erthwrks

AIR EMISSIONS TESTING FOR INDUSTRY

Relative Accuracy Test Audit (RATA)

for

Marathon Petroleum Company LP

at the

Marathon Detroit Refinery in Detroit, MI

on the

Fluid Catalytic Cracking Unit (FCCU)
Regenerator Stack
Unit: EU-11-FCCU-S1/SVFCCU
Permit No. MI-ROP-A9831-2012c

Prepared for:

MARATHON Marathon Petroleum Company LP

Test Date: March 1, 2023
Erthwrks Project No. 9284.1.A2

STAC STACK TESTING ACCREDITATION COUNCIL

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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 Fluid Catalytic Cracking Unit (FCCU) in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on March 1, 2023.

1.2 Purpose of Testing

The exhaust from FCCU Stack, also known as the FCC Regen Unit, was sampled and analyzed to determine the relative accuracy of the associated CEMS 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, testing was conducted to determine the emissions of Sulfuric Acid (H_2SO_4) from the exhaust stack.

1.3 Description of Source

Marathon Petroleum Company LP operates the Fluid Catalytic Cracking Unit (FCCU) designated as EU-11-FCCU-S1/SVFCCU in the refinery. This report addresses the RATA for the CEMS associated with the unit as well as the required test for H_2SO_4. Table 1.1 below details the CEMS analyzer information.

Table 1.1—Marathon FCC Regen CEMS Details

FCCU CEMS	Tag No.	Manufacturer	Model No.	S/N
NO_X	11AT0813	ABB	Uras 26	3.417667.1
O_2	11AT0816	ABB	Magnos 28	3.417670.1
CO	11AT0814	ABB	Uras 26	3.417669.1
SO_2	11AT0812			
CO_2	11AT0815			

1.4 Contact Information

Marathon Petroleum Company LP
Emily Mattson
Environmental Professional
Michigan Refining Division
O: (313)236-1501
EGMattson@marathonpetroleum.com

Erthwrks, Inc.
John Wood
Technical Director
P.O. Box 150549
Austin, TX 78745
512-585-1685 office
888-573-9994 fax
jwood@erthwrks.com

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

2.0 SUMMARY OF RESULTS

Table 2.1—Marathon FCC Regen (EU-11-FCCU-S1/SVFCCU) CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO_X	Performance Spec. 2	7.6% RA_{RM}	<20%	Pass
SO_2	Performance Spec. 2	3.8% RA_{AS}	<10%	Pass
O_2	Performance Spec. 3	0.1% *RA*	<1%	Pass
CO_2	Performance Spec. 3	0.02% *RA*	<1%	Pass
CO	Performance Spec. 4	2.1% RA_{AS}	<5%	Pass

Table 2.2—Marathon FCC Regen (EU-11-FCCU-S1/SVFCCU) Compliance Test Results

Pollutant Measured	Methodology	Measured Results	Applicable Limit
H_2SO_4	EPA Method CTM-013	1.33E-03 lb/MMBtu	Not Applicable

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.

Marathon Petroleum Company LP operates the Fluid Catalytic Cracking Unit which uses a catalyst in a process that converts heavier hydrocarbons into lighter products. In the process coke is deposited onto the catalyst. The spent catalyst is then moved to a regenerator where the coke is burned off using air. The hot flue gas from the regenerator is directed to a cooler where the heat is recovered as steam. Before existing the stack, the gas passes through electrostatic precipitators to reduce particulate matter.

3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the FCC Regen (EU-11-FCCU-S1/SVFCCU) 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 H_2SO_4 exhaust emissions.

3.3 Type and quantity of materials processed during tests

During the emission testing on March 1, 2023, at the Marathon Petroleum Company LP Refinery, the FCC Regen was tested while operating at greater than 50% of load condition. **NOTE:** For this testing program, the average FCCU Charge Rate was 42,476 BPD, the average Coke Burn was 21,283 lb/hr, and the NH_3 Injection Rate was 49.3 lb/hr. 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 – NOx, CO, SO, 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 ≤ 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 ≤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 ≤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.

