

# erthwrks

AIR EMISSIONS TESTING FOR INDUSTRY

## *US EPA Part 60 & 75 Relative Accuracy Test Audit and Performance Testing*

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MAY 02 2023

for

**Marathon Petroleum Company LP**

AIR QUALITY DIVISION

at the

**Marathon Detroit Refinery in Detroit, MI**

on the

**B&W Boiler  
(EU27-B&WBOILER1-S1)**

Prepared for:



**Marathon  
Petroleum Company LP**

**Test Date: February 28, 2023**

**Erthwrks Project No. 9284.1.A2**

A9831-test-20230228



## 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: Quality Assurance Manager

Signature: 

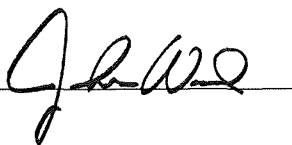
This report has been reviewed for accuracy and completeness. The actions presented in this report are, to the best of my knowledge, an accurate representation of the results and findings of the test campaign. Erthwrks, Inc. operates in conformance with the requirements on ASTM D7036-04 Standard Practice 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.

### 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. Sampling Datasheets
- E. Raw Datalog Records
- F. Calibrations and Certifications
- G. CEMS Logs and Operational Data
- H. Particulate Matter Laboratory Analysis
- I. Method 18 Analysis
- J. Erthwrks AETB and QI Personnel Certifications

## 1.0 INTRODUCTION

### 1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the B&W Boiler in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on February 28, 2023.

### 1.2 Purpose of Testing

A relative accuracy test audit (RATA) was conducted to demonstrate the accuracy and reliability of the Marathon Petroleum Company LP nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO) and oxygen (O<sub>2</sub>) continuous emissions monitoring system (CEMS) in operation on the B&W Boiler. This program was conducted to satisfy the requirements of the facility's operating permit. All audit procedures were conducted in accordance with the requirements set forth in the USEPA Title 40 CFR Part 75, which defines the CEMS specifications and testing procedures.

In addition, compliance testing was conducted to determine the compliance status of the unit's particulate matter (PM), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and volatile organic compounds (VOCs) emissions. For this test program, VOCs are defined as total hydrocarbons (THC), minus methane and ethane.

### 1.3 Description of the Participants

Marathon Petroleum Company LP operates Detroit Refinery located in Detroit Refinery. Within this facility there are numerous combustion emission sources. Associated with these emission points, Marathon Petroleum Company LP has installed continuous emission monitoring systems, or CEMS, that continuously record all data for emissions control and emissions reporting.

Erthwrks, Inc. integrates our Quality Management Plan (QMP) into every aspect of our testing service. The procedures specified in the current published versions of the test Method(s) referenced in this report are followed by all Erthwrks' personnel. Any modifications or deviations are specifically identified in the body of the report. We routinely participate in independent, third-party audits of our activities, and maintain:

- Accreditation from the Stack Testing Accreditation Council (STAC) and the American Association for Laboratory Accreditation (A2LA) that our operations conform with the requirements of ASTM D 7036 as an Air Emission Testing Body (AETB).

This accreditation demonstrates that systems for training, equipment maintenance and calibration, document control and project management will fully ensure that project

objectives are achieved in a timely and efficient manner with a strict commitment to quality.

All calibrations are performed in accordance with the test method(s) identified in this report. If a method allows for more than one calibration approach, or if approved alternatives are available, the calibration documentation in the appendices specifies which approach was used. All measurement devices are calibrated or verified at set intervals against standards traceable to the National Institute of Standards and Technology (NIST). NIST traceability information is available upon request.

All testing performed by Erthwrks is supervised on site by at least one Qualified Individual (QI) as defined in D7036-04 Section 8.3.2. Data quality objectives for estimating measurement uncertainty within the documented limits in the test methods are met by using approved test protocols for each project as defined in D7036-04 Sections 7.2.1 and 12.10. Additional quality assurance information is presented in the report appendices. Conformance with this section may be demonstrated using approved test protocols for all tests. When such protocols are used, reference shall be made to published literature, when available, where estimates of uncertainty for test methods may be found. Erthwrks, Inc. conforms to this section by using approved test protocols for all tests.

