy Test Audit (RATA) and Performance Testing

for
Marathon Petroleum Company LP

at the
Marathon Detroit Refinery in Detroit, MI

on the
FCCU Charge Heater
Unit: EU11-FCCUCHARHTR-S1
Permit No. MI-ROP-A9831-2012c

Prepared for:

MARATHON
Marathon
Petroleum Company LP

Test Date: July 20-21, 2022
Erthwrks Project No. 9049.1.C1

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1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the FCCU Charge Heater in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on July 20-21, 2022.

1.2 Purpose of Testing

The exhaust from FCCU Charger Heater Stack was sampled and analyzed to determine the compliance status of the units' emission for Particulate Matter (PM), Volatile Organic Compounds (VOC), and Sulfur Dioxides (SO_2)

1.3 Description of Source

Marathon Petroleum Company LP operates the FCCU Charge Heater designated as EU11-FCCUCHARHTR-S1 in the refinery. This report addresses the compliance test for PM, SO_2 and VOC.

1.4 Contact Information

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2.0 SUMMARY OF RESULTS

Table 2.1—Marathon FCCU Chg Htr (EU11-FCCUCHARHTR-S1) Compliance Test Results Fuel Gas + Disulfide Off Gas

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
PM	EPA Method 5	0.0016 lb/MMBtu	N/A	N/A
PM/PM_{10}	EPA Method 202	0.0053 lb/MMBtu	N/A	N/A
H2SO4	EPA Method CTM-013	0.44 ppm	N/A	N/A

Table 2.2—Marathon FCCU Chg Htr (EU11-FCCUCHARHTR-S1) Compliance Test Results Fuel Gas Only

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
PM	EPA Method 5	0.0015 lb/MMBtu	0.0019 lb/MMBtu	Pass
PM/PM_{10}	EPA Method 202	0.0053 lb/MMBtu	0.0076 lb/MMBtu	Pass

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 FCCU Charge Heater preheats the feed to the FCCU. The unit can be fired by a combination of refinery fuel gas, disulfide off-gas and natural gas. Emission are vented to the atmosphere at the FCCU Charge Heater Stack (SV11-H1).

3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the FCCU Charger Heater (EU11-FCCUCHARHTR-S1) under EGLE Renewable Operating Permit No. MI-ROP-A9831-2012c and is required to periodically determine the PM exhaust emissions.

3.3 Type and quantity of materials processed during tests

During the emission testing on July 20-21, 2022, at the Marathon Petroleum Company LP Refinery, the FCC Charge Heater was tested while operating at the maximum achievable load condition. **NOTE:** For this testing program, the average Crude Charge was approximately 40,800 BPD. 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 – 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 $\leq$ 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 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 $\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 ±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.

The figure below details the Erthwrks Gaseous Sampling System.

