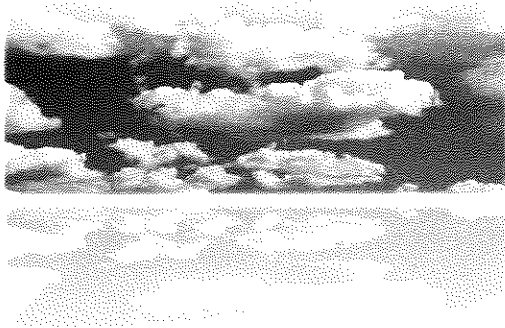




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REPORT ON COMPLIANCE &  
RATA TESTING

Detroit Refinery  
Crude/Vacuum Heater Stack

Marathon Petroleum Company LP  
1300 South Fort Street  
Detroit, MI 48217  
Client Reference No. 4101379616

CleanAir Project No. 13582-2  
A2LA ISO 17025 Certificate No. 4342.01  
A2LA / STAC Certificate No. 4342.02  
Revision 1, Final Report  
August 2, 2018

## 1. PROJECT OVERVIEW

### Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to complete testing on the Crude/Vacuum Heater (EU05-CRUDEHTR-S1 & EU04-VACHTR-S-1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>), and volatile organic compound (VOC) testing to demonstrate compliance with the MDEQ Permit No. MI-ROP-A9831-2012c;
- Perform a relative accuracy test audit (RATA) on the facility's continuous emissions monitoring system (CEMS) for oxygen (O<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>) and carbon monoxide (CO).

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis. Test program information, including the test parameters, on-site schedule and a project discussion, begins on page 2.

**Table 1-1:  
Summary of Compliance Results**

| Source<br>Constituent                     | Sampling Method<br>(USEPA) | Average<br>Emission | Permit Limit <sup>1</sup> |
|---|----------------------------|---------------------|---------------------------|
| <u>Crude/Vacuum Heater</u>                |                            |                     |                           |
| FPM (lb/MMBtu)                            | USEPA M-5                  | 0.0016              | N/A                       |
| H <sub>2</sub> SO <sub>4</sub> (lb/MMBtu) | Draft ASTM CCM             | 0.0008              | N/A                       |
| PM (lb/MMBtu) <sup>2</sup>                | USEPA M-5 / Draft ASTM CCM | 0.0008              | 0.0019                    |
| VOC (lb/MMBtu)                            | USEPA M-18 / 25A           | <0.0008             | 0.0055                    |

<sup>1</sup> Permit limits obtained from MDEQ Renewable Operating Permit No. MI-ROP-A9831-2012c.

<sup>2</sup> PM assumed equivalent to FPM less H<sub>2</sub>SO<sub>4</sub>. The letter from MDEQ referenced in Appendix K further outlines the correction of particulate emission for H<sub>2</sub>SO<sub>4</sub> bias.

**Table 1-2:  
Summary of RATA Results**

| Source<br>Constituent                         | Reference Method<br>(USEPA) | Relative<br>Accuracy (%) | Applicable<br>Specification | Specification<br>Limit <sup>1</sup> |
|---|-----------------------------|--------------------------|-----------------------------|-------------------------------------|
| <u>Crude/Vacuum Heater</u>                    |                             |                          |                             |                                     |
| O <sub>2</sub> (% dv)                         | 3A                          | 0.03                     | PS3                         | ±1.0% dv                            |
| NO <sub>x</sub> (ppm dv @ 0% O <sub>2</sub> ) | 7E                          | 3.0                      | PS2                         | 20% of RM                           |
| NO <sub>x</sub> (lb/MMBtu)                    | 7E                          | 5.5                      | PS2                         | 20% of RM                           |
| CO (lb/MMBtu)                                 | 10                          | 0.0                      | PS4A <sup>2</sup>           | 10% of RM                           |

<sup>1</sup> Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

<sup>2</sup> For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4A RA limit is either < 10% of RM, < 5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

## Test Program Details

### Parameters

The test program will include the following emissions measurements:

- filterable particulate matter (FPM)
- sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>) (conducted concurrently with FPM measurements)
- particulate matter (PM), assumed equivalent to FPM minus H<sub>2</sub>SO<sub>4</sub>
- nitrogen oxides (NO<sub>x</sub>)
- carbon monoxide (CO)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
  - methane (CH<sub>4</sub>)
  - ethane (C<sub>2</sub>H<sub>6</sub>)
- flue gas composition (e.g., O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O)
- flue gas temperature
- flue gas flow rate

### Schedule

Testing was performed on June 6 and 13, 2018. The on-site schedule followed during the test program is outlined in Table 1-3.

**Table 1-3:  
Test Schedule**

| Run Number | Location            | Method                | Analyte  | Date     | Start Time | End Time |
|------------|---------------------|-----------------------|--|----------|------------|----------|
| 1          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 08:35      | 08:56    |
| 2          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 09:07      | 09:28    |
| 3          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 09:38      | 09:59    |
| 4          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 10:09      | 10:30    |
| 5          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 10:42      | 11:03    |
| 6          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 11:14      | 11:35    |
| 7          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 11:46      | 12:07    |
| 8          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 12:17      | 12:38    |
| 9          | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 12:50      | 13:11    |
| 10         | Crude/Vacuum Heater | USEPA Method 3A/7E/10 | O <sub>2</sub> /CO <sub>2</sub> /NO <sub>x</sub> /CO | 6/06/18  | 13:24      | 13:45    |
| 1          | Crude/Vacuum Heater | USEPA Method 5        | FPM  | 06/13/18 | 08:06      | 10:14    |
| 2          | Crude/Vacuum Heater | USEPA Method 5        | FPM  | 06/13/18 | 10:45      | 12:51    |
| 3          | Crude/Vacuum Heater | USEPA Method 5        | FPM  | 06/13/18 | 13:25      | 15:35    |
| 4          | Crude/Vacuum Heater | USEPA Method 5        | FPM  | 06/13/18 | 16:16      | 18:23    |
| 0          | Crude/Vacuum Heater | Draft ASTM CCM        | Sulfuric Acid  | 06/12/18 | 15:30      | 16:30    |
| 1          | Crude/Vacuum Heater | Draft ASTM CCM        | Sulfuric Acid  | 06/13/18 | 08:06      | 10:14    |
| 2          | Crude/Vacuum Heater | Draft ASTM CCM        | Sulfuric Acid  | 06/13/18 | 10:45      | 12:52    |
| 3          | Crude/Vacuum Heater | Draft ASTM CCM        | Sulfuric Acid  | 06/13/18 | 13:25      | 15:35    |
| 4          | Crude/Vacuum Heater | Draft ASTM CCM        | Sulfuric Acid  | 06/13/18 | 16:16      | 18:23    |
| 1          | Crude/Vacuum Heater | USEPA Method 25A/18   | VOC  | 06/13/18 | 10:46      | 11:46    |
| 2          | Crude/Vacuum Heater | USEPA Method 25A/18   | VOC  | 06/13/18 | 11:59      | 12:59    |
| 3          | Crude/Vacuum Heater | USEPA Method 25A/18   | VOC  | 06/13/18 | 13:46      | 14:46    |

## Discussion

### *Project Synopsis*

#### PM Testing

A total of four (4) 120-minute EPA Method 5 test runs were performed. FPM emission results were calculated in units of pounds per million Btu (lb/MMBtu). The final result was expressed as the average of the three (3) valid runs (Runs 2-4).