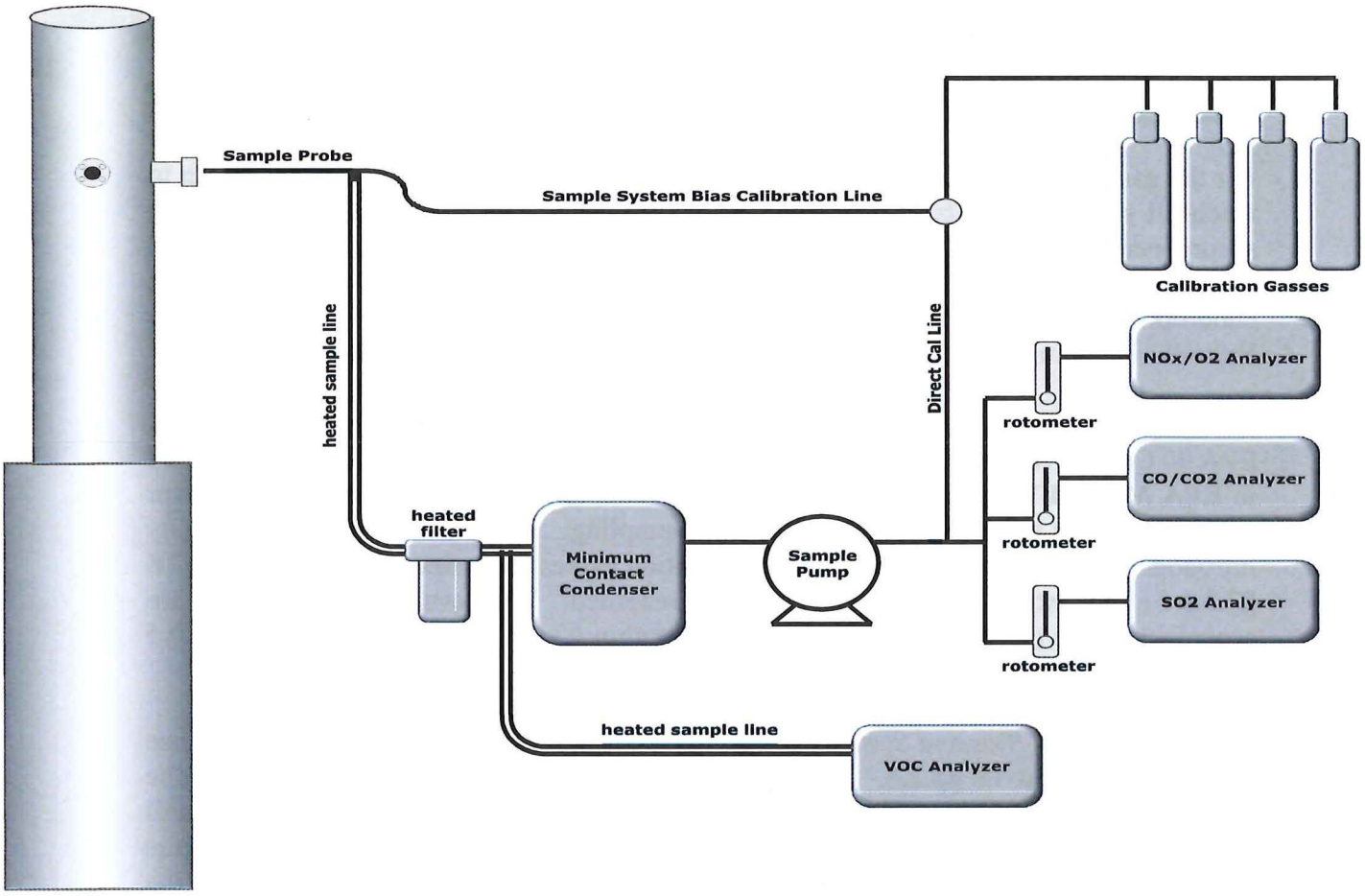

Figure 1: Example Erthwrks Gaseous Sampling System Diagram

4.2 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.