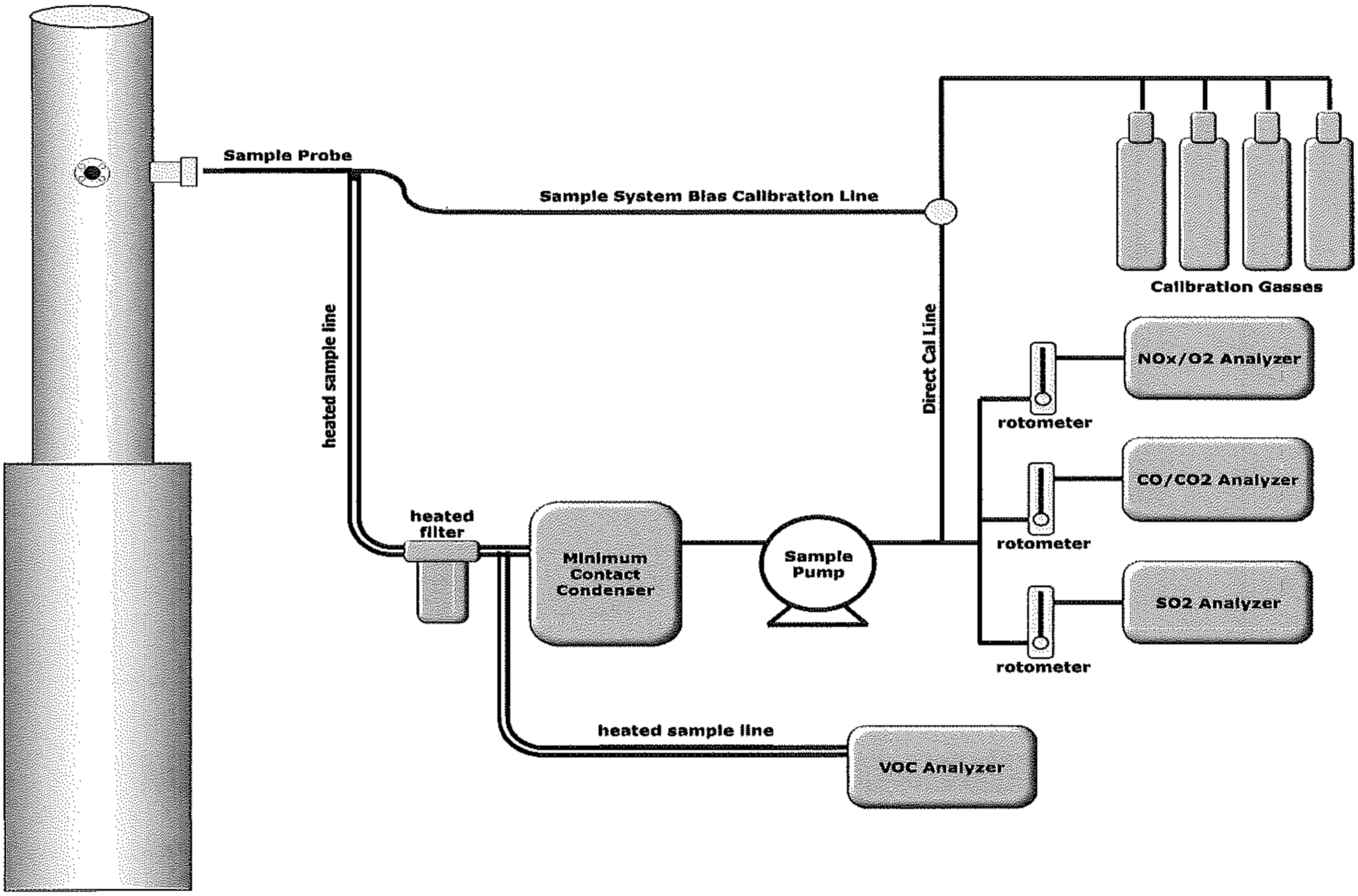
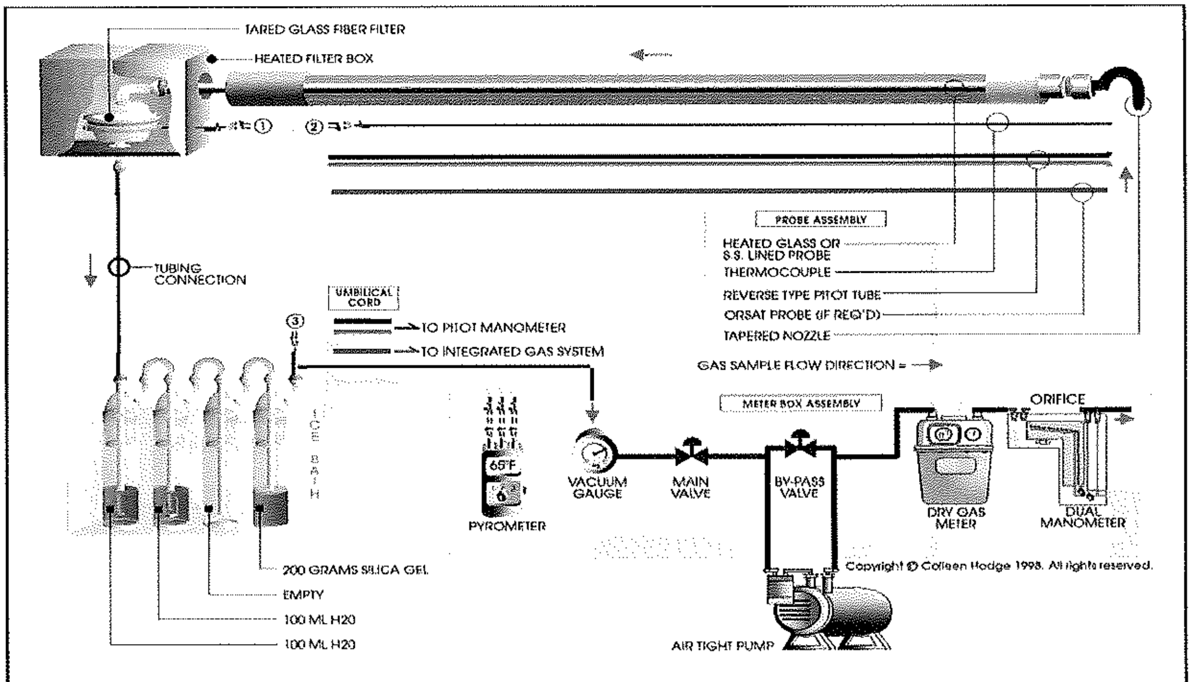


Figure 1: Example Erthwrks Gaseous Sampling System Diagram

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.



