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URS 40942612

Source Test Report

Delayed Coking Unit
Atmospheric Depressurization Vent

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Prepared for:

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1.0 Introduction

Marathon Petroleum Company LLC, Michigan Refining Division (MPC Detroit), operates a petroleum refinery in Detroit, Michigan. The MPC-Detroit Refinery is a petroleum refinery with the capacity to convert approximately 120,000 barrels of crude oils per calendar day (bbl/cd) into finished products. The new EG70-Coker delayed coking unit (DCU) was commissioned in November 2012 and is covered under the Michigan Department of Environmental Quality (MDEQ) Permit 63-08D.

URS prepared a Test Plan that described the sampling and analytical methodologies to be employed to measure non-methane, non-ethane volatile organic compounds (NMNE VOCs), hydrogen sulfide (H_2S), and total filterable particulate matter (FPM) mass emission rates from the DCU Vent during a normal venting cycle (see Section 1.2). Molecular weight, moisture (H_2O) concentrations, and DCU Vent exhaust gas flow rate were also measured to develop target compound mass emission rates. The Test Plan was approved by the MDEQ in May 2014.

Because of the unique nature of this intermittent process vent, modifications to existing U.S. EPA-approved reference methods were made to collect accurate and precise data from this source. Due to the extremely high moisture content (greater than 99%) and the high velocity (greater than 200 mph) of the gas stream, the dynamic nature of the gas stream's characteristics, and the variable batch nature of the delayed coking process, URS implemented the modified reference methods and alternative quality assurance/quality control (QA/QC) criteria discussed in the Test Plan (see Section 5.0).

This *Source Test Report for Atmospheric Depressurization Vent* presents the results of the 2014 Source Test in the following sections:

- Section 2.0 – Summary of Results;
- Section 3.0 – Sampling and Analytical Procedures;
- Section 4.0 – Calculations; and
- Section 5.0 – Quality Assurance Objectives for Measurement Data.

Report appendices provide copies of raw data, including chain-of-custody forms, sampling logs, raw analytical instrument output, laboratory reports, DCU process data, and sampling equipment calibration forms. General information regarding the testing is summarized in Table 1-1.

Table 1-1. Source Test Information

Facility Name	Marathon Petroleum Company, Michigan Refining Division
Contact Person(s)	Crystal Davis
Telephone Number	313-297-6115
Facility Address	1300 South Fort Street, Detroit, Michigan 48217
Types of Process Sampled	DCU Atmospheric Depressurization Vent Gas Stream
Person Responsible for Conducting Source Test	Jesse Rocha
Telephone Number	512-419-5726
Testing Company Name	URS Corporation
Testing Company Address	9400 Amberglen Boulevard Austin, Texas 78729
Person(s) Conducting Source Test	Jesse Rocha Kevin McGinn Carl Galloway Dave Maxwell Megan Bowien Levi Wolfe
Modified U.S. EPA Reference Methods Performed	U.S. EPA Methods 1, 2, 3, 4, 5, 18, and 25A U.S. EPA Other Test Method 12
Dates of Source Testing	July 8 through 11, 2014

1.1 Delayed Coking Unit – Process Description

The EG70 Delayed Coker converts Vacuum Resid (Crude Vacuum Tower Bottoms), a product normally sold as asphalt or blended into residual fuel oil, into lighter, more valuable products. The Vacuum Resid feedstock is heated before it enters the main fractionator, where lighter material vaporizes. The fractionator bottoms are routed through a fired heater (Coker Charge Heater) and then into a coke drum. The heat within the coke drum causes cracking reactions to produce the coke, which accumulates in the coke drum, and hydrocarbon vapors which are carried overhead from the coke drum back to the fractionator. The fractionator produces gasoil, distillate, and naphtha streams which are sent to downstream units for additional processing. The fractionator overhead is directed to the Coker Gas Plant where it is separated into LPG and offgas streams. The LPG and offgas streams are sent to downstream units for additional processing.

Petroleum (pet) coke eventually fills the coke drum; subsequently the drum is isolated, purged of hydrocarbon vapors, cooled, and opened. A typical Delayed Coker uses at least two coking drums so that one can be filled while the other is being de-coked.

At the end of each coke drum filling cycle, the full coke drum is switched off-line, stripped with steam to remove residual hydrocarbons, flooded with quench water, and depressured. Coke is cut from the drum with high pressure water jets.

The MPC Detroit coker includes two redundant vapor recovery compressors. The compressors allow the coke drums to be vented to atmosphere only after the drum pressure decreases to two pounds per square inch gauge (psig).

1.2 Source Test Objectives

The objective of the source test is to quantify emissions from the DCU vent. The DCU vent gas stream was tested pursuant to the Test Plan using direct source testing methodologies. The sampling and analytical methods employed during the source test and any modifications to the EPA-approved reference methods (RMs) are presented in subsequent sub-sections.

The DCU vent gas stream was sampled pursuant to the Test Plan using direct source testing methodologies to quantify the emissions of the following target compounds:

- NMNE VOC;
- Methane;
- Ethane;
- Hydrogen sulfide (H_2S); and
- Total particulate matter (Total PM).

Table 1-2 presents the sampling durations for each target compound during the batch cycle of the DCU vent.