Run 1 was excluded from final results because the sample was compromised with foreign particulate matter of metallic composition not otherwise consistent with a combustion process. Composition analysis of the foreign matter revealed it was mainly comprised of iron and sulfur; elements that are consistent with originating from degradation of the duct sample ports. The composition analysis report is presented in Appendix L of this report. It was also determined on-site by DEQ personnel that Run 1 was an outlier. It should be noted that the average emission for all runs, including Run 1, is 0.0011 lb/MMBtu, which also meets PM limit criteria.

PM is assumed equivalent to the difference of FPM and H<sub>2</sub>SO<sub>4</sub> emissions. This is recommended in a letter from the DEQ, dated December 18, 2017; "Marathon Petroleum, Crude/Vacuum Heater Stack, Request to Substitute Method 5B for Method 5, Permit: MI-ROP-A9831-2012c, SRN: A9831." H<sub>2</sub>SO<sub>4</sub> emissions were determined concurrently with FPM emissions, converted to units of lb/MMBtu and subtracted from total FPM emissions from each respective run.

#### H<sub>2</sub>SO<sub>4</sub> Testing – Draft ASTM Controlled Condensation Method

H<sub>2</sub>SO<sub>4</sub> emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM). Four (4) 120-minute Draft ASTM CCM test runs were performed concurrently with all Method 5 runs. H<sub>2</sub>SO<sub>4</sub> emission results were calculated in units of lb/MMBtu. The H<sub>2</sub>SO<sub>4</sub> final results were expressed as the average of four (4) valid runs.

Diluent concentrations (%O<sub>2</sub>, %CO<sub>2</sub>) from concurrent Method 5 runs were utilized to convert H<sub>2</sub>SO<sub>4</sub> concentrations to units of lb/MMBtu. There was no diluent concentration data collected during H<sub>2</sub>SO<sub>4</sub> runs because there was insufficient sample flow to create pressure drop to collect a slip stream of the sample gas.

Prior to the first official test run, a 60-minute sample conditioning run (Run 0) was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H<sub>2</sub>SO<sub>4</sub>-collecting portion of the sample train). The conditioning run was recovered in the same manner as the official test runs.

#### VOC Testing – USEPA Methods 25A and 18

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 60-minute test runs. The Method 25A test runs were performed concurrently with three (3) 60-minute Method 18 bag collections. The final result for each VOC run was expressed as the average of three (3) runs.

For all Method 25A runs, the measured concentrations of THC were below the detection limit defined as 'less than 1%' of the calibration span of the THC instrument. Assuming worst-case scenario, the resultant VOC emissions are reported as 'less than' the defined THC detection limit and Method 18 analyses are deemed extraneous. The Method 18 bag collections have been archived.

VOC emission results were calculated in units of lb/MMBtu as propane. O<sub>2</sub> concentrations from concurrent Method 3A runs were utilized to convert VOC results to lb/MMBtu. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from nearly concurrent Method 5 runs.

### RATA Testing – USEPA Methods 3A, 7E and 10

Minute-average data points for O<sub>2</sub>, NO<sub>x</sub> and CO (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A, 7E and 10. Unless statistically inconsequential (CO), relative accuracy was determined based on nine (9) of 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

Sampling occurred at the three (3) points as specified in Section 8.1.3.2 of PS 2 during each run. The average result for each run was converted to identical units of measurement as the facility CEMS and compared for relative accuracy.

### Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm<sub>dv</sub>) were converted into units of pounds per million Btu (lb/MMBtu) by calculating an oxygen-based fuel factor (F<sub>d</sub>) for refinery gas per EPA Method 19 specifications. The heat content and F<sub>d</sub> factor were calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents.

### Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions compliance test runs and RATA test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test report.

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*End of Section*

## 2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

**Table 2-1:  
Crude/Vacuum Heater – FPM Emissions**

| Run No.                   |   | 1*       | 2        | 3        | 4        | Average         |
|---------------------------|---|----------|----------|----------|----------|-----------------|
| Date (2018)               |   | Jun 13   | Jun 13   | Jun 13   | Jun 13   |                 |
| Start Time (approx.)      |   | 08:06    | 10:45    | 13:25    | 16:16    |                 |
| Stop Time (approx.)       |   | 10:14    | 12:51    | 15:35    | 18:23    |                 |
| <b>Process Conditions</b> |   |          |          |          |          |                 |
| P <sub>1</sub>            | Charge rate (BPD)                                   | 145,500  | 145,400  | 145,300  | 145,100  | <b>145,300</b>  |
| F <sub>d</sub>            | Oxygen-based F-factor (dscf/MMBtu)                  | 8,319    | 8,319    | 8,319    | 8,319    |                 |
| H <sub>i</sub>            | Actual heat input (MMBtu/hr)                        | 300      | 296      | 295      | 300      | <b>297</b>      |
| <b>Gas Conditions</b>     |   |          |          |          |          |                 |
| O <sub>2</sub>            | Oxygen (dry volume %)                               | 7.6      | 7.3      | 8.0      | 7.4      | <b>7.6</b>      |
| CO <sub>2</sub>           | Carbon dioxide (dry volume %)                       | 7.7      | 8.0      | 7.7      | 8.0      | <b>7.9</b>      |
| T <sub>s</sub>            | Sample temperature (°F)                             | 292      | 291      | 293      | 293      | <b>292</b>      |
| B <sub>w</sub>            | Actual water vapor in gas (% by volume)             | 14.4     | 15.4     | 13.9     | 15.2     | <b>14.8</b>     |
| <b>Gas Flow Rate</b>      |   |          |          |          |          |                 |
| Q <sub>a</sub>            | Volumetric flow rate, actual (acfm)                 | 113,000  | 112,000  | 112,000  | 104,000  | <b>109,000</b>  |
| Q <sub>s</sub>            | Volumetric flow rate, standard (scfm)               | 77,400   | 76,200   | 76,400   | 71,000   | <b>74,500</b>   |
| Q <sub>std</sub>          | Volumetric flow rate, dry standard (dscfm)          | 66,300   | 64,500   | 65,800   | 60,200   | <b>63,500</b>   |
| <b>Sampling Data</b>      |   |          |          |          |          |                 |
| V <sub>mstd</sub>         | Volume metered, standard (dscf)                     | 85.79    | 83.13    | 84.59    | 77.64    | <b>81.79</b>    |
| %I                        | Isokinetic sampling (%)                             | 103.6    | 103.2    | 103.0    | 103.2    | <b>103.1</b>    |
| <b>Laboratory Data</b>    |   |          |          |          |          |                 |
| m <sub>filter</sub>       | Matter collected on filter(s) (g)                   | 0.00332  | 0.00248  | 0.00180  | 0.00177  |                 |
| m <sub>s</sub>            | Matter collected in solvent rinse(s) (g)            | 0.00446  | 0.00193  | 0.00255  | 0.00328  |                 |
| m <sub>n</sub>            | Total FPM (g)                                       | 0.00778  | 0.00441  | 0.00435  | 0.00505  |                 |
| <b>FPM Results</b>        |   |          |          |          |          |                 |
| C <sub>sd</sub>           | Particulate Concentration (lb/dscf)                 | 2.00E-07 | 1.17E-07 | 1.13E-07 | 1.43E-07 | <b>1.25E-07</b> |
| E <sub>lb/hr</sub>        | Particulate Rate (lb/hr)                            | 0.796    | 0.453    | 0.447    | 0.518    | <b>0.473</b>    |
| E <sub>Fd</sub>           | Particulate Rate - F <sub>d</sub> -based (lb/MMBtu) | 0.00261  | 0.00150  | 0.00153  | 0.00185  | <b>0.00162</b>  |

