



AIR EMISSIONS TESTING FOR INDUSTRY

*Relative Accuracy Test Audit
and Performance Testing*

for

Marathon Petroleum Company LP

at the

Marathon Detroit Refinery in Detroit, MI

on the

BR-10 (Zurn) Boiler

Unit: EU27-ZURNBOILER-S1

Permit No. MI-ROP-A9831-2012c

Prepared for:



**Marathon
Petroleum Company LP**

Test Date: July 19, 2022

Erthwrks Project No. 9049.1.C1



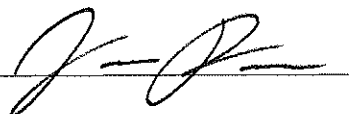
Endorsement Page

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: QA Specialist

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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ATTACHMENTS

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

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the BR-10 (Zurn) Boiler in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on July 19, 2022.

1.2 Purpose of Testing

The exhaust from BR-10 (Zurn) Boiler was sampled and analyzed to determine the relative accuracy of the associated carbon monoxide (CO), oxides of nitrogen (NOx), and oxygen (O₂) 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. In addition, compliance testing was conducted to determine the compliance status of the units' emission for sulfuric acid (H₂SO₄), particulate matter (PM) and volatile organic compounds (VOC).

1.3 Description of Source

Marathon Petroleum Company LP operates the BR-10 (Zurn) Boiler designated as EU27-ZURNBOILER-S1 in the refinery. This report addresses the RATA for the CEMS associated with the unit as well as the required compliance test for PM and VOC. Table 1.1 below details the CEMS analyzer information.

Table 1.1—Marathon BR-10 (Zurn) Boiler CEMS Details

BR-10 (Zurn) Boiler CEMS	Manufacturer	Model No.	S/N	Install Date
NOx	ABB	Limas 11	3.342678.1	2012
CO	ABB	Uras 26	3.342694.1	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 BR-10 (Zurn) Boiler (EU27-ZURNBOILER-S1) CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO _x	Performance Spec. 2	10.6% RA_{RM}	20%	Pass
CO	Performance Spec. 4A	0.8 ppm RA_{AA}	<5 ppm	Pass
O ₂	Performance Spec. 3	0.05% RA	1%	Pass

Table 2.2—Marathon BR-10 (Zurn) Boiler (EU27-ZURNBOILER-S1) Compliance Test Results

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
VOC	EPA Method 25A/4	0.0001 lb/MMBtu	0.0055 lb/MMBtu	Pass
PM	EPA Method 5	0.0016 lb/MMBtu	0.0019 lb/MMBtu	Pass
PM/PM ₁₀	EPA Method 5/202	0.0042 lb/MMBtu	0.0076 lb/MMBtu	Pass
H ₂ SO ₄	EPA Method CTM-013	0.004 ppm	n/a	n/a

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.

As required in the Tier 3 Gasoline Project Permit (PTI 118-15), the BR-10 (Zurn) Boiler (EU27-ZURNBOILER-S1) utilizes low NO_x burners. This boiler generates steam required by other refinery process components. The unit is fired by natural gas. Emissions are vented to the atmosphere via the BR-10 (Zurn) Boiler Stack (SV22-BR7) where testing was performed.

3.2 Applicable permit and source designation

Marathon Petroleum Company LP operates the BR-10 (Zurn) Boiler (EU27-ZURNBOILER-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 periodically determine the PM and VOC exhaust emissions.

3.3 Type and quantity of materials processed during tests

During the emission testing on July 19, 2022, at the Marathon Petroleum Company LP Refinery, the BR-10 (Zurn) Boiler was tested while operating at the maximum achievable load condition. **NOTE:** For this testing program, the average steam production was approximately 155 mlb/hr and the average unit firing rate was 178 MMBtu/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 – NO_x, CO, and 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)

The determination of the VOC as total hydrocarbon compounds (THC) concentration followed 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 or Method 5 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.