Valid gas samples were collected during three (3) separate venting cycles of the DCU (Runs 2, 3, and 4). A complete set of valid results for Run 1 was not collected due to loss of data from one of the THC analyzers.

1.3 Source Test Strategy

A venting cycle is defined in the Test Plan as the period of time between the activation of the vent (i.e., opening) and the optimal depressurization of a coke drum to atmosphere that is necessary before the draining and coke-cutting cycles can begin.

Table 1-2 presents the test run durations of each modified sampling system during a given test run. Modified sampling methods are described in detail in Section 3.0. URS began collecting all gas samples within one (1) minute of vent activation during each test run unless otherwise noted. Gas samples were collected until the coke drum reached optimal depressurization, for as long as the sampling equipment remained operable within acceptable performance ranges, or until health and safety limitations were encountered.

Results for Run 1 are not reported because a complete set of valid samples was not collected during this sampling interval.

Section 2.0 of this report presents the averages of target compound mass emission rates measured during each venting condition.

Table 1-2. Sampling Train Durations

Run No.	Date	Time	Sampling Duration (min)	Sampling Method
2	7/9/14	16:37-17:30	53	U.S. EPA Method 5
	7/9/14	16:37-17:30	53	U.S. EPA Methods 18/25A/OTM 12
3	7/10/14	13:05-13:27	22	U.S. EPA Method 5
	7/10/14	13:05-13:27	22	U.S. EPA Methods 18/25A/OTM 12
4	7/11/14	08:32-09:10	38	U.S. EPA Method 5
	7/11/14	08:32-09:10	38	U.S. EPA Methods 18/25A/OTM 12

1.4 Quality Assurance Summary

Any sampling and/or analytical QA/QC issues associated with the data obtained through the 2014 Source Test are described in Section 5.0. Table 1-3 presents QA summaries for each of the modified U.S. EPA reference methods performed on the DCU.

A review of the data quality associated with the measurements performed during all runs indicates that these data are supportable and usable for the purpose intended. A full set of data could not be obtained during Run 1 due to the loss of data from one of the THC analyzers.

Table 1-3. Quality Assurance Summary

Parameter	Deviations from the Test Plan and Quality Assurance/Quality Control Issues
Sampling Points, Velocity and Volumetric Flow Rate, Dry Gas Molecular Weight, and Moisture Concentration	None
Total Particulate Matter Determination	The Test Plan describes a single PM sampling train per vent cycle. During the 2014 Source Test, two PM sampling trains (A and B for each run) were collected simultaneously in order to minimize the potential for collecting an incomplete set of data for a given vent cycle. The replicate sample that resulted in the greater sample volume was chosen for analysis, and the other sample was archived by the laboratory. As a result, the reported PM results from Runs 2, 3, and 4 were derived using samples Train 1, Train 2, and Train 2, respectively. Minor temperature excursion for probe temperature during Run 3 Train 2. The target sample time of 30-45 minutes was not met for Runs 1 and 3 due to a short vent cycle (24 and 22 minutes respectively). Field blank results for probe and nozzle rinse are similar to the results for the vent gas. Vent gas results are considered conservative and are not qualified.
Methane and Ethane Concentrations and Dilution Sampling System	None
Hydrogen Sulfide Concentrations and Dilution Sampling System	None
Total Hydrocarbon Concentration and Dilution Sampling System	During Run 1, the signal output of the high level THC analyzer was lost. As hydrocarbon readings entered this range, this run was not used in emissions calculations, and Run 4 performed to replace it. The THC2 analyzer response to the mid-level calibration gas at the conclusion of Runs 1 and 4 were outside of the 3.0% drift check criteria (-3.6 and -4.7% respectively). The Run 1 data was not used, and has no effect on data quality. Following Run 4, a 4-point post test calibration was performed as per EPA Method 25A. The data were evaluated against the resulting curve. The data were then corrected to the new calibration curve, providing the more conservative emissions measurement. The use of the revised, bias corrected data may provide a positive bias to the data. The THC1 analyzer response to the mid-level calibration gas at the conclusion of Run 4 was outside of the 3.0% drift check criteria (-8.7%). Following Run 4, a 4-point post test calibration was performed as per EPA Method 25A. The data were evaluated against the resulting curve. The data were then corrected to the new calibration curve, providing the more conservative emissions measurement. The use of the revised, bias corrected data may provide a positive bias to the data.

2.0 Summary of Results

This section presents a summary of process operations during the Source Test as well as selected methane, ethane, hydrogen sulfide, NMNE VOC, and PM emissions data. Valid NMNE VOC results could not be obtained during Run 1 due to the loss of data from one of the THC analyzers. The valid PM, methane, ethane, and hydrogen sulfide samples collected during Run 1 were archived as a complete data set could not be collected. Table 2-1 presents the summary of results for this test program.