#### **1.4 Contact Information**

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## 2.0 SUMMARY OF RESULTS

**Table 2.1—B&W Boiler CEMS RATA Results**

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NO <sub>x</sub>	Performance Spec. 2	0.007 lb/MMBtu $RA_{MD}$	<0.02 lb/MMBtu	Pass
CO	Performance Spec. 4A	6.6% $RA_{RM}$	<10%	Pass
O <sub>2</sub>	Performance Spec. 3	0.04% $RA_{MD}$	<1%	Pass

Standard (subscript "PS") is 10% relative accuracy; for the Alternative Standard (subscript AS) the mean difference must be <15 ppm (1% for O<sub>2</sub>) or 0.02 lb/MMBtu.

**NOTE:** In accordance with §2.3.1.2(f) of Part 75, Appendix B, the unit qualifies for the reduced RATA frequencies due to the mean-difference resulting value is within ±0.015 lb/mmBtu (± 0.7 % for O<sub>2</sub>).

**Table 2.2—B&W Boiler Compliance Test Results**

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
VOC	EPA Method 25A/18	0.0006 lb/MMBtu	0.0055 lb/MMBtu	Pass
H <sub>2</sub> SO <sub>4</sub>	EPA Method CTM-013	5.33E-05 lb/MMBtu	Not Applicable	NA
Filterable PM	EPA Method 5	0.0010 lb/MMBtu	0.0019 lb/MMBtu	Pass
PM/PM <sub>10</sub>	EPA Method 5/202	0.0024 lb/MMBtu	0.0076 lb/MMBtu	Pass

## 3.0 SOURCE DESCRIPTION

### 3.1 Description of the Source

Marathon Petroleum Company LP B&W Boiler provides steam for process heat throughout the refinery. The boiler has Low NO<sub>x</sub> burners and Selective Catalytic Reduction (SCR) and is fired with refinery fuel gas and natural gas.

**Table 3.1: Detroit Refinery B&W CEMS Description**

Pollutant Measured	Analyzer Manufacturer	Analyzer Model	Serial Number
NO <sub>x</sub>	ABB	Uras 26	3.417674.1
O <sub>2</sub>	ABB	Magnos 28	3.417676.1
CO	ABB	Uras 26	3.417674.1

### **3.2 Applicable permit and source designation**

The Marathon Petroleum Company LP operates the B&W Boiler following the parameters required by facility permit and 40 CFR Part 75, Appendix A. Under these regulations, the Detroit Refinery 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 Marathon Petroleum Company LP, Detroit Refinery emission testing on February 28, 2023, the B&W Boiler was tested while producing an average of 202,462 lbs/hr of steam. It most frequently produces 102,000 – 152,000 lbs/hr of steam, followed by 50,000-101,999 lbs/hr of steam.

The actual load conditions during the testing were documented by Marathon Petroleum Company LP, personnel and provided in Appendix G.

## **4.0 SAMPLING AND ANALYTICAL PROCEDURES**

### **4.1 Gaseous Sampling – NO<sub>x</sub>, CO, 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 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  $\leq 0.5$  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  $\pm 3.0\%$  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.

