



AIR EMISSIONS TESTING FOR INDUSTRY

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Emissions Compliance Test Report

for the
**Fluid Catalytic Cracking Unit (FCCU)
Regenerator Stack
EU-11-FCCU-S1/SVFCCU**

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 18, 2023
Erthwrks Project No. 9284.1.B1**



A9831-TEST-20230418

Endorsement Page

This report was developed in accordance with the requirements designated in the applicable regulatory permit(s) and or regulatory rules. To the best of my knowledge the techniques, instrumentation, and calculations presented in this report will serve to accurately and efficiently detail the results of the test campaign requirements.

Erthwrks, Inc.

Name: Jason Dunn

Title: QAQC Manager

Signature: 

This report has been reviewed for accuracy and completeness. The actions presented in this report are, to the best of my knowledge, an accurate representation of the results and findings of the test campaign. Erthwrks, Inc. operates in conformance with the requirements on ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies and is accredited as such by the Stack Testing Accreditation Council (STAC) and the American Association for Laboratory Accreditation (A2LA).

Erthwrks, Inc.

Name: John Wood

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Signature: 

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- A. Detailed Results of Emissions Test
- B. Quality Control Documentation
- C. Example Calculations
- D. Field Sampling Worksheets
- E. Raw Datalog Records
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- H. Laboratory Analysis Report

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) Regenerator Stack in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on April 18, 2023.

1.2 Purpose of Testing

This test was conducted to determine the FCCU Regenerator Stack mass emission rates of volatile organic compounds (VOCs), ammonia (NH₃), particulate matter (PM), and non-sulfate particulate matter.

Oxygen (O₂), carbon dioxide (CO₂), moisture content, and stack flow rate were also measured to calculate mass emission rates in pounds per hour (lb/hr) and tons per year (tpy).

1.3 Contact Information

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2.0 SUMMARY OF RESULTS

Table 2.1: FCCU Regenerator Stack Compliance Test Results

Pollutant Measured	EPA Methodology	Measured Result	Applicable Limit	Pass/Fail
VOC	Method 25A	5.87 tpy	21 tpy	Pass
NH ₃	CTM-027	4.27 lb/hr	n/a	n/a
Non-Sulfate PM/PM ₁₀	Method 5F/202	0.83 lb/1000 lb of coke burn	1.1 lb/1000 lb of coke burn	Pass
Non-Sulfate Filterable PM	Method 5F	0.46 lb/1000 lb of coke burn	0.8 lb/1000 lb of coke burn	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.

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

The FCCU Regenerator Stack is identified as EU-11-FCCU-S1/SVFCCU and is operated under Permit No. MI-ROP-A9831-2012c.

3.3 Type and quantity of materials processed during tests

During the emission testing on April 18, 2023, at the Marathon Petroleum Company LP refinery, the FCCU Regenerator Stack 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 – O₂ and CO₂

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

- EPA Method 3A for the determination of O₂ and CO₂ 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.

A stratification test was conducted in accordance with EPA Method 7E §8.1.2 at the beginning of Run 1. The results were determined to be unstratified and single-point sampling was utilized throughout the remainder of the test. The results of the stratification test is included in Attachment B of this report.

See Figure 1 below for a sample system diagram.