Table 2-1. Summary of Results

Run No.	Date	Methane Mass Emission Rate (lbs/cycle)	Ethane Mass Emission Rate (lbs/cycle)	H_2S Mass Emission Rate (lbs/cycle)	NMNE VOC Mass Emission Rate (lbs/cycle)	Particulate Matter Mass Emission Rate (lbs/cycle)
2	7/09/14	52.3	10.7	<0.84	0.0	<0.0424
3	7/10/14	5.1	1.1	<0.03	0.18	<0.0623
4	7/11/14	18.9	3.8	0.276	53.9	<0.0456

2.1 DCU Process Operations

The DCU was operated at conditions reflective of "normal" unit operations during the source test. During the source test, the DCU was vented to atmosphere after the internal pressure of the coke drum reached approximately 2 psig. This venting pressure is consistent with the normal operation of the DCU.

Sampling durations were determined using the venting cycle start and end times recorded by URS scientists. The venting cycle start times corresponded to the initial differential pressure increase within the vent duct, as reported by sampling instrumentation, rounded to the nearest whole minute. In many cases, the venting cycle end times corresponded to the measurement of zero (0) differential pressure in the vent pipe using U.S. EPA Method 2, "*Determination of Stack Gas Velocity and Flow Rate from Stationary Sources (Type-S Pitot Tube).*"

2.2 Data Reduction Approach

Mass emission rates are typically expressed using an industry standard of mass per unit time, such as pounds per hour (lbs/hr), by relating the average concentration of a target compound to the average volumetric flow rate of a gas stream through a stack or vent. However, the use of a simple average is inappropriate for developing an emissions profile for the intermittent and dynamic characteristics of the atmospheric depressurization vent source, so the duration and profile of each complete venting cycle varied according to the batch process.

The data reduction approach used in this report integrates target compound mass emission rates as pounds per minute (lbs/min) throughout the complete venting cycle, starting at the point of vent activation and ending at the point of optimal depressurization of the coke drum. Total mass emission rates are expressed in this report as mass per batch cycle (lbs/cycle).

2.3 Results for Vent Gas Volumetric Flow Rate

Vent gas volumetric flow rate was measured according to modified U.S. EPA Methods 2, "*Determination of Stack Gas Velocity and Volumetric Flow Rate*," 3, "*Gas Analysis for the Determination of Dry Molecular Weight*," and 4, "*Determination of Moisture Content in Stack Gases*." These methods were performed in conjunction with each modified U.S. EPA Method 5 sampling train. Table 2-2 presents average volumetric flow rate and other operating data associated with the modified sampling train.

It was not practicable to measure the oxygen or carbon dioxide concentrations in the sample gas using U.S. EPA Method 3 due to the low dry gas percentage (less than 2% of the total). The molecular weight of the dry fraction of the DCU gas was therefore assumed to be equal to methane (16.0 g/g-mol), the most abundant compound detected in the vent gas stream after water. The estimated dry gas molecular weight had an insignificant impact on the calculation of wet gas molecular weight as the average moisture concentration was slightly in excess of 99%.

Table 2-2. Isokinetic Sampling Data

Run No.	Analytical Parameter	Average Vent Temperature (°F)	Velocity (ft/sec)	Vent Gas Moisture (%)	Avg Flow Rate (acfm)	Avg Flow Rate (dscfm)	Volume at Meter (dscf)	Isokinetic Sampling Rate (%)
2[a]	Particulate Matter	255	228	99.3	10,723	51	1.153	84.2
3[b]	Particulate Matter	231	342	99.2	16,116	95	0.550	50.8
4[b]	Particulate Matter	237	232	98.9	10,955	89	1.329	76.0

[a] Results from PM Train 1

[b] Results from PM Train 2

2.4 Results for Methane, Ethane, and Hydrogen Sulfide Emissions

Methane, ethane, and hydrogen sulfide concentrations were measured according to modified U.S. EPA Method 18, "*Measurement of Gaseous Organic Compound Emissions by Gas Chromatography*" and the dilution sampling system procedures described in U.S. EPA Other Test Method 12, "*Protocol for the Source Testing, Analysis, and Reporting of VOC Emissions from Hot Mix Asphalt Plant Dryers*."

2.4.1 Results for Methane and Ethane

Bag samples were collected from the same dilution sampling system used for the measurement of total hydrocarbon (THC) concentrations by modified U.S. EPA Method 25A, "*Determination of Total Gaseous Organic Concentrations Using a Flame Ionization Analyzer*," and modified Other Test Method 12. An integrated bag sample of vent gas was collected during a venting cycle and analyzed for methane and ethane by gas chromatograph with flame ionization detector (GC/FID) and for hydrogen sulfide (H_2S) by a gas chromatograph with flame photometric detector (GC/FPD). All analyses were performed in triplicate. Concentration results are presented as parts per million by volume, wet basis (ppmvw).

Raw GC/FID results were multiplied by the dilution ratios (DR) developed on a test run-specific basis through the operation of the dilution sampling system (see Section 2.5).

Based on past practices, URS assumed methane/propane and ethane/propane equivalency factors to be 1/3 and 2/3, respectively. These factors were multiplied by the methane and ethane concentrations (quantified by GC/FID), respectively, to determine methane/propane equivalent and ethane/propane equivalent concentrations. Methane/propane equivalent and ethane/propane equivalent concentrations were then subtracted from average THC concentrations to develop average NMNE VOC concentrations during a given sampling interval.