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U.S. EPA Method 5 Sampling Train

4.3 EPA Method 202 – Condensable Particulate Matter

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° – 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.

4.4 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.

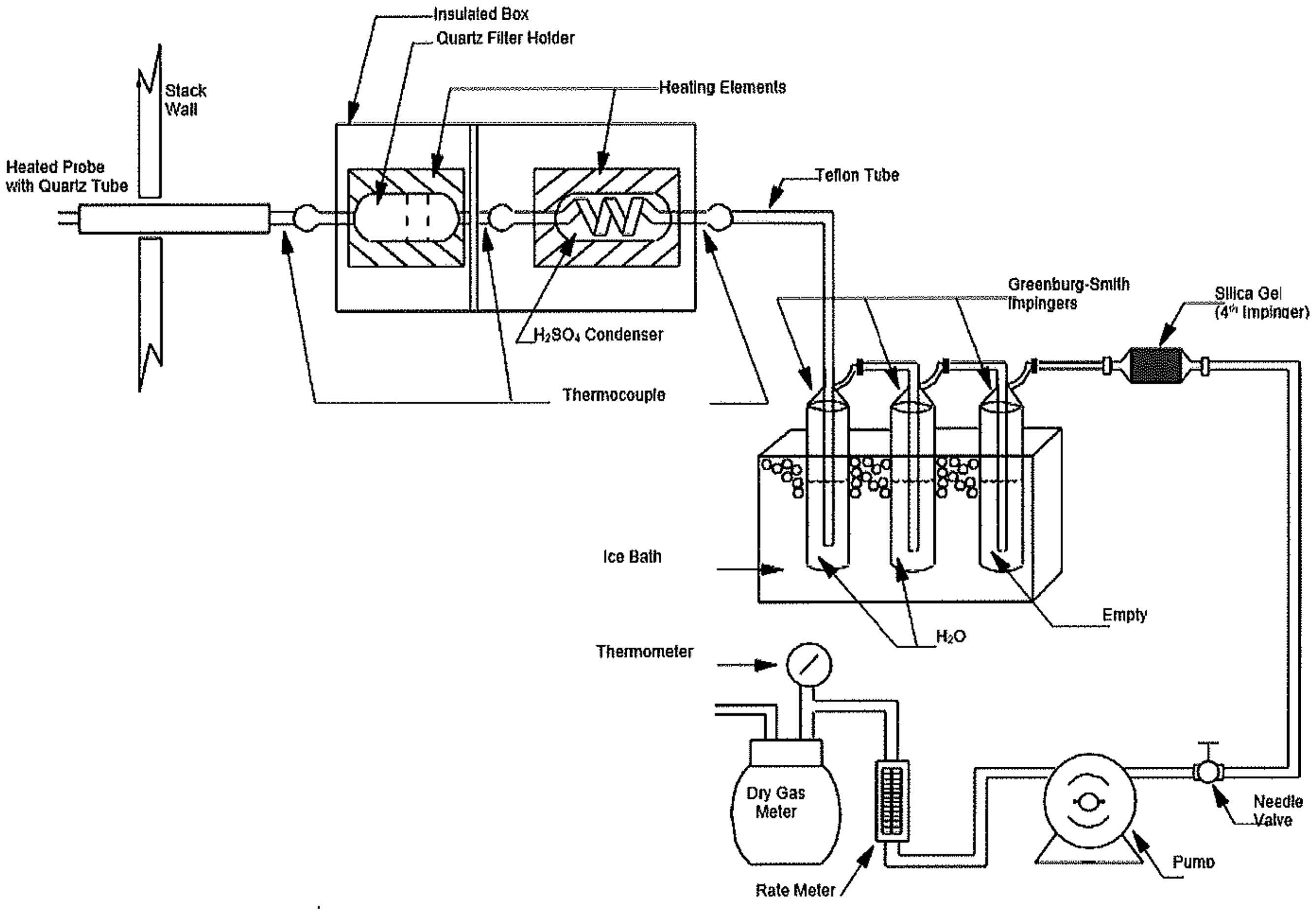

Figure 3: Example Erthwrks H_2SO_4 System Diagram

4.5 Discussion of sampling procedure or operational variances

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

During the PM testing on July 21, 2022, the Run 1 filter temperature exceeded the required temperature range required by the method. This run was discarded and not recovered. The Run 2 filter appeared to be unusually discolored compared to that of the visual appearance of Runs 3 and 4. Therefore, MPC requested that a 5th run be conducted in case the results of Run 2 are in question. Upon receipt of the laboratory results, Run 2 did not appear to be an outlier and all four test runs were averaged for the determination of PM compliance.