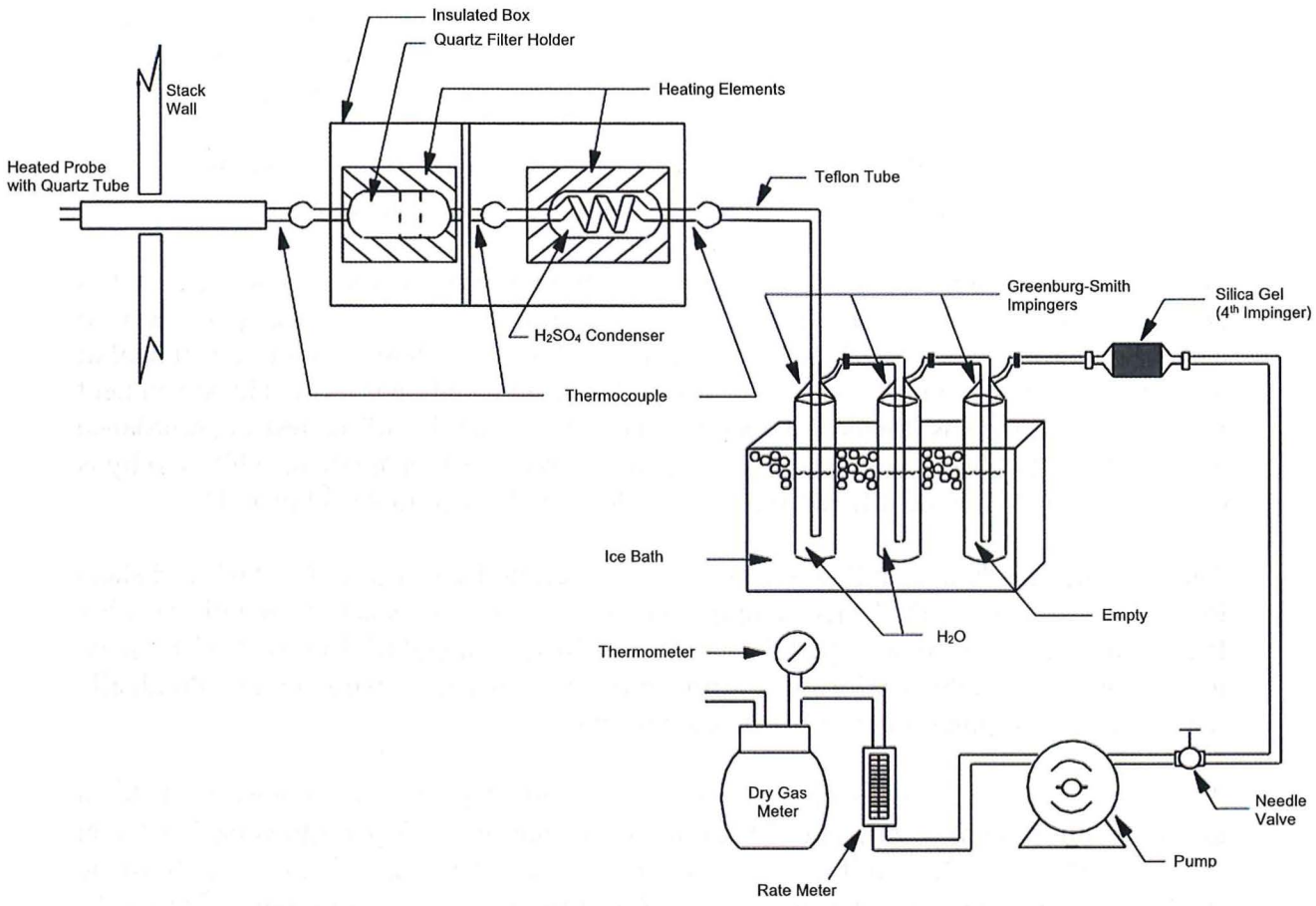

Figure 2: Example Erthwrks CTM-013 Sample System Diagram

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 will be used during this testing program.

- EPA Performance Specification 2 for NOx and SO_2 relative accuracy
- EPA Performance Specification 3 for O_2 and CO_2 relative accuracy
- EPA Performance Specification 4/4A 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.

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 O_2 and CO_2 concentration
- EPA Method 6C for the determination of SO_2 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 E. 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 D.

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.

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). 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 and SO_2, 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 CO, the results of the RATA test is 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 can also be considered acceptable if the absolute average difference between the RM and CEMS is within ±5 ppmv.

For O_2 and CO_2, 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.

4.2 Discussion of sampling procedure or operational variances

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

Attachment A
Detailed Results of Emission Test