The methane and ethane concentration data from each test run are presented in Table 2-3. Methane/propane and ethane/propane equivalent concentrations are presented in Table 2-4. A full set of data could not be obtained during Run 1 due to loss of data from the high range THC analyzer. See Section 5.0 for details. Raw data associated with the operation of the GC/FID, including all chromatograms, are included in Appendix 2-1.

Methane and ethane mass emission rates are presented in Tables 2-5 and 2-6, respectively. Section 2.2 discusses the development of target compound mass emission rates. Two bags were collected sequentially during Run 2, only the time-weighted average for Run 2 is presented below. The individual bag results, as well as the time-weighted average are presented in Appendix 2-1.

Table 2-3. Concentration Results for Methane and Ethane

Run No.	Date	Sampling Interval (hh:mm)	Methane Conc. (ppmvw)	Ethane Conc. (ppmvw)
2[a]	7/09/14	16:37-17:30	3123	341
3	7/10/14	13:05-13:27	471	54
4	7/11/14	08:32-09:10	1,495	159

[a] Time weighted average of Bag A and Bag B of Run 2.

Table 2-4. Methane/Propane and Ethane/Propane Equivalent Concentrations

Run No.	Date	Sampling Interval (hh:mm)	Methane Conc. (ppmvw)	Methane/ Propane Equivalent Conc. (ppmvw)	Ethane Conc. (ppmvw)	Ethane/ Propane Equivalent Conc. (ppmvw)
2[a]	7/09/14	16:37-17:30	863	1,041	85	227
3	7/10/14	13:05-13:27	471	157	54	36
4	7/11/14	08:32-09:10	1,495	498	159	106

[a] Time weighted average of Bag A and Bag B of Run 2.

Table 2-5. Mass Emission Rate Results for Methane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet Methane Conc. (ppmvw)	Vent Gas Moisture (%)	Dry Methane Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	Methane Mass Emission Rate (lbs/min)	Methane Mass Emission Rate (lbs/cycle)
2[a]	7/09/14	16:37-17:30	53	3,123	99.3	465,868	51	0.988	52.3
3	7/10/14	13:05-13:27	22	471	99.2	58,462	95	0.231	5.1
4	7/11/14	08:32-09:10	38	1,495	98.9	134,947	89	0.498	18.9

[a] Time weighted average of Bag A and Bag B of Run 2.

Table 2-6. Mass Emission Rate Results for Ethane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet Ethane Conc. (ppmvw)	Vent Gas Moisture (%)	Dry Ethane Conc. (ppmvd)[a]	Volumetric Flow Rate (dscfm)	Ethane Mass Emission Rate (lbs/min)	Ethane Mass Emission Rate (lbs/cycle)
2[a]	7/09/14	16:37-17:30	53	341	99.3	50,830	51	0.202	10.7
3	7/10/14	13:05-13:27	22	54	99.2	6,709	95	0.0496	1.1
4	7/11/14	08:32-09:10	38	159	98.9	14,332	89	0.0992	3.8

[a] Time weighted average of Bag A and Bag B of Run 2.

2.4.2 Results for Hydrogen Sulfide

Bag samples were collected from the same dilution sampling system used for the measurement of total hydrocarbon (THC) concentrations by modified U.S. EPA Method 25A, and modified U.S. EPA Other Test Method 12. As discussed earlier, two (2) integrated bag samples of vent gas were collected simultaneously during a venting cycle. One bag was analyzed for methane and ethane by gas chromatograph with flame ionization detector (GC/FID) and for hydrogen sulfide (H_2S) by a gas chromatograph with flame photometric detector (GC/FPD). The second bag was only analyzed if there was an issue with the first. All analyses were performed in triplicate. Concentration results are presented as parts per million by volume, wet basis (ppmvw).

Raw GC/FPD results were multiplied by the dilution ratios (DR) developed on a test run-specific basis through the operation of the dilution sampling system (see Section 2.5).

The hydrogen sulfide concentration data from each test run are presented in Table 2-7. Raw data associated with the operation of the GC/FPD, including all chromatograms, are included in Appendix 2-2.

Hydrogen sulfide mass emission rates are presented in Table 2-8. Section 2.2 discusses the development of target compound mass emission rates. The hydrogen sulfide concentration for Bag A of Run 2 and for Run 3 were below the applicable method detection limit and are reported as a maximum ("<"). All results calculated from this maximum are also reported as maxima ("<").

Table 2-7. Concentration Results for Hydrogen Sulfide

Run No.	Date	Sampling Interval (hh:mm)	Hydrogen Sulfide Conc. (ppmvw)[a]
2[b]	7/09/14	16:37-17:30	<23.5
3	7/10/14	13:05-13:27	<1.31
4	7/11/14	08:32-09:10	10.3

[a] The hydrogen sulfide concentration for Bag A of Run 2 and for Run 2 were below the applicable method detection limit and are reported as a maximum ("<"). All results calculated from this maximum are also reported as maxima ("<").

[b] Time weighted average of Bag A and Bag B of Run 2.

