



*Relative Accuracy Test Audit*

for  
**Marathon Petroleum Company LP**

at the  
**Marathon Detroit Refinery in Detroit, MI**

on the  
**Alky DIB Reboiler**  
**Unit: EU09-ALKYDIBREBHTR-S1**  
**Permit No. MI-ROP-A9831-2012c**

Prepared for:



**Marathon  
Petroleum Company LP**

**Test Date: September 13, 2023**  
Erthwrks Project No. 9284.1.C3



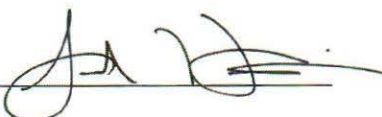
## Endorsement Page

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: Jarrold Hoskinson

Title: Senior Project 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

Title: Technical Director

Signature: 

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### ATTACHMENTS

- A. Detailed Results of Emissions Test
- B. Quality Control Documentation
- C. Example Calculations
- D. Raw Datalog Records
- E. Calibrations and Certifications
- F. CEMS Logs and Operational Data



## 1.0 INTRODUCTION

### 1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emissions testing on the Alky DIB Reboiler in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on September 13, 2023.

### 1.2 Purpose of Testing

The exhaust from Alky DIB Reboiler was sampled and analyzed to determine the relative accuracy of the associated oxides of nitrogen (NO<sub>x</sub>), and oxygen (O<sub>2</sub>) continuous emissions monitoring system (CEMS) in accordance with the requirements in the Marathon Permit No. MI-ROP-A9831-2012c and the Title 40 CFR Part 60, Appendix F.

### 1.3 Description of Source

Marathon Petroleum Company LP operates the Alky DIB Reboiler designated as EU09-ALKYDIBREBHTR-S1 in the refinery. Table 1.1 below details the CEMS analyzer information.

**Table 1.1—Marathon Alky DIB Reboiler CEMS Details**

Alky DIB Reboiler CEMS	Manufacturer	Model No.	S/N	Install Date
NO <sub>x</sub>	ABB	Limas 11	3.343232.1	2012
O <sub>2</sub>	ABB	Magnos 206	3.343209.1	2012

## 1.4 Contact Information

### **Marathon Petroleum Company LP**

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### **Facility Location:**

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



## 2.0 SUMMARY OF RESULTS

Table 2.1—Marathon Alky DIB Reboiler (EU09-ALKYDIBREBHTR-S1)  
CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO <sub>x</sub> (lb/MMBtu)	Performance Spec. 2	7.4% <i>RA<sub>RM</sub></i>	20%	Pass
O <sub>2</sub> (%vd)	Performance Spec. 3	0.13% <i>RA<sub>MD</sub></i>	1%	Pass

## 3.0 SOURCE DESCRIPTION

### 3.1 Description of the process

The Alkylation Unit (EU09 ALKYLATION) reacts isobutene with olefins in the presence of sulfuric acid to produce alkylate, a high-octane gasoline blending component. Reaction products are sent for further processing and separation in the fractionating section. Products from the unit include off gas, alkylate, butane, isobutene, and propane. Off gas is routed to the refinery fuel gas system. Alkylate, butane, and propane are directed to storage. Isobutene is recycled through the system for further processing. The alkylation unit consists of process vessels (including fractionators, reactor and caustic scrubber), the Alkylation Deisobutanizer (DIB) Reboiler Heater (EU09 ALKYDIBREBHTR S1), tanks, containers, cooling tower, flare, compressors, pumps, piping, drains, and other various components.

The Alky DIB Reboiler is fired by refinery fuel gas. Emissions are vented to the atmosphere via the Alky DIB Reboiler Stack (SV09 H7), where testing was performed.



### 3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the Alky DIB Reboiler (EU09-ALKYDIBREBHT-R-S1) under Michigan Department of Environment, Great Lakes, and Energy (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.

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

During the emission testing on September 13, 2023, at the Marathon Petroleum Company LP Refinery, the Alky DIB Reboiler was tested while operating at load conditions representative of normal conditions. The load conditions during the testing were documented by Marathon Detroit Refinery and provided in Appendix F.