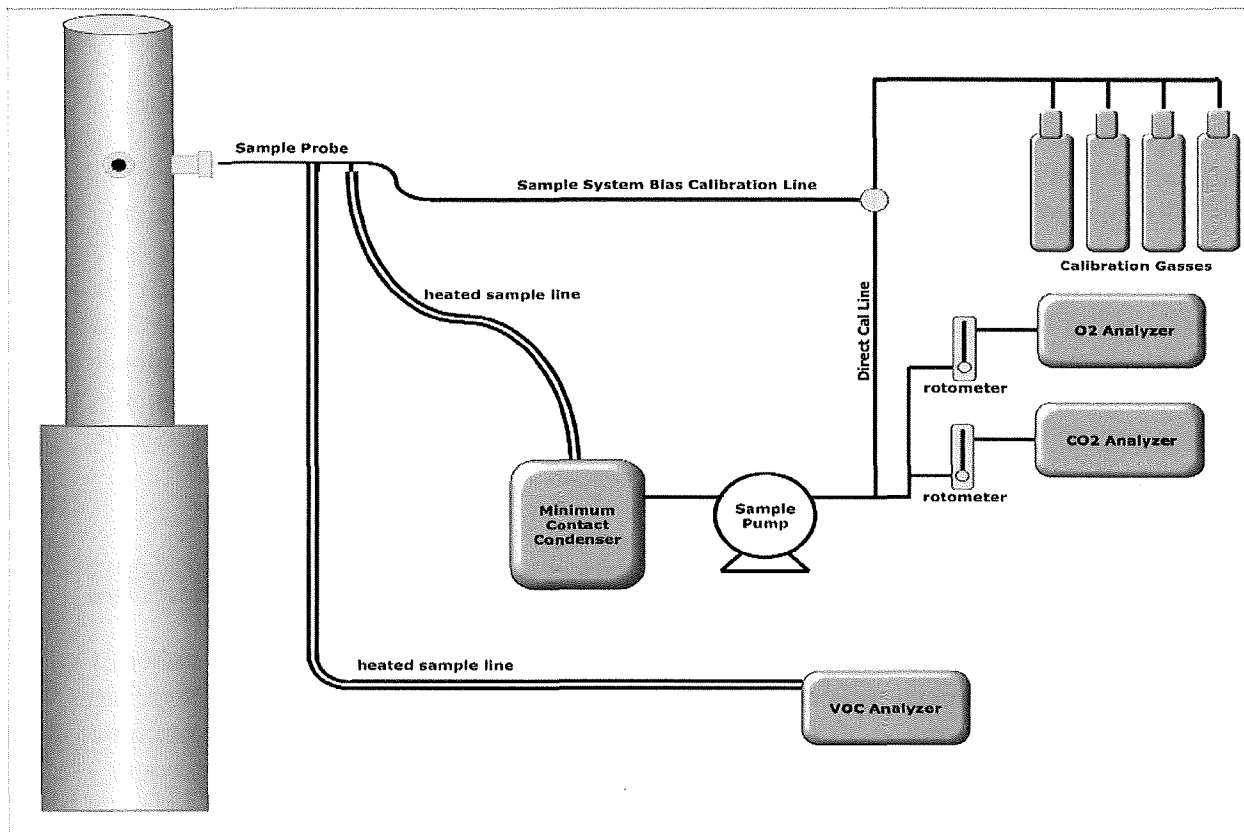


Figure 1: Example Erthwrks Gaseous Sampling System Diagram

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

The determination of the VOC concentration was determined by measuring total hydrocarbon compound (THC) and followed all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A with the exception of the EGLE requirement to adjust the final results for drift using Equation 7E-5B. 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 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. The sample system response time was also 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 $\pm 3.0\%$ of the span value (EPA Method 25A §13.1.2). The THC was measured on a wet basis and was converted to a dry basis using moisture data from the concurrently run Method 5 sampling train.

4.3 EPA Methods CTM-027 – NH₃ Concentration Determination

During the particulate matter sampling, Erthwrks utilized EPA CTM-027 for the determination of Ammonia Slip. A quartz nozzle and in-stack filter, charged with a glass fiber thimble filter, was used to extract the flue gas sample into the CTM-027 collection system. This system is a series of impingers wherein the first two are charged with 0.1 N sulfuric acid, the third being empty and the fourth containing a known amount of silica gel. Three 60-minute, isokinetic sampling runs were conducted concurrently during the particulate matter sampling. Upon the completion of each test run, the nozzle, filter housing and probe were rinsed with DI H₂O and combined with the first impinger contents into a 250 ml high density polyethylene (HDPE) bottle. The second impinger was rinsed into a second HDPE bottle and both were analyzed for NH₃ content, as ammonium ion, by Ion Chromatography. The samples were kept cold until analysis within 2 weeks of sample collection.