#### 4.2 Gaseous Emissions – VOC as THC (Method 18 and 25A)

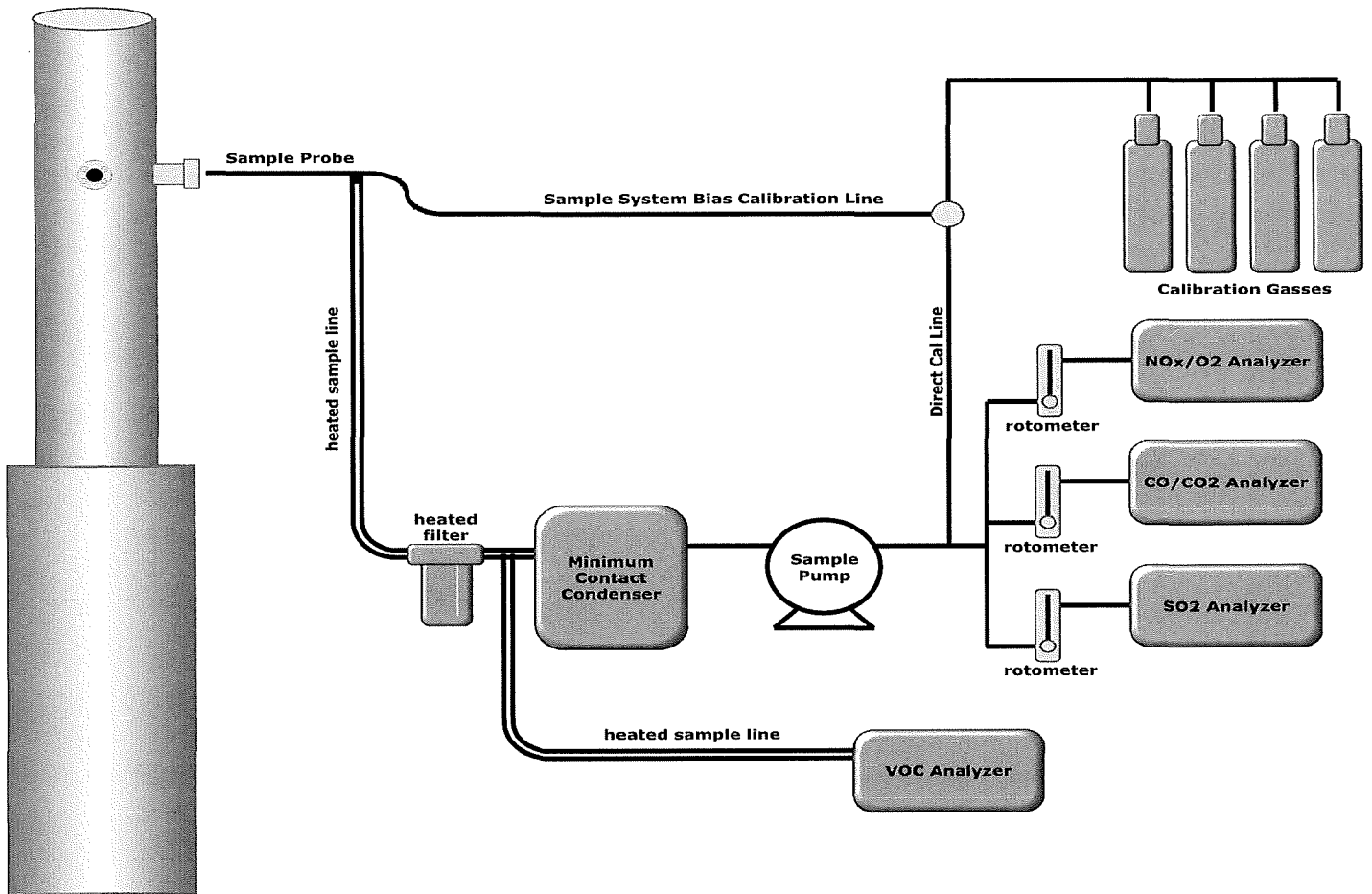
The determination of concentration follows all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A and Method 18. The calibration error (CE) test was conducted following the procedures specified in EPA Method 25A §8.4. In accordance with this requirement, a four-point analyzer 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 VOC raw data is corrected for analyzer drift using EPA Method 7E Equation 7E-B5. The VOC is measured on a wet basis and is converted to a dry basis using moisture data from a Method 5 sampling train.

In order to subtract methane and ethane from the THC value generated by Method 25A, bag samples of the stack gas were collected during each run. The bag samples were shipped overnight to the Erthwrks base laboratory analyzed for methane and ethane using Method 18.

The figure below details the Erthwrks Gaseous Sampling System.