## 4.0 SAMPLING AND ANALYTICAL PROCEDURES

### 4.1 Gaseous Sampling – NO<sub>x</sub> and O<sub>2</sub>

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  $\leq 0.5$  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 was repeated with the low-level gas and the response recorded. During this activity, the sample system response time was also 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  $\leq 0.5$  ppmv).

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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  $\leq 0.5$  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:

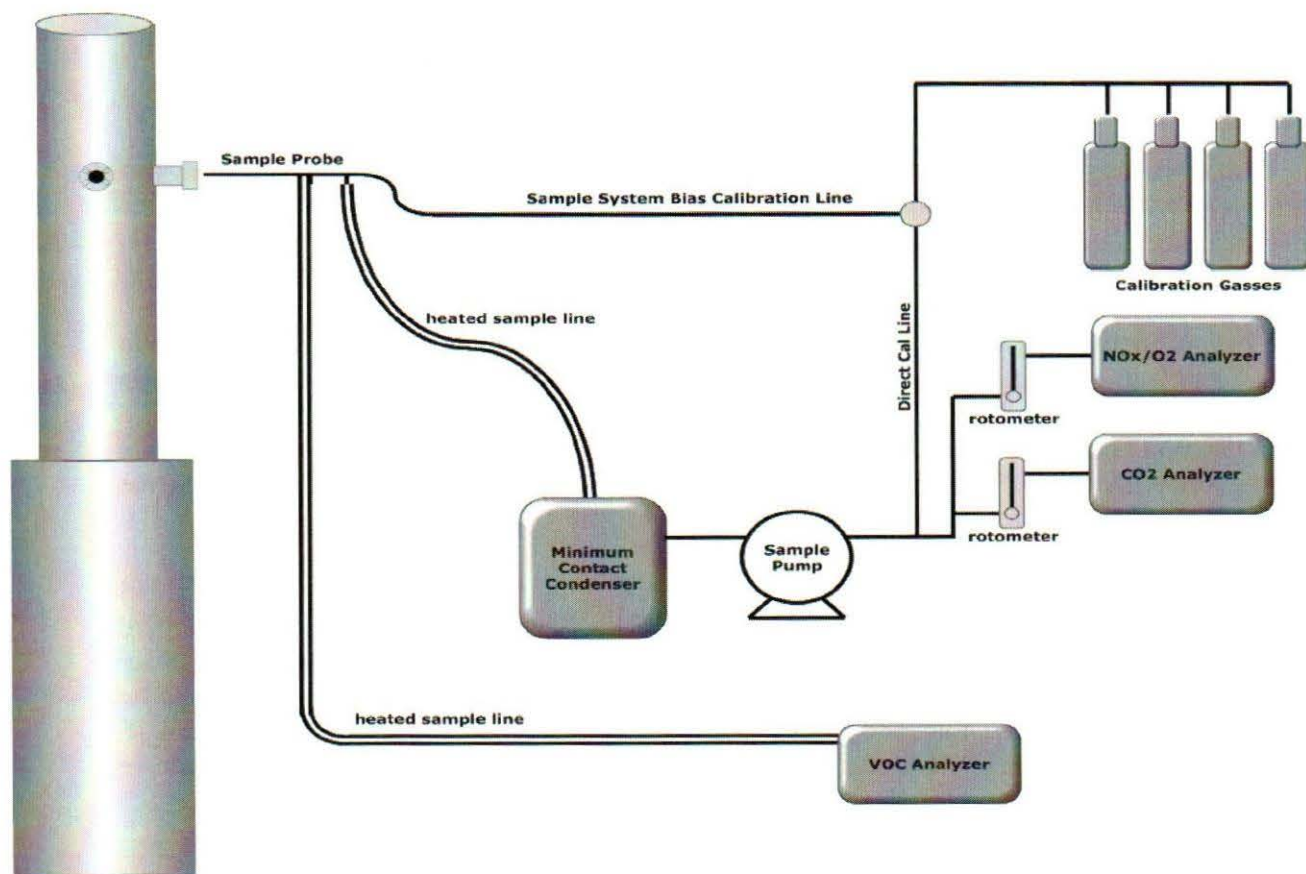


Figure 1: Example Erthwrks Gaseous Sampling System Diagram



## 4.2 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<sub>x</sub> relative accuracy
- EPA Performance Specification 3 for O<sub>2</sub> 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 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 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.