Table 2-8. Mass Emission Rate Results for Hydrogen Sulfide (H_2S)

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet H_2S Conc. (ppmvw)[a]	Vent Gas Moisture (%)	Dry H_2S Conc. (ppmvd)[a]	Volumetric Flow Rate (dscfm)	H_2S Mass Emission Rate (lbs/min)[a]	H_2S Mass Emission Rate (lbs/cycle)[a]
2[b]	7/09/14	16:37-17:30	53	<23.5	99.3	<3,507	51	<0.0158	<0.84
3	7/10/14	13:05-13:27	22	<1.31	99.2	<163	95	<0.0014	<0.03
4	7/11/14	08:32-09:10	38	10.3	98.9	926	89	0.0073	0.276

[a] The hydrogen sulfide concentration for Bag A of Run 2 and for Run 3 were below the applicable method detection limit and are reported as a maximum ("<"). All results calculated from this maximum are also reported as maxima ("<").

[b] Time weighted average of Bag A and Bag B of Run 2.

2.5 Results for NMNE Volatile Organic Compounds (NMNE VOC)

The total hydrocarbon (THC) concentration in the DCU gas stream was measured conservatively during the 2014 Source Test as THC using FID-based portable gas analyzers. THC concentrations were measured according to modified U.S. EPA Method 25A and the dilution sampling system procedures described in U.S. EPA Other Test Method 12.

Samples of the DCU gas stream were extracted using the same dilution sampling system used to collect methane, ethane, and hydrogen sulfide samples by modified U.S. EPA Method 18 (see Section 2.4). The diluted sample gas was routed to two (2) gas analyzers that measured THC concentrations as parts per million by volume, wet basis (ppmvw), continuously during the venting cycle. Standards of propane in a balance of nitrogen were used to calibrate two (2) THC analyzers at three (3) different ranges (0-3,500, 0-10,000, and 0-35,000 ppmvw). Nitrogen was also used as the diluent with the dilution sampling system. The dilution ratio developed on a test run-specific basis was multiplied by the average THC concentration result per sample run.

Based on prior experience and as presented in the Test Plan, URS assumed methane/propane and ethane/propane equivalency factors to be 1/3 and 2/3, respectively. Methane/propane equivalent and ethane/propane equivalent concentrations were subtracted from THC concentrations to develop NMNE VOC concentrations during a given sample run. Section 2.4.1 describes this calculation process in detail.

During Run 2, the total methane/propane equivalents concentrations exceeded total VOC concentration. In this case, subsequent calculations for NMNE VOC mass emission rate calculations applied a concentration of zero ppmvw for NMNE VOC.

THC and NMNE VOC concentrations data for each test run are presented in Table 2-9. Raw data associated with the operation of the THC analyzers is included in Appendix 2-3. NMNE VOC (as propane) mass emission rates are presented in Table 2-10. Section 2.2 discusses the development of target compound mass emission rates.

Table 2-9. Concentration Results for NMNE VOC, as Propane

Run No.	Date	Sampling Interval (hh:mm)	THC Conc. (ppmvw, as propane)	Methane/ Propane Equivalent Conc. (ppmvw)	Ethane/ Propane Equivalent Conc. (ppmvw)	NMNE VOC Conc. (ppmvw, as propane)[a]
2[b]	7/09/14	16:37-17:30	1,140	1,041	227	0.0
3	7/10/14	13:05-13:27	199	157	36	6.0
4	7/11/14	08:32-09:10	2,152	498	106	1,548

[a] During Run 2 the total of methane/propane equivalent concentrations and ethane/propane equivalent concentrations exceeded THC concentration. In these cases, subsequent calculations for NMNE VOC mass emission rates apply a concentration of zero (0) ppmvw for NMNE VOC.

[b] Time weighted average of Bag A and Bag B of Run 2.

Table 2-10. Mass Emission Rate Results for NMNE VOC, as Propane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet NMNE VOC Conc. (ppmvw, as propane)[a]	Vent Gas Moisture (%)	Dry NMNE VOC Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	NMNE VOC Mass Emission Rate (lbs/min)	NMNE VOC Mass Emission Rate (lbs/cycle)
2[b]	7/09/14	16:37-17:30	53	0.0	99.3	0.0	51	0.0	0.0
3	7/10/14	13:05-13:27	22	6.0	99.2	747	95	0.0081	0.18
4	7/11/14	08:32-09:10	38	1,548	98.9	139,707	89	1.42	53.9

[a] During Run 2 the total of methane/propane equivalent concentrations and ethane/propane equivalent concentrations exceeded THC concentration. In these cases, subsequent calculations for NMNE VOC mass emission rates apply a concentration of zero (0) ppmvw for NMNE VOC.

[b] Time weighted average of Bag A and Bag B of Run 2.

2.6 Results for Particulate Matter

Total particulate matter was measured according to modified U.S. EPA Method 5, "*Determination of Particulate Matter Emissions from Stationary Sources*." Particulate matter samples were extracted from the DCU gas stream isokinetically.

Following each test run, the PM samples were recovered separately into the following components:

- Front-half (nozzle, probe liner and front-half of the filter holder) rinse with acetone; and
- Quartz-fiber filter.

The minimum dry gas sample volumes typically associated with sampling for total PM were not obtained due to the limited sampling durations, the minimal dry gas fraction of the vent gas stream (less than 2%), and the large volume of water that was condensed in a relatively short period of time. As an alternative, the target wet gas sample volume of greater than 0.25 cubic feet (corrected to standard conditions) was used for this source testing project.