Average includes 3 runs. \* indicates that the run is not included in the average due to interferences from foreign matter comprised of metal not otherwise consistent with combustion process.

**Table 2-2:  
Crude/Vacuum Heater – H<sub>2</sub>SO<sub>4</sub> Emissions**

| Run No.  |  | 1        | 2        | 3        | 4        | Average         |
|--|--|----------|----------|----------|----------|-----------------|
| Date (2018)  |  | Jun 13   | Jun 13   | Jun 13   | Jun 13   |                 |
| Start Time (approx.)   |  | 08:06    | 10:45    | 13:25    | 16:16    |                 |
| Stop Time (approx.)  |  | 10:14    | 12:52    | 15:35    | 18:23    |                 |
| <b>Process Conditions</b>  |  |          |          |          |          |                 |
| P <sub>1</sub>   | Charge rate (BPD)  | 145,500  | 145,400  | 145,300  | 145,100  | <b>145,300</b>  |
| F <sub>d</sub>   | Oxygen-based F-factor (dsct/MMBtu)                                     | 8,319    | 8,319    | 8,319    | 8,319    |                 |
| H <sub>i</sub>   | Actual heat input (MMBtu/hr)   | 300      | 296      | 295      | 300      | <b>298</b>      |
| <b>Gas Conditions<sup>1</sup></b>                                |  |          |          |          |          |                 |
| O <sub>2</sub>   | Oxygen (dry volume %)  | 7.6      | 7.3      | 8.0      | 7.4      | <b>7.6</b>      |
| CO <sub>2</sub>  | Carbon dioxide (dry volume %)  | 7.7      | 8.0      | 7.7      | 8.0      | <b>7.9</b>      |
| T <sub>s</sub>   | Sample temperature (°F)  | 295      | 296      | 297      | 296      | <b>296</b>      |
| B <sub>w</sub>   | Actual water vapor in gas (% by volume)                                | 14.3     | 14.3     | 13.4     | 13.0     | <b>13.7</b>     |
| <b>Sampling Data</b>   |  |          |          |          |          |                 |
| V <sub>metd</sub>  | Volume metered, standard (dsct)  | 40.66    | 40.38    | 40.19    | 40.25    | <b>40.37</b>    |
| <b>Laboratory Data (Ion Chromatography)</b>                      |  |          |          |          |          |                 |
| m <sub>n</sub>   | Total H <sub>2</sub> SO <sub>4</sub> collected (mg)                    | 1.0053   | 1.1125   | 1.1867   | 1.0440   |                 |
| <b>Sulfuric Acid Vapor (H<sub>2</sub>SO<sub>4</sub>) Results</b> |  |          |          |          |          |                 |
| C <sub>sd</sub>  | H <sub>2</sub> SO <sub>4</sub> Concentration (lb/dsct)                 | 5.45E-08 | 6.07E-08 | 6.51E-08 | 5.72E-08 | <b>5.94E-08</b> |
| C <sub>sd</sub>  | H <sub>2</sub> SO <sub>4</sub> Concentration (ppmdv)                   | 0.214    | 0.239    | 0.256    | 0.225    | <b>0.233</b>    |
| E <sub>Fd</sub>  | H <sub>2</sub> SO <sub>4</sub> Rate - F <sub>d</sub> -based (lb/MMBtu) | 0.000713 | 0.000777 | 0.000878 | 0.000737 | <b>0.000776</b> |

<sup>1</sup> Diluent concentrations from concurrent EPA Method 5 runs.

**Table 2-3:  
Crude/Vacuum Heater – PM Emissions**

| Run No.                                    |  | 1*       | 2        | 3        | 4        | Average         |
|--|--|----------|----------|----------|----------|-----------------|
| Date (2018)                                |  | Jun 13   | Jun 13   | Jun 13   | Jun 13   |                 |
| Start Time (approx.)                       |  | 08:06    | 10:45    | 13:25    | 16:16    |                 |
| Stop Time (approx.)                        |  | 10:14    | 12:51    | 15:35    | 18:23    |                 |
| <b>Process Conditions</b>                  |  |          |          |          |          |                 |
| P <sub>1</sub>                             | Charge rate (BPD)  | 145,490  | 145,445  | 145,306  | 145,094  | <b>145,282</b>  |
| F <sub>d</sub>                             | Oxygen-based F-factor (dscf/MMBtu)                                     | 8,319    | 8,319    | 8,319    | 8,319    | <b>8,319</b>    |
| H <sub>i</sub>                             | Actual heat input (MMBtu/hr)   | 300      | 296      | 295      | 300      | <b>297</b>      |
| <b>Gas Conditions</b>                      |  |          |          |          |          |                 |
| O <sub>2</sub>                             | Oxygen (dry volume %)  | 7.6      | 7.3      | 8.0      | 7.4      | <b>7.6</b>      |
| CO <sub>2</sub>                            | Carbon dioxide (dry volume %)  | 7.7      | 8.0      | 7.7      | 8.0      | <b>7.9</b>      |
| T <sub>s</sub>                             | Sample temperature (°F)  | 292      | 291      | 293      | 293      | <b>292</b>      |
| <b>FPM Results</b>                         |  |          |          |          |          |                 |
| E <sub>Fd</sub>                            | Filterable Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)         | 0.00261  | 0.00150  | 0.00153  | 0.00185  | <b>0.00162</b>  |
| <b>H<sub>2</sub>SO<sub>4</sub> Results</b> |  |          |          |          |          |                 |
| E <sub>Fd</sub>                            | H <sub>2</sub> SO <sub>4</sub> Rate - F <sub>d</sub> -based (lb/MMBtu) | 0.000706 | 0.000769 | 0.000869 | 0.000730 | <b>0.000790</b> |
| <b>PM Results<sup>1</sup></b>              |  |          |          |          |          |                 |
| E <sub>Fd</sub>                            | Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)                    | 0.00191  | 0.000726 | 0.000659 | 0.00112  | <b>0.000834</b> |

Average includes 3 runs. \* indicates that the run is not included in the average.