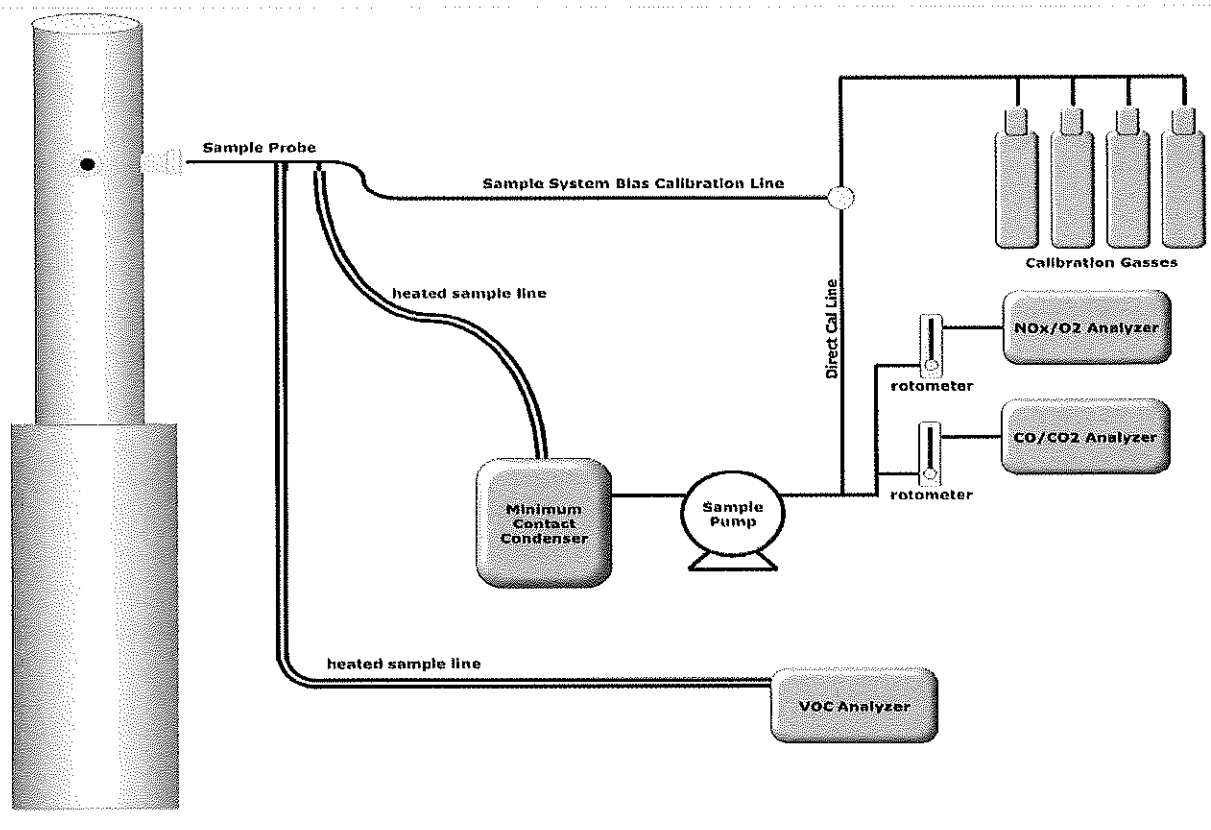