Table 2-2 presents a summary of modified U.S. EPA Method 5 sampling train operating data such as dry and wet gas volumes collected and isokinetic sampling rates achieved. Particulate mass loadings are presented in Table 2-11. The full laboratory report detailing the analyses of vent gas samples for particulate loading is presented in Appendix 2-4.

Total PM mass emission rates are also presented in Table 2-11. Section 2.2 discusses the development of target compound mass emission rates.

Table 2-11. Mass Loading and Mass Emission Rate Results for Total PM

	Run 2[a]	Run 3[b]	Run 4[b]	Average
Date	**7/09/2014**	**7/10/2014**	**7/11/2014**	-
Time	**16:37-17:30**	**13:05-13:27**	**08:32-09:10**	-
Duration (mins)	53	22	38	38
Volume Collected (dscf)	1.153	0.550	1.329	1.011
Flow Rate (dscfm)	51	95	89	78
Mass Found (mg)				
PM - Filter	<0.5	<0.5	<0.5	<0.5
PM - PNR	7.7	7.1	7.6	7.5
Particulate Matter - Total	<8.2	<7.6	<8.1	<8.0
Stack Gas Concentration (mg/dscf)				
Particulate Matter	<7.1	<14	<6.1	<9.1
Mass Emission Rate (lb/min)				
Particulate Matter	<0.0008	<0.0028	<0.0012	<0.0016
Mass Emission Rate (lb/cycle)				
Particulate Matter	<0.0424	<0.0623	<0.0456	<0.0501

[a] Results from PM Train 1

[b] Results from PM Train 2

3.0 Sampling and Analytical Procedures

Emissions from the DCU were tested according to the Test Plan using direct source testing methodologies. The sampling and analytical procedures followed during the 20143 Source Test are presented in this section and outlined in Table 3-1. Any deviations from the modified U.S. EPA reference methods described in the Test Plan are identified in this section and discussed in Section 5.0. Appendix 3-1 presents the field sample logbook.

Table 3-1. Summary of Modified Sampling and Analytical Methods

Parameter	Sampling Method	Analytical Method
Sampling Location	U.S. EPA Method 1	N/A
Velocity and Volumetric Flow Rate	U.S. EPA Method 2	N/A
Molecular Weight	U.S. EPA Method 3	N/A
Moisture	U.S. EPA Method 4	Gravimetric by U.S. EPA Method 4
Total PM	U.S. EPA Method 5	Gravimetric by U.S. EPA Method 5
Hydrogen Sulfide	U.S. EPA Method 18 and Other Test Method 12	Gas Chromatography/ Flame Photometric Detector by U.S. EPA Method 18
Methane and Ethane	U.S. EPA Method 18 and Other Test Method 12	Gas Chromatography/ Flame Ionization Detector by U.S. EPA Method 18
Total Hydrocarbons and NMNE VOC	U.S. EPA Method 25A and Other Test Method 12	Flame Ionization Detector by U.S. EPA Method 25A

3.1 Sampling Location by Modified U.S. EPA Method 1

MPC Detroit installed five sampling ports on both the A Coke Drum Vent and the B Coke Drum Vent to allow sequential sampling of both emission sources during the source test. The A and B Vents are identical in design and have diameters of twelve inches. The ports were installed on the same measurement plane of each DCU vent. Four of the sampling ports are situated roughly 12" apart from one another along the horizontal run of the vent pipe. The fifth port is located on the horizontal run of the port but is situated approximately 24" upstream of the next port. Of the five sampling ports, Port #1 and #2 were dedicated for the sampling of the gas stream for total PM according to modified EPA Method 5. The next three ports served as spares (Ports #3 and #4). A dilution sampling system operated according to guidance in U.S. EPA Other Test Method 12 was used to sample the gas stream for hydrogen sulfide, methane, ethane, total VOCs, and NMNE VOCs according to modified U.S. EPA Methods 18 and 25A. This dilution sampling system was inserted in Port #5, furthest upstream from the opening of the DCU vent to atmosphere.

Each sampling port is located in compliance with EPA Method 1, "*Sample and Velocity Traverses for Stationary Sources.*" EPA Method 1 was modified to allow for the use of a single traverse point at the center of the vent pipe by the modified EPA Method 5 sampling train in Port #1.

3.2 Velocity, Volumetric Flow Rate, Dry Gas Molecular Weight, and Moisture Concentration by Modified U.S. EPA Methods 2, 3, and 4

The DCU atmospheric depressurization vent gas velocities and volumetric flow rates were measured according to modified U.S. EPA Method 2, and the moisture concentration was measured according to modified U.S. EPA Method 4. U.S. EPA Methods 2 and 4 were performed concurrently with the modified U.S. EPA Method 5 sampling train. In lieu of performing oxygen and carbon dioxide measurements per U.S. EPA Method 3, the molecular weight of methane (16.0 g/g-mol) was assigned to the entire dry gas fraction during all test runs. The modified procedures by which velocity, volumetric flow rate, dry gas molecular weight, and moisture concentration data were obtained on the DCU gas stream are described in detail in the Test Plan, and any deviations from those modified procedures are discussed in this section.