<sup>1</sup> PM assumed equivalent to FPM less H<sub>2</sub>SO<sub>4</sub>.



**Table 2-4:  
Crude/Vacuum Heater – VOC Emissions**

| Run No.                          |   | 1          | 2          | 3          | Average    |
|----------------------------------|---|------------|------------|------------|------------|
| Date (2018)                      |   | Jun 13     | Jun 13     | Jun 13     |            |
| Start Time (approx.)             |   | 10:46      | 11:59      | 13:46      |            |
| Stop Time (approx.)              |   | 11:46      | 12:59      | 14:46      |            |
| <b>Process Conditions</b>        |   |            |            |            |            |
| P <sub>1</sub>                   | Charge rate (BPD)                                       | 145,100    | 145,800    | 145,600    | 145,500    |
| F <sub>d</sub>                   | Oxygen-based F-factor (dscf/MMBtu)                      | 8,319      | 8,319      | 8,319      | 8,319      |
| H <sub>i</sub>                   | Actual heat input (MMBtu/hr)                            | 297        | 295        | 295        | 296        |
| <b>Gas Conditions</b>            |   |            |            |            |            |
| O <sub>2</sub>                   | Oxygen (dry volume %)                                   | 6.9        | 6.9        | 6.9        | 6.9        |
| CO <sub>2</sub>                  | Carbon dioxide (dry volume %)                           | 8.3        | 8.4        | 8.3        | 8.3        |
| B <sub>w</sub>                   | Actual water vapor in gas (% by volume) <sup>1</sup>    | 15.4       | 15.4       | 13.9       | 14.9       |
| <b>THC Results<sup>2,3</sup></b> |   |            |            |            |            |
| C <sub>sd</sub>                  | Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> ) | <0.555     | <0.555     | <0.546     | <0.552     |
| C <sub>sd</sub>                  | Concentration (lb/dscf)                                 | <6.36E-08  | <6.36E-08  | <6.25E-08  | <6.32E-08  |
| E <sub>Fd</sub>                  | Emission Rate - F <sub>d</sub> -based (lb/MMBtu)        | < 0.000791 | < 0.000787 | < 0.000777 | < 0.000785 |

<sup>1</sup> Moisture data used for ppmv to ppmdv correction obtained from nearly-concurrent M-4 runs.<sup>2</sup> For THC, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).<sup>3</sup> VOC is reported as THC since all THC results were non-detect.

**Table 2-5:  
 Crude/Vacuum Heater – O<sub>2</sub> (%dv) Relative Accuracy**

| Run No.        | Start Time | Date (2018) | RM Data (%dv) | CEMS Data (%dv) | Difference (%dv) | Difference Percent |
|----------------|------------|-------------|---------------|-----------------|------------------|--------------------|
| 1              | 08:35      | Jun 6       | 9.05          | 9.02            | 0.03             | 0.3%               |
| 2 *            | 09:07      | Jun 6       | 9.00          | 8.95            | 0.05             | 0.6%               |
| 3              | 09:38      | Jun 6       | 8.97          | 8.92            | 0.05             | 0.6%               |
| 4              | 10:09      | Jun 6       | 8.97          | 8.94            | 0.03             | 0.3%               |
| 5              | 10:42      | Jun 6       | 8.58          | 8.55            | 0.03             | 0.3%               |
| 6              | 11:14      | Jun 6       | 8.49          | 8.45            | 0.04             | 0.5%               |
| 7              | 11:46      | Jun 6       | 8.63          | 8.60            | 0.03             | 0.3%               |
| 8              | 12:17      | Jun 6       | 8.54          | 8.50            | 0.04             | 0.5%               |
| 9              | 12:50      | Jun 6       | 8.37          | 8.34            | 0.03             | 0.4%               |
| 10             | 13:24      | Jun 6       | 8.27          | 8.25            | 0.02             | 0.2%               |
| <b>Average</b> |            |             | <b>8.65</b>   | <b>8.62</b>     | <b>0.03</b>      | <b>0.4%</b>        |

**Relative Accuracy Test Audit Results**

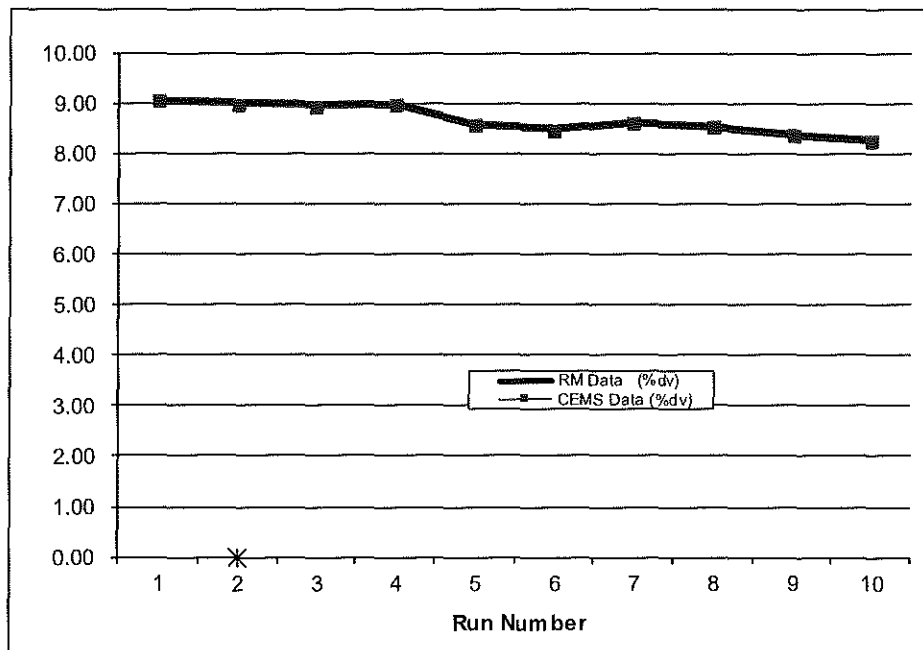
|                                   |             |                     |
|-----------------------------------|-------------|---------------------|
| Standard Deviation of Differences | 0.0087      |                     |
| Confidence Coefficient (CC)       | 0.0067      |                     |
| t-Value for 9 Data Sets           | 2.306       |                     |
| Avg. Abs. Diff. (%dv)             | <b>0.03</b> | Limit<br><b>1.0</b> |