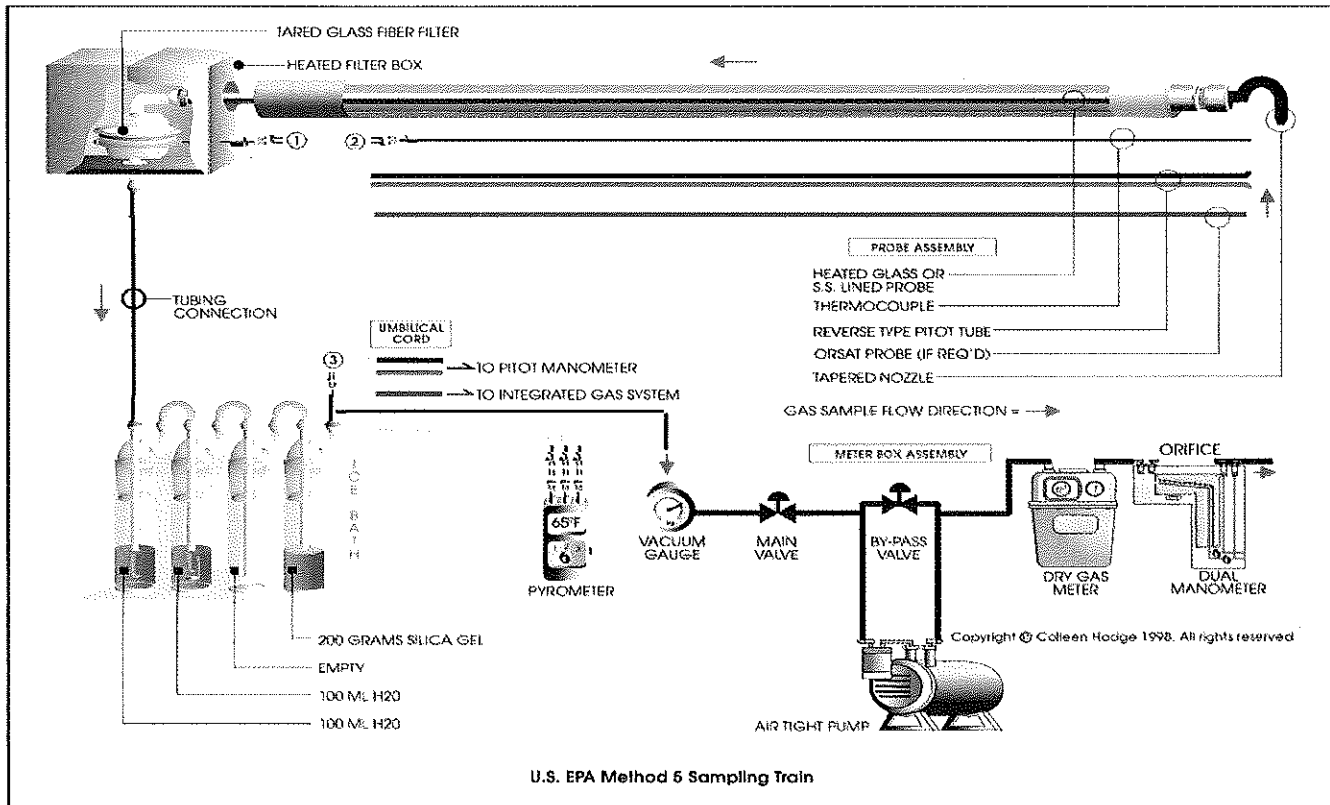