There were no deviations from the Test Plan that were solely associated with U.S. EPA Method 1.

3.2.1 Sampling Train Design

The modified U. S. EPA Method 2 sampling system consisted of a sampling probe equipped with a Type-S pitot tube and instruments to measure the differential pressure, static pressure, and temperature of the vent gas stream. Gravimetric analysis of the impinger trains was used to determine moisture concentrations.

3.2.2 Sampling Train Operation

Differential pressure measurements across a Type-S pitot tube were made with a gauge-oil manometer or a digital manometer (when the differential pressure exceeded 10 inches of H_2O). The vent gas static pressure was recorded using a gauge-oil manometer or magnehelic gauge (when the static pressure exceeded 10 inches of H_2O). Before and after each sampling run, a calibration check was performed on the magnehelic gauge and digital manometer according to U.S. EPA Method 2, Section 6.2.1. The vent gas differential pressure, static pressure, temperature, and dry gas sample volume readings were recorded nominally every two (2) minutes during the operation of the isokinetic sampling trains. Due to the high velocity, high moisture concentration, and limited duration of the venting cycle, it was not practicable to check for the presence of cyclonic flow. Per the Test Plan, U.S. EPA Method 2 was modified such that the extent of cyclonic flow was not determined as part of this sampling program.

3.2.3 Sample Analysis

All data collected using modified U.S. EPA Method 2 was recorded real-time and no samples were collected for recovery and analysis. The moisture content of the gas stream was determined from the total weight gain of the impingers utilized in each sampling train according to modified U.S. EPA Method 4.

Vent gas velocity, static pressure, temperature, dry gas molecular weight, and moisture concentration data collected by the modified U.S. EPA Method 5 sampling train were used to calculate vent gas volumetric flow rates per U.S. EPA Method 2.

Appendix 3-2 includes calibration data for sampling equipment used with modified U.S. EPA Methods 2 and 4.

There were no deviations from the Test Plan that were solely associated with U.S. EPA Methods 2, 3, and 4.

3.3 Methane, Ethane, and Hydrogen Sulfide Concentrations by Modified U.S. EPA Method 18 and Other Test Method 12

The concentrations of methane, ethane, and hydrogen sulfide compounds in the DCU gas stream were measured during the 2014 Source Test according to modified U.S. EPA Method 18 and the dilution sampling system procedures described in U.S. EPA Other Test Method 12. The modified procedures by which methane, ethane, and hydrogen sulfide concentration data were obtained on the vent gas stream are described in detail in the Test Plan, and any deviations from those modified procedures are discussed in this section.

3.3.1 Sampling System Design

Samples of the DCU gas streams were extracted continuously using the modified U.S. EPA Methods 18/25A/OTM 12 dilution sampling system (equipped with a glass critical orifice) and diluted with high-purity nitrogen at dilution ratios (DR) of approximately 25:1. A heated particulate filter was placed immediately downstream of the inlet to the stainless steel dilution sampling probe tip and upstream of the glass critical orifice. The diluted sample gas passed from the glass critical orifice through a heated Teflon sampling line to a sample bag. An integrated bag sample was collected during each venting cycle. The bag samples were then transported to the URS on-site laboratory until analysis on a wet basis by GC/FID (methane and ethane) and GC/FPD (H_2S). All bag samples were analyzed within 3 hours of collection.

3.3.2 Sampling System Operation

A stable dilution air pressure and critical orifice vacuum greater than 14.7" Hg (manufacturer's specification) were maintained throughout all calibrations and sampling periods during valid test runs.

Prior to the start of sampling, the GC/FID and GC/FPD were calibrated using Custom Certified (±2% accuracy) calibration gas standards for the target analytes in a balance of nitrogen. Stainless steel or Teflon sample loops of various sizes were used to inject target concentrations of calibration gas to the GC/FID and GC/FPD. Bags were used to store and introduce calibration gas from the gas cylinder to the GC to mimic sample conditions as closely as possible. After all sample analyses, a post-test calibration was performed using calibration gas standards identical to the ones used during the pre-test run calibration.

The following calibration and quality assurance procedures described in U.S. EPA Method 18 were followed, with exceptions noted in Section 3.3.4:

- The instrument was calibrated at three points for each species before sample analyses;
- The analysis of each of three consecutive calibration injections differed by ≤5% from the average result at each concentration level;
- The calibration drift of the instrument was determined at one point (mid-level) after sample analyses; and
- The average analyses of the mid-level calibration standard before sample analyses and after sample analyses differed by ≤5% from their average, or a complete three-point post calibration was performed and all pre-test and post-test calibration results were used to develop a calibration curve to correct the test run results.

3.3.3 Sample Analysis

For each run, a single bag sample was analyzed in triplicate and the final concentration result was calculated as the average. The raw GC/FID and GC/FPD results were multiplied by the average dilution ratios developed on a test run-specific basis through the operation of the dilution sampling system and the THC analyzers (see Section 3.4). These results (GC raw data x DR) were then corrected to the average percent recovery achieved through the dilution system. The average percent recoveries were developed on a test run-specific basis by performing a modified Recovery Study based upon Section 8.4 of U.S. EPA Method 18.