RM = Reference Method (CleanAir Data)

062018 104217

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-6:  
 Crude/Vacuum Heater – NO<sub>x</sub> (ppmdv @ 0%O<sub>2</sub>) Relative Accuracy**

| Run No.        | Start Time | Date (2018) | RM Data (ppm@0%O <sub>2</sub> ) | CEMS Data (ppm@0%O <sub>2</sub> ) | Difference (ppm@0%O <sub>2</sub> ) | Difference Percent |
|----------------|------------|-------------|---------------------------------|-----------------------------------|------------------------------------|--------------------|
| 1              | 08:35      | Jun 6       | 41.1                            | 41.6                              | -0.5                               | -1.2%              |
| 2              | 09:07      | Jun 6       | 40.7                            | 41.6                              | -0.9                               | -2.2%              |
| 3              | 09:38      | Jun 6       | 40.0                            | 41.0                              | -1.0                               | -2.5%              |
| 4              | 10:09      | Jun 6       | 40.5                            | 41.8                              | -1.3                               | -3.2%              |
| 5 *            | 10:42      | Jun 6       | 38.6                            | 39.9                              | -1.3                               | -3.4%              |
| 6              | 11:14      | Jun 6       | 38.3                            | 39.5                              | -1.2                               | -3.1%              |
| 7              | 11:46      | Jun 6       | 39.5                            | 40.6                              | -1.1                               | -2.8%              |
| 8              | 12:17      | Jun 6       | 38.0                            | 39.2                              | -1.2                               | -3.2%              |
| 9              | 12:50      | Jun 6       | 37.4                            | 38.4                              | -1.0                               | -2.7%              |
| 10             | 13:24      | Jun 6       | 37.0                            | 37.8                              | -0.8                               | -2.2%              |
| <b>Average</b> |            |             | <b>39.2</b>                     | <b>40.2</b>                       | <b>-1.0</b>                        | <b>-2.6%</b>       |

**Relative Accuracy Test Audit Results**

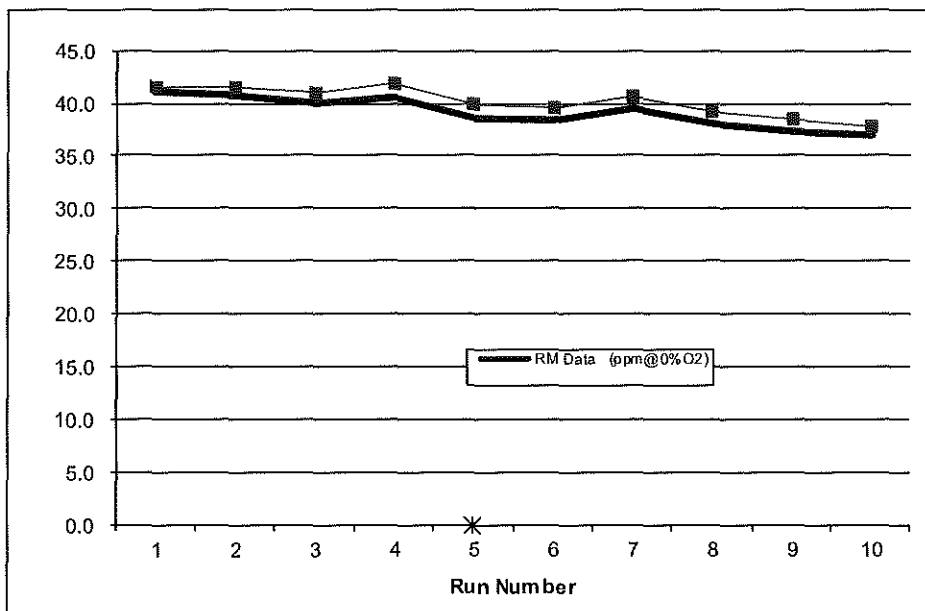
|  |       |       |
|--|-------|-------|
| Standard Deviation of Differences      | 0.245 |       |
| Confidence Coefficient (CC)            | 0.188 |       |
| t-Value for 9 Data Sets                | 2.306 |       |
|  |       | Limit |
| Relative Accuracy (as % of RM)         | 3.0%  | 20.0% |
| Relative Accuracy (as % of Appl. Std.) | 2.0%  | 10.0% |
| Appl. Std. = 60 ppm@0%O <sub>2</sub>   |       |       |

RM = Reference Method (CleanAir Data)

062018 104217

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-7:  
 Crude/Vacuum Heater – NO<sub>x</sub> (lb/MMBtu) Relative Accuracy**

| Run No.        | Start Time | Date (2018) | RM Data (lb/MMBtu) | CEMS Data (lb/MMBtu) | Difference (lb/MMBtu) | Difference Percent |
|----------------|------------|-------------|--------------------|----------------------|-----------------------|--------------------|
| 1              | 08:35      | Jun 6       | 0.0407             | 0.0422               | -0.0015               | -3.7%              |
| 2              | 09:07      | Jun 6       | 0.0403             | 0.0422               | -0.0019               | -4.7%              |
| 3              | 09:38      | Jun 6       | 0.0396             | 0.0416               | -0.0020               | -5.1%              |
| 4              | 10:09      | Jun 6       | 0.0402             | 0.0424               | -0.0022               | -5.5%              |
| 5 *            | 10:42      | Jun 6       | 0.0382             | 0.0405               | -0.0023               | -6.0%              |
| 6              | 11:14      | Jun 6       | 0.0380             | 0.0401               | -0.0021               | -5.5%              |
| 7              | 11:46      | Jun 6       | 0.0391             | 0.0412               | -0.0021               | -5.4%              |
| 8              | 12:17      | Jun 6       | 0.0377             | 0.0398               | -0.0021               | -5.6%              |
| 9              | 12:50      | Jun 6       | 0.0371             | 0.0390               | -0.0019               | -5.1%              |
| 10             | 13:24      | Jun 6       | 0.0367             | 0.0384               | -0.0017               | -4.6%              |
| <b>Average</b> |            |             | <b>0.0388</b>      | <b>0.0408</b>        | <b>-0.0019</b>        | <b>-5.0%</b>       |