Figure 1: Example Erthwrks Gaseous Sampling System Diagram

4.3 Filterable Particulate Matter Sampling – EPA Method 5

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.

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.



4.4 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.

4.5 EPA Method CTM-013 (ALT-133 Analysis) H₂SO₄ Determination

The H₂SO₄ 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 Graham condenser (H₂SO₄ Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing condenser coil. The H₂SO₄ condenser is maintained between 167 to 185 °F. Because SO₂ 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.

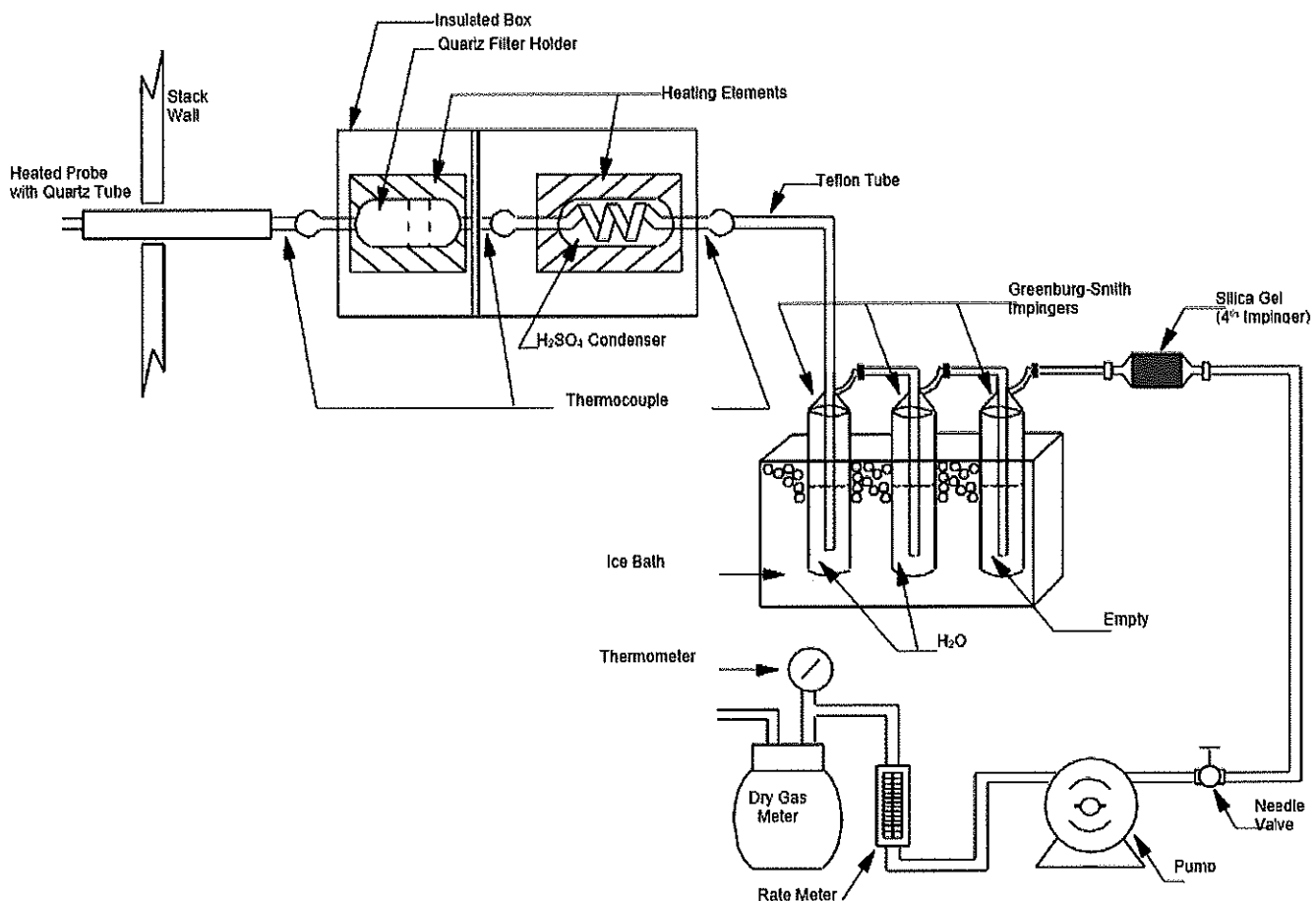


Figure 3: Example Erthwrks H₂SO₄ System Diagram

4.6 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
- 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.

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_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.

For CO, the results of the RATA test are 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 are considered acceptable if the absolute average difference between the RM and CEMS is within 5 ppmv.

4.7 Discussion of sampling procedure or operational variances

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

Ten (10) RATA runs were conducted, and the first nine (9) runs were used to determine relative accuracy of the NO_x, CO, and O₂ CEMS.

Attachment A
Detailed Results of Emission Test