Method detection limits (MDL) were developed using the approach described in 40 CFR §136, Appendix B. According to this methodology, each standard is analyzed seven (7) times, and the MDL is defined as the standard deviation times the student T value at the 99% confidence limit. The MDL was developed at the instrument using direct injection of calibration gas, transferred from the calibration gas cylinder or calibration gas dilution system to the GC via a bag. The analyte-specific method detection limits established through the calibration of the GC/FID and GC/FPD are presented in Appendices 2-1 and 2-2, respectively.

Raw GC/FID and GC/FPD calibration and analysis data is included in Appendices 2-1 and 2-2, respectively. Sampling data sheets used for the operation of the modified U.S.EPA Methods 18/25A/OTM 12 dilution sampling system are presented in Appendix 3-3.

There were no deviations from the Test Plan that were solely associated with the determination of methane and ethane or hydrogen sulfide.

3.4 NMNE VOC Concentration by Modified U.S. EPA Method 25A and Other Test Method 12

THC concentrations in the DCU gas streams were measured according to modified U.S. EPA Methods 25A and the dilution sampling system procedures described in U.S. EPA Other Test Method 12. NMNE VOC concentration results were reported by subtracting the methane and ethane concentrations (as propane) from the average THC concentrations measured during a given sampling period. The modified procedures by which NMNE VOC concentration data were obtained on the DCU gas streams are described in detail in the Test Plan, and any deviations from those modified procedures are discussed in this section.

3.4.1 Sampling System Design

Samples of the DCU gas stream were extracted continuously using the modified U.S. EPA Methods 18/25A/OTM 12 dilution sampling system (equipped with a glass critical orifice) and diluted with high-purity nitrogen at known dilution ratios of approximately 25:1. A heated particulate filter was placed immediately downstream of the inlet to the stainless steel dilution sampling probe tip and upstream of the glass critical orifice. The diluted sample gas passed from the glass critical orifice through a heated Teflon sampling line to two (2) THC analyzers equipped with FIDs. One THC analyzer was calibrated at two low-level ranges (0-3,500 and 0-10,000 ppmvw), and a second THC analyzer was calibrated at a single high-level range (0-35,000 ppmvw). THC concentrations in the diluted sample gas were measured continuously on a wet basis.

3.4.2 Sampling System Operation

Samples of the DCU gas streams were extracted using the same dilution sampling system used to collect methane, ethane, and hydrogen sulfide samples by modified U.S. EPA Method 18 (see Section 3.3). A stable dilution air pressure and critical orifice vacuum greater than 14.7" Hg (manufacturer's specification) were maintained throughout all calibrations and sampling periods during valid test runs.

Prior to the start of sampling, THC analyzers were calibrated using either U.S. EPA Protocol or Primary Standard (±1% accuracy) calibration gas standards for propane in a balance of nitrogen. Following sample analyses and unless otherwise noted, a Drift Test was performed using calibration gas standards identical to the ones used during the pre-test run Calibration Error Test. U.S. EPA OTM 12 requires that the Calibration Error Test and Drift Test be performed with U.S. EPA Protocol calibration gases introduced as close to the probe tip as possible and upstream of the dilution sampling system.

The following calibration and quality assurance procedures described in U.S. EPA Method 25A were followed, with exceptions noted in Section 3.4.4:

- A pre-test run Calibration Error Test was performed at four (4) points for each THC analyzer before sample analyses;
- The analysis of each calibration gas during the Calibration Error Test differed by <5% error from the certified concentration;
- The post-test run Drift Test of the instrument was determined at two (2) points (zero and either low- or mid-level) after sample analyses;
- The analysis of each calibration gas during the Drift Test differed by <5% error from the certified concentration;
- The analyses of each calibration gas during the Drift Test differed by <3% of the instrument's calibration span from the Calibration Error Test results; and
- A response time test was conducted on each THC analyzer.

3.4.3 Sample Analysis

THC concentrations were recorded at 10-second intervals throughout each vent sampling run. A run average THC was developed by averaging these data over the course of the sampling run. The raw GC/FID and GC/FPD results were multiplied by the average dilution ratios developed on a test run-specific basis. Average dilution ratios were also applied to raw GC/FID and GC/FPD data collected using modified U.S. EPA Method 18. Average methane/propane and average ethane/propane equivalent concentrations were calculated using response factor per carbon data applied to average methane and ethane concentration results from GC/FID analyses. Finally, average methane/propane equivalent and average ethane/propane equivalent concentrations were subtracted from average THC concentrations to develop average NMNE VOC concentrations during a given sampling interval.

Raw and corrected THC analyzer data are included in Appendix 2-3. Sampling data sheets used for the operation of the modified U.S. EPA Methods 18/25A/OTM 12 dilution sampling system are presented in Appendix 3-3. THC analyzer calibration information associated with the performance of modified U.S. EPA Method 25A is included in Appendix 2-3.

There were no deviations from the Test Plan that were solely associated with the determination of THC concentration.

3.5 Total PM Concentration by Modified U.S. EPA Method 5

Total PM in the DCU gas stream was measured according to U.S. EPA Method 5, "*Determination of Particulate Matter Emissions from Stationary Sources*." Total PM