**Relative Accuracy Test Audit Results**

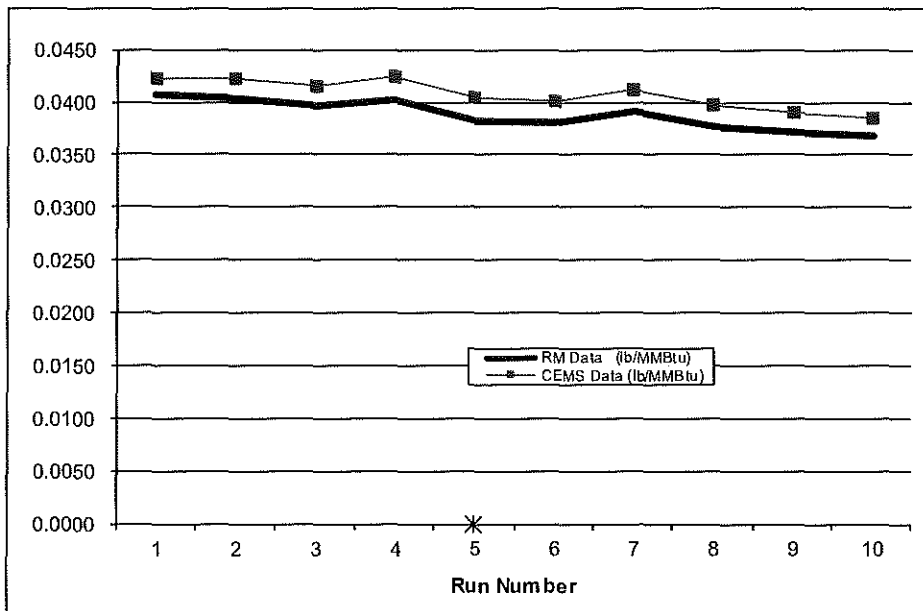
|  |          |       |
|--|----------|-------|
| Standard Deviation of Differences      | 0.000224 |       |
| Confidence Coefficient (CC)            | 0.000172 |       |
| t-Value for 9 Data Sets                | 2.306    |       |
|  |          | Limit |
| Relative Accuracy (as % of RM)         | 5.5%     | 20.0% |
| Relative Accuracy (as % of Appl. Std.) | 4.2%     | 10.0% |
| Appl. Std. = 0.05 lb/MMBtu             |          |       |

RM = Reference Method (CleanAir Data)

062018 104217

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-8:  
 Crude/Vacuum Heater – CO (lb/MMBtu) Relative Accuracy**

| Run No.        | Start Time | Date (2018) | RM Data (lb/MMBtu) | CEMS Data (lb/MMBtu) | Difference (lb/MMBtu) | Difference Percent |
|----------------|------------|-------------|--------------------|----------------------|-----------------------|--------------------|
| 1              | 08:35      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 2              | 09:07      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 3              | 09:38      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 4              | 10:09      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 5              | 10:42      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 6              | 11:14      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 7              | 11:46      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 8              | 12:17      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 9              | 12:50      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| 10             | 13:24      | Jun 6       | 0.0000             | 0.0000               | 0.0000                | 0.0%               |
| <b>Average</b> |            |             | <b>0.0000</b>      | <b>0.0000</b>        | <b>0.0000</b>         | <b>0.0%</b>        |

**Relative Accuracy Test Audit Results**

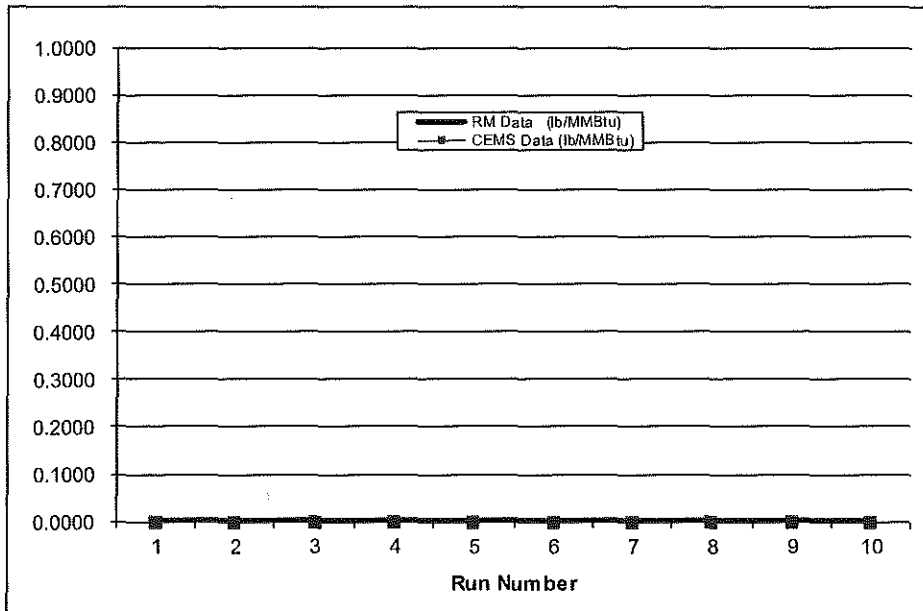
|  |          |       |
|--|----------|-------|
| Standard Deviation of Differences      | 0.000000 |       |
| Confidence Coefficient (CC)            | 0.000000 |       |
| t-Value for 10 Data Sets               | 2.262    |       |
|  |          | Limit |
| Relative Accuracy (as % of RM)         | 0.0%     | 10.0% |
| Relative Accuracy (as % of Appl. Std.) | 0.0%     | 5.0%  |
| Appl. Std. = 1 lb/MMBtu                |          |       |
| Avg. Abs. Diff. + CC (lb/MMBtu)        | 0.000    | 5.0   |

RM = Reference Method (CleanAir Data)

062018 104217

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)

RATA calculations are based on all 10 runs.



AUG 10 2018

CleanAir Project No. 13582-2

Marathon Petroleum Company LP

Detroit Refinery

Revision 0, Final Report

Report on Compliance &amp; RATA Testing

AIR QUALITY DIVISION

Page 13

### 3. DESCRIPTION OF INSTALLATION

#### Process Description

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to other units in the refinery for further processing. The Crude Unit consists of process vessels (including heat exchangers and fractionation columns), the Alcorn Heater (EU05-CRUDEHTR-S1), tanks, containers, compressors, pumps, piping drains, and various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Vacuum Unit (EU04-VACUUM) separates the reduced crude from the crude unit through the use of a vacuum column. The reduced crude is separated into light vacuum gas oil, medium vacuum gas oil, heavy vacuum gas oil and a bottoms product called flux. The various fractions are sent to other units in the refinery for further processing. The vacuum unit consists of process vessels (including heat exchangers and vacuum column), two process heaters, tanks, containers, two cooling towers, flare, compressors, pumps, piping drains and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

Both the Crude Heater (EU05-CRUDEHTR-S1) and the Vacuum Heater (EU04-VACHTR-S1) are fired by refinery fuel gas. Emissions are vented to the atmosphere via a common stack known as the Crude/Vacuum Heater Stack (SV04-H1-05-H1) where testing was performed.