## 4.3 Discussion of sampling procedure or operational variances

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

**Attachment A**  
**Detailed Results of Emission Test**



## Erthwrks Relative Accuracy Test Audit--NOx RATA Performance Specification 2

Alky DIB Reboiler							NOx CEMS RATA - lb/mmBTU			
Test Run	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Date	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023
Start Time	10:30	10:51	11:12	11:42	12:03	12:24	12:54	13:15	13:36	14:04
End Time	10:51	11:12	11:33	12:03	12:24	12:45	13:15	13:36	13:57	14:25
RM NOx (ppmvd)	21.98	21.32	22.90	23.03	23.10	23.11	23.21	23.37	23.23	23.40
RM O <sub>2</sub> Results (%vd)	7.27	7.24	7.27	6.99	6.86	6.92	7.06	7.44	6.81	7.03
RM NOx (lb/mmBTU)	<b>0.0340</b>	<b>0.0329</b>	<b>0.0355</b>	<b>0.0349</b>	<b>0.0347</b>	<b>0.0349</b>	<b>0.0354</b>	<b>0.0366</b>	<b>0.0348</b>	<b>0.0356</b>
CEMS NOx (lb/mmBTU)	<b>0.0367</b>	<b>0.0366</b>	<b>0.0366</b>	<b>0.0368</b>	<b>0.0367</b>	<b>0.0370</b>	<b>0.0370</b>	<b>0.0383</b>	<b>0.0365</b>	<b>0.0367</b>
Difference	-0.0026	-0.0036	-0.0011	-0.0019	-0.0020	-0.0021	-0.0016	-0.0016	-0.0017	-0.0011
Accept or Reject	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Reject

Applicable Standard (lb/mmBTU)

Mean of the Difference ( $d_{avg}$ )

Standard Deviation ( $S_d$ )

Confidence Coefficient (CC)

Relative Accuracy via RM,  $RA_{RM}^*$

\* $RA_{RM}$  (Reference Method) must be less than 20%

† $RA_{AS}$  (Applicable Standard) must be less than 10%

0.04
-0.0020
0.0007
0.0006
<b>7.44%</b>

← Pass

## Erthwrks Relative Accuracy Test Audit--O<sub>2</sub> RATA Performance Specification 3

Alky DIB ReboilerO<sub>2</sub> CEMS RATA

Test Run	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Date	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023	9/13/2023
Start Time	10:30	10:51	11:12	11:42	12:03	12:24	12:54	13:15	13:36	14:04
End Time	10:51	11:12	11:33	12:03	12:24	12:45	13:15	13:36	13:57	14:25
RM O <sub>2</sub> Result (%vd)	7.27	7.24	7.27	6.99	6.86	6.92	7.06	7.44	6.81	7.03
CEMS O <sub>2</sub> Data (%vd)	6.94	6.88	6.90	7.02	6.84	6.96	7.02	7.37	6.77	6.94
Difference	0.33	0.36	0.37	-0.03	0.02	-0.04	0.04	0.07	0.04	0.09
Accept or Reject	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Accept	Reject

Mean of the Difference ( $d_{avg}$ )

0.13
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Standard Deviation ( $S_d$ )

0.17
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Confidence Coefficient (CC)

0.13
------

Relative Accuracy via RM,  $RA_{RM-CEMS}^*$

0.13%
-------

← Pass

\* $RA_{RM-CEMS}$  (Reference Method - CEMS) Absolute difference must be less than 1.0%



**Attachment B**  
**Quality Control Documentation**

## Erthwrks Method 1 Traverse Point Location Worksheet

**Client:** Marathon Petroleum Company  
**Project #:** 9284.1.C3  
**Facility:** Detroit Refinery  
**Unit ID:** Alky DIB Reboiler  
**Technician:** M. Oleszko

**Stack ID Measurements**

Stack ID + Port (inches):	<b>79</b>
Port Extension (inches):	<b>9</b>
Stack Diameter (inches):	<b>70</b>