4.4 Filterable Particulate Matter Sampling – EPA Method 5/5F

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. All pre-test measurements and calculations to determine sample traverse points in accordance with EPA Method 1 are included with this final test report.

EPA Test Methods 2, 3A, and 4 were used to determine the flow rate, gas composition, and moisture content of the gas stream.

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 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, was 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.

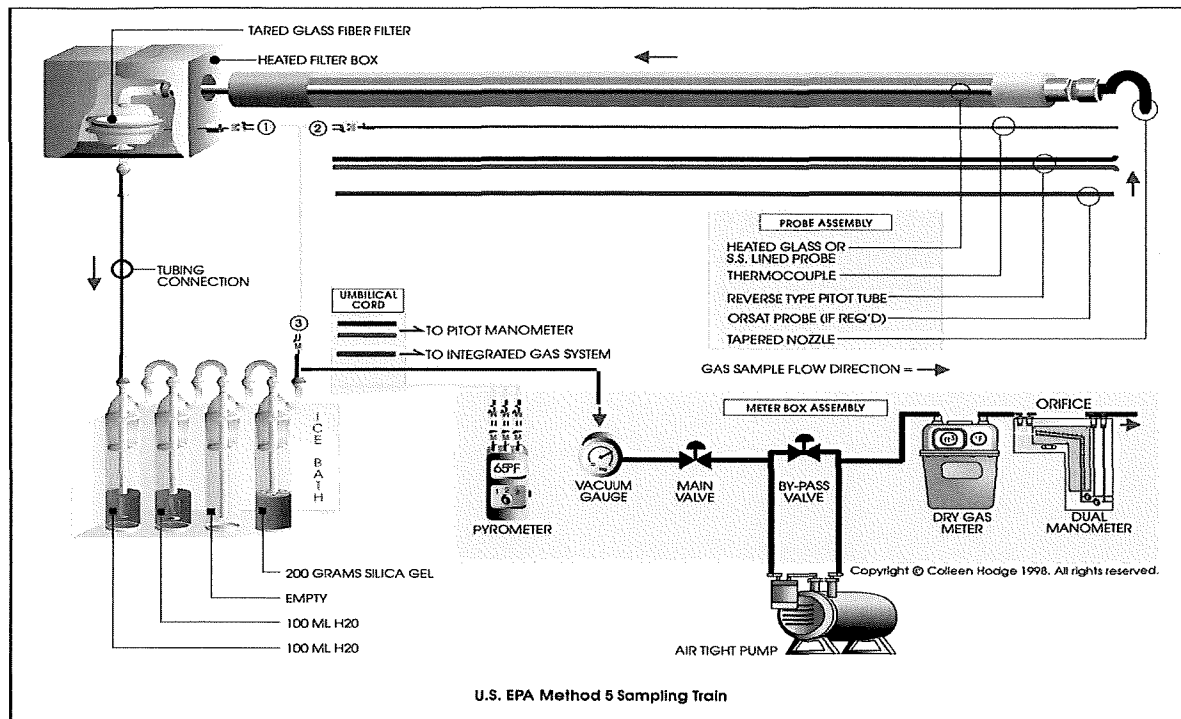


Figure 2: EPA Method 5 Sample System Diagram

EPA Method 5F was used on the FCCU Regen unit in lieu of Method 5. Method 5F is the determination of non-sulfate particulate matter. This sampling methodology is analogous to Method 5 as described above, except that the filter is baked at 320 °F prior to obtaining a tare weight and the probe and filter temperature is maintained at 320 °F during the test run. In addition, the post run sample recovery is conducted with water solvent instead of acetone. A portion of this sample is analyzed for sulfate content by ion chromatography. The weight of the sulfate content is then subtracted from the total weight gain for the determination of non-sulfate particulate matter.

4.5 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.

4.6 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted four (4) test runs for PM and NH₃ instead of the three (3) that were protocolled. This decision was made because it was observed during the sample recovery that the thimble filter for the CTM-027 train was cracked. This observance threw into question the validity of the Run 1 NH₃ data. Therefore, a fourth run for PM and NH₃ were conducted. All four runs were averaged to comply with compliance with the permitted limit.