#### Test Location

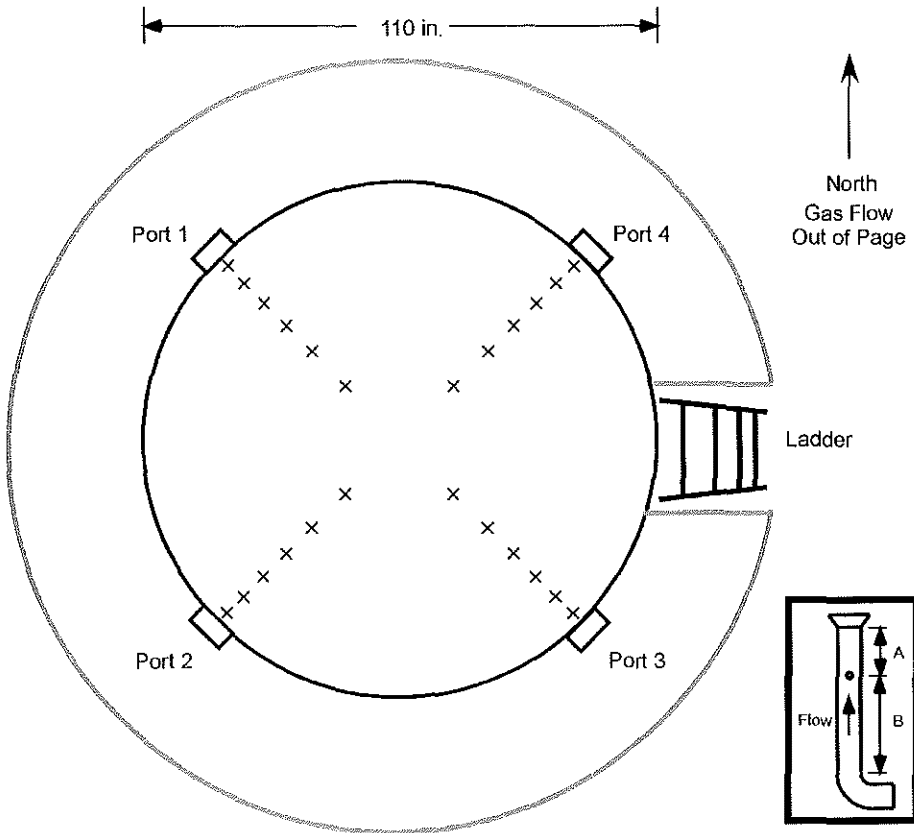
The sample point locations were determined by EPA Method 1 and Performance Specification 2. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 14 and 15 represent the layout of the test location.

**Table 3-1:  
Sampling Point Information**

| Source   | Method (USEPA) | Run No. | Ports | Points per Port | Minutes per Point | Total Minutes | Figure           |
|--|----------------|---------|-------|-----------------|-------------------|---------------|------------------|
| <u>Crude/Vacuum Heater</u>   |                |         |       |                 |                   |               |                  |
| FPM  | 5              | 1-4     | 4     | 6               | 5                 | 120           | 3-1              |
| H <sub>2</sub> SO <sub>4</sub>   | Draft ASTM CCM | 1-4     | 1     | 1               | 120               | 120           | N/A <sup>1</sup> |
| O <sub>2</sub> / CO <sub>2</sub> / CH <sub>4</sub> / C <sub>2</sub> H <sub>6</sub> / THC | 3A / 18 / 25A  | 1-3     | 1     | 3               | 20                | 60            | N/A <sup>1</sup> |
| O <sub>2</sub> / CO <sub>2</sub> / NO <sub>x</sub> / CO                                  | 3A / 7E / 10   | 1-10    | 1     | 3               | 7                 | 21            | 3-2              |

<sup>1</sup> Draft ASTM CCM and EPA Method 25A sampling occurred at a single point near the center of the duct.

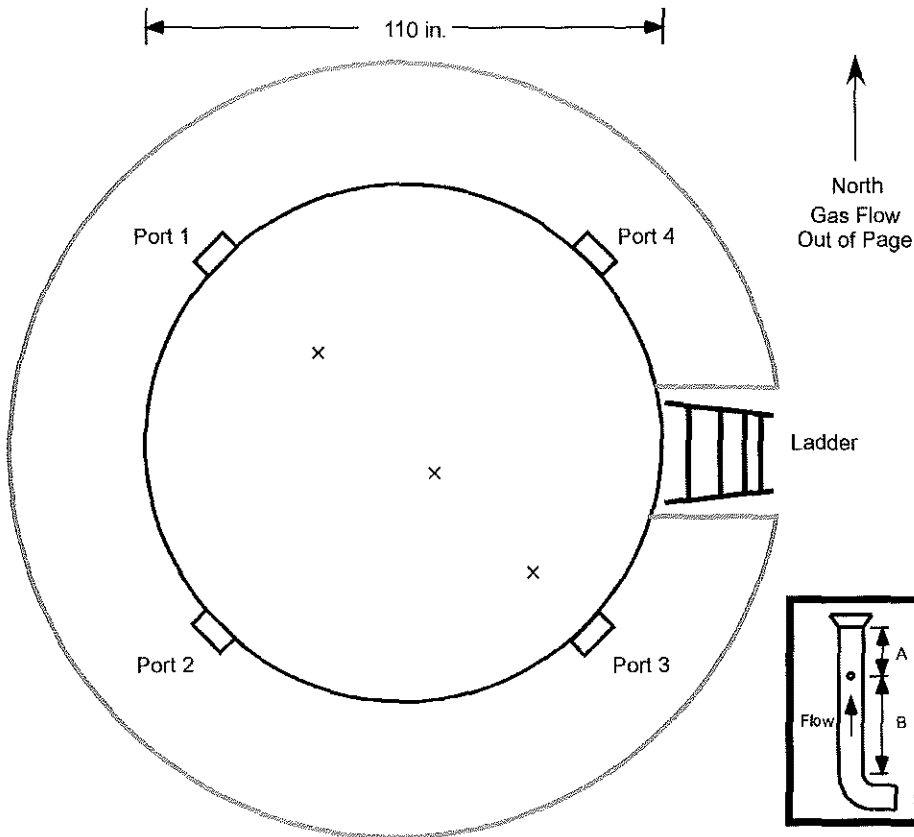
**Figure 3-1:  
 PM Sample Point Layout**



| Sampling Point | % of Stack Diameter | Port to Point Distance (inches) |
|----------------|---------------------|---------------------------------|
| 1              | 35.6                | 39.2                            |
| 2              | 25.0                | 27.5                            |
| 3              | 17.7                | 19.5                            |
| 4              | 11.8                | 13.0                            |
| 5              | 6.7                 | 7.4                             |
| 6              | 2.1                 | 2.3                             |

Duct diameters upstream from flow disturbance (A): 5.3      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 2.4      Limit: 2.0

**Figure 3-2:  
 O<sub>2</sub>, CO<sub>2</sub> & NO<sub>x</sub> Sample Point Layout**



| Sampling Point | Port to Point Distance (meters) | Port to Point Distance (inches) |
|----------------|---------------------------------|---------------------------------|
| 1              | 2.0                             | 78.7                            |
| 2              | 1.2                             | 47.2                            |
| 3              | 0.4                             | 15.7                            |

Duct diameters upstream from flow disturbance (A): 5.3      Limit: 0.5  
 Duct diameters downstream from flow disturbance (B): 2.4      Limit: 2.0

End of Section



## 4. METHODOLOGY

### Procedures and Regulations

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The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environmental Quality (DEQ). These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix.