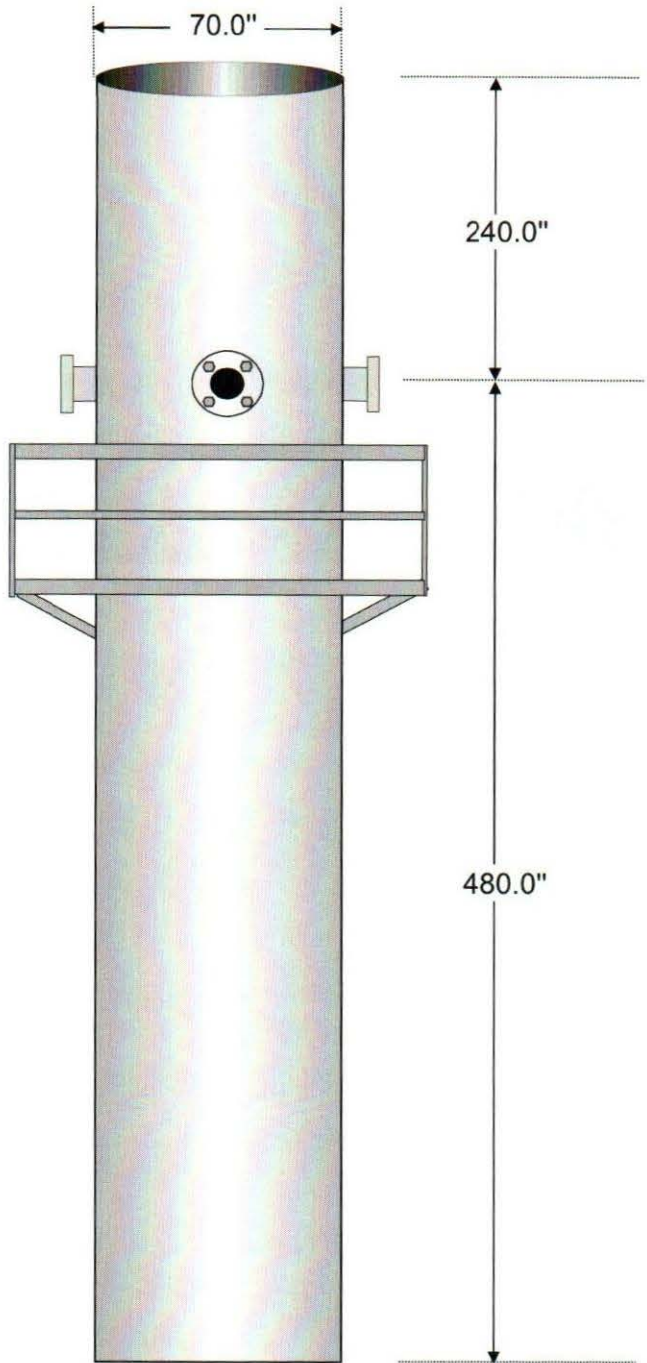
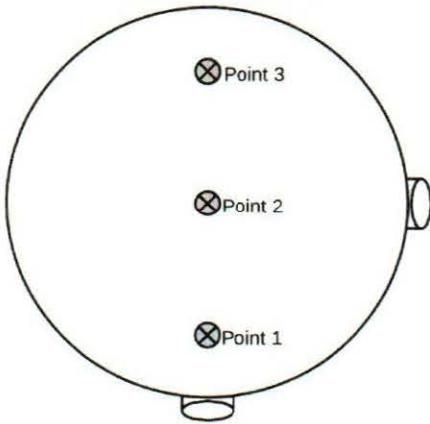
**Port Location Measurements**

Distance Upstream (A) (inches):	<b>240</b>
Distance Downstream (B) (inches):	<b>480</b>
Stack Diameters Upstream (A):	<b>3.4</b>
Stack Diameters Downstream (B):	<b>6.9</b>

Total Traverse Points to be used:	<b>3</b>
Traverse Points per Diameter:	<b>3</b>

Traverse Point Locations <sup>(1)(2)</sup>	
Point 1:	11.69"
Point 2:	35.00"
Point 3:	58.31"

**Stack Cross Section View**



<sup>(1)</sup>For stack diameter >4.0" and <2.4 meters, stratification is measured at 16.7%, 50.0%, and 83.3" of stack diameter (M7E, §8.1.2).

<sup>(2)</sup>For stack diameter >2.4 meters, stratification is measured at 0.4, 1.2, and 2.0 meters from stack wall (M7E, §8.1.2).