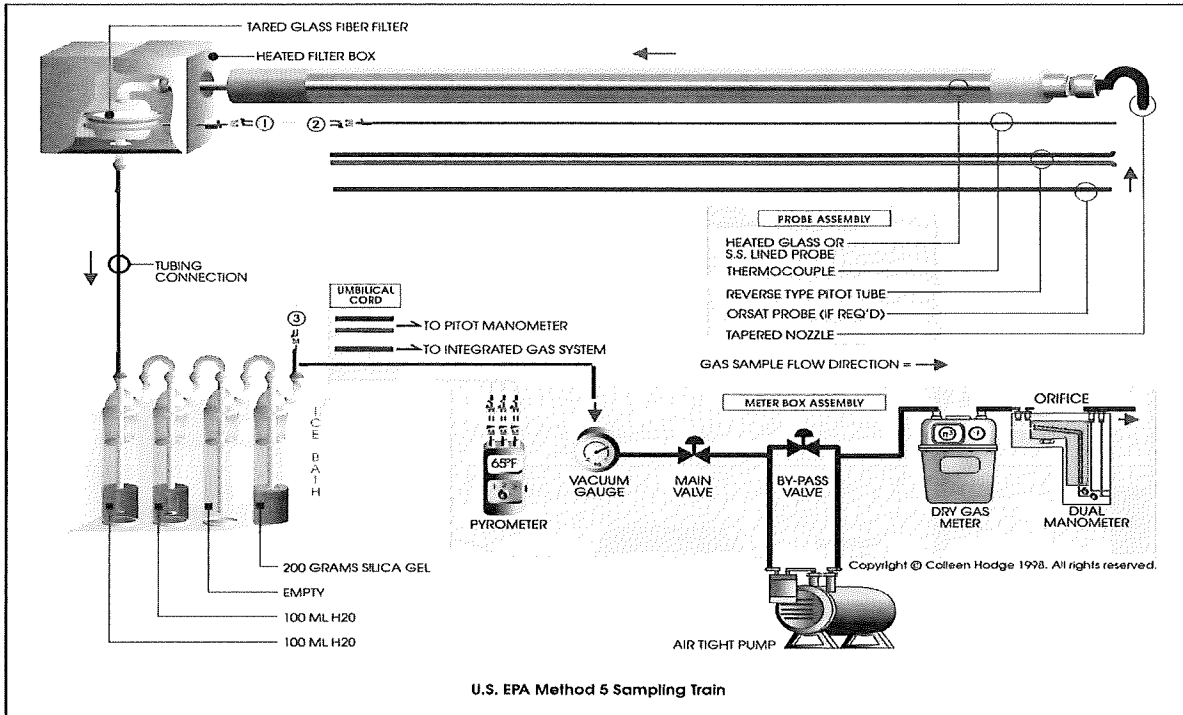


**Figure 1: Example Erthwrks Gaseous Sampling System Diagram**

### 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 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, is 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.



For the determination of PM/PM10, the 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<sub>2</sub>SO<sub>4</sub> Determination

The H<sub>2</sub>SO<sub>4</sub> emissions were determined utilizing 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 (H<sub>2</sub>SO<sub>4</sub> Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing condenser coil. The H<sub>2</sub>SO<sub>4</sub> condenser is maintained between 167 to 185 °F. Because SO<sub>2</sub> 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.

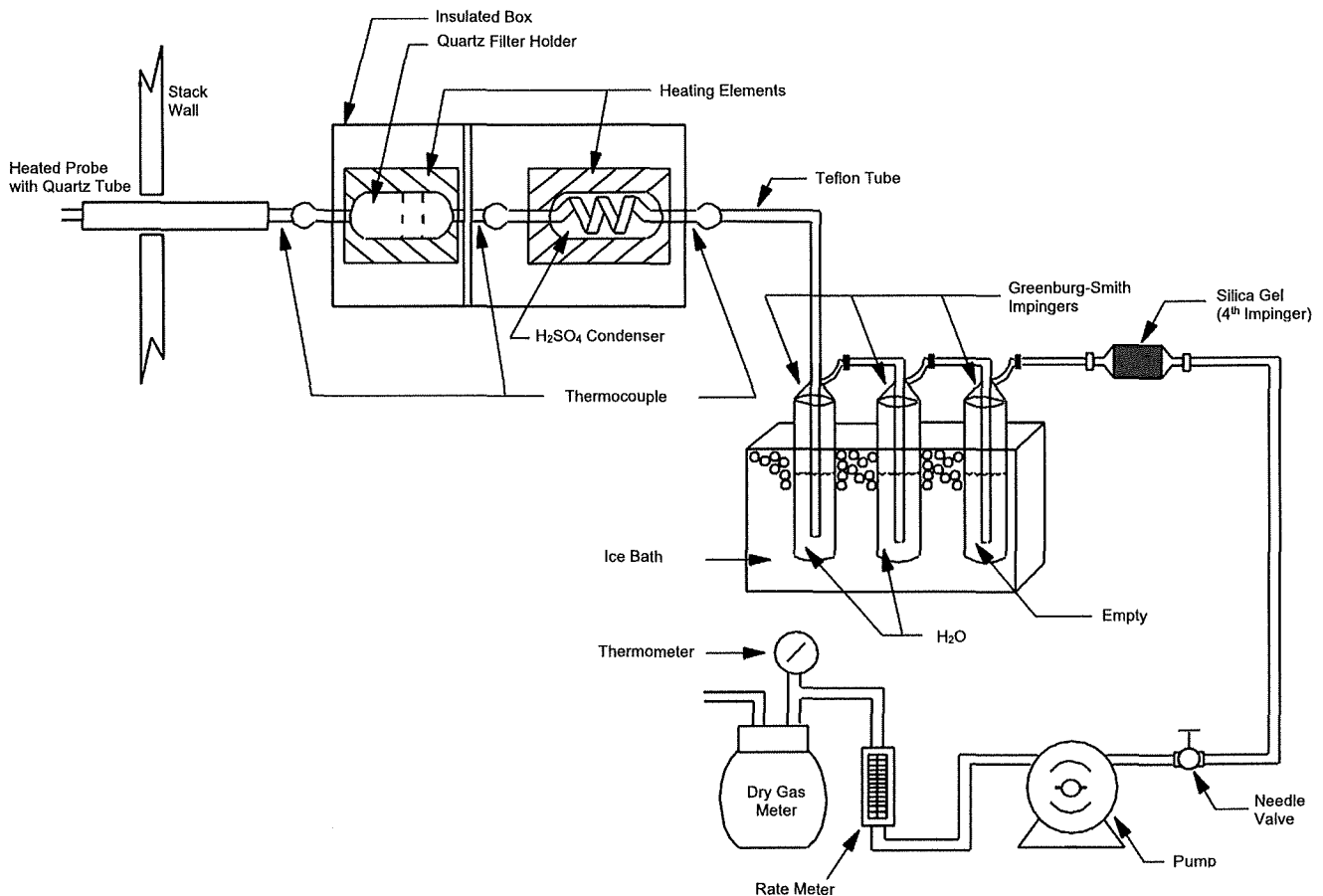


Figure 2: Example Erthwrks CTM-013 Sample System Diagram

## 4.5 RATA Procedures – O<sub>2</sub> and CO

The RATA testing for CO and O<sub>2</sub> 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 was used during this testing program.

- EPA Performance Specification 3 for O<sub>2</sub> relative accuracy
- EPA Performance Specification 4A for CO relative accuracy

As required by these specifications, 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.

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.

#### 4.6 RATA Procedures – NO<sub>x</sub>

As required by the USEPA Part 75 test procedures, a minimum of nine (9) EPA reference method tests were conducted for each pollutant monitored by the CEMS system. Each of these test runs were conducted for a minimum duration of twenty-one (21) minutes. The results of these reference method tests were compared to CEMS measurement data from the same time periods to determine the relative accuracy of the CEMS. The results of the RATA test is considered acceptable if the calculated relative accuracy does not exceed 10.0%. Alternatively, for affected units where the average of the reference method measurements of NO<sub>x</sub> concentration during the RATA is less than or equal to 250.0 ppm, the difference between the mean value of the CEMS measurements and the mean value of the reference method shall not exceed  $\pm 15.0$  ppm ( $\pm 1.0\%$  for O<sub>2</sub>).

The bias test was performed upon review of the RATA results. This test consists of calculations only without any further physical measurement. If the mean difference of the reference method values and the corresponding CEMS data collected during the RATA is less than or equal to the absolute value of the confidence coefficient, the monitor has passed the bias test. If the mean difference is greater than the confidence coefficient, a bias adjustment factor (BAF) will be required to be applied to the CEMS results. The bias adjustment factor (BAF) was calculated in accordance with the equation defined in USEPA Part 75, Appendix A, §7.6.4 (Eq. A-12).

#### 4.7 Discussion of sampling procedure or operational variances

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

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