In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications, along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's AZLA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

#### Title 40 CFR Part 60, Appendix A

|            |  |
|------------|--|
| Method 1   | "Sample and Velocity Traverses for Stationary Sources"   |
| Method 2   | "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"   |
| Method 3   | "Gas Analysis for the Determination of Dry Molecular Weight"   |
| Method 3A  | "Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)" |
| Method 3B  | "Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air"  |
| Method 4   | "Determination of Moisture Content in Stack Gases"   |
| Method 5   | "Determination of Particulate Matter Emissions from Stationary Sources"  |
| Method 7E  | "Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"                              |
| Method 10  | "Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"                             |
| Method 18  | "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"  |
| Method 25A | "Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"   |

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## Title 40 CFR Part 60, Appendix B Performance Specifications

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- PS 2 "Specifications and Test Procedures for SO<sub>2</sub> and NO<sub>x</sub> Continuous Emission Monitoring Systems in Stationary Sources"
- PS 3 "Specifications and Test Procedures for O<sub>2</sub> and CO<sub>2</sub> Continuous Emission Monitoring Systems in Stationary Sources"
- PS 4A "Specifications and Test Procedures for CO Continuous Emission Monitoring Systems in Stationary Sources"

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## CTM-013 (Mod.)/Draft ASTM Controlled Condensation Method (Draft ASTM CCM)

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"Determination of Sulfur Oxides Including Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Vapor and Mist from Stationary Sources Using a Controlled Condensation Sampling Apparatus"

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## Methodology Discussion

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### *FPM – USEPA Method 5*

FPM emissions were determined using EPA Method 5.

The front-half of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 248°F ± 25°F and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

After exiting the front-half filter, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars were collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters dessicated for 24 hours at ambient temperature. The front-half rinses were evaporated at ambient temperature and pressure. The masses from each fraction were then summed for a total FPM mass.

### *H<sub>2</sub>SO<sub>4</sub> Testing – Draft ASTM CCM*

H<sub>2</sub>SO<sub>4</sub> emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM).

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of 650°F ± 25°F and a quartz fiber filter (to remove particulate matter) maintained at the same temperature as the probe. The sample was then passed through a glass coil condenser for collection of sulfuric acid vapor and/or mist.

A second quartz fiber filter (referred to as the sulfuric acid mist (SAM) filter) is located at the condenser outlet for the collection of residual SAM not collected by the condenser. The condenser temperature is regulated by a water jacket and the SAM filter is regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at  $140^{\circ}\text{F} \pm 9^{\circ}\text{F}$  plus  $2^{\circ}\text{F}$  for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved sulfur dioxide ( $\text{SO}_2$ ) into the  $\text{H}_2\text{SO}_4$ -collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then continued through a series of four (4) glass knock-out jars; two (2) containing water, one (1) empty and one (1) containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set is maintained below  $68^{\circ}\text{F}$ . The sample gas then flowed into a dry gas meter, where the collected sample gas volume was determined by means of a calibrated, dry gas meter or an orifice-based flow meter.

The  $\text{H}_2\text{SO}_4$ -collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI  $\text{H}_2\text{O}$  as the recovery/extraction solvent; any  $\text{H}_2\text{SO}_4$  disassociates into sulfate ion ( $\text{SO}_4^{2-}$ ) and is stabilized in the  $\text{H}_2\text{O}$  matrix until analysis.

Samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for ion chromatography (IC) analysis.

#### *O<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub> and CO Testing – USEPA Methods 3A, 7E and 10; Performance Specifications 2, 3 and 4A*

Reference method (RM) oxygen ( $\text{O}_2$ ) concentrations were determined using a paramagnetic analyzer per EPA Method 3A. RM  $\text{NO}_x$  emissions were determined using a chemiluminescent analyzer per EPA Method 7E. RM CO emissions were determined using an infrared analyzer per EPA Method 10. Carbon dioxide ( $\text{CO}_2$ ) concentrations were determined using an NDIR analyzer per EPA Method 3A for supplemental purposes.

Sample gas was extracted at a constant rate, conditioned to remove moisture, and delivered to an analyzer bank which measured concentration on a dry basis (units of %dv or ppm<sub>dv</sub>).

Calibration error checks were performed by introducing zero nitrogen ( $\text{N}_2$ ), high and mid-range calibration gases to the inlet of each analyzer during calibration error checks. Bias checks were performed before and after each sampling run by introducing calibration gas to the inlet of the sampling system's heated filter. Documentation of interference checks and  $\text{NO}_2$  converter efficiency checks are included in Appendix D of this report.

Minute-average data points for  $\text{O}_2$ ,  $\text{NO}_x$  and CO (dry basis) were collected over a period of 21 minutes for each RATA run. Sampling occurred at the three points specified in Section 8.1.3.2 of Performance Specification (PS) 2 during each run. A single port was used for each run.

Per EPA Methods 3A, 7E and 10, the average results for each run was drift-corrected. The average result for each run was converted to identical units of measurement as the facility CEMS and compared for relative accuracy (RA).

*VOC Testing – USEPA Methods 18 and 25A*

VOC emissions were determined using EPA Method 25A to quantify THC emissions which were assumed equivalent to VOC emissions.

The Method 25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was delivered at 250°F to a flame ionization analyzer (FIA), which continuously measured minute-average THC concentration expressed in terms of propane (C<sub>3</sub>H<sub>8</sub>) on an actual (wet) basis. FIA calibration was performed by introducing zero air, high, mid- and low range C<sub>3</sub>H<sub>8</sub> calibration gases to the inlet of the sampling system's heated filter. Bias checks were performed before and after each sampling run in a similar manner.

The Method 18 sampling system consisted of a gas conditioner (for moisture removal), TFE sample lines, TFE-coated diaphragm pump and a mass flow meter ("Direct Pump Sampling Procedure"). This system pulled a slipstream of the flue gas from the Method 25A sample delivery system and delivered it into a Tedlar bag at a constant rate. The moisture condensate was not collected for analysis as CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are insoluble in water. Each bag was filled over a period of 60 minutes for each test run. The Tedlar bags were not analyzed because all Method 25A runs resulted in non-detect concentrations.

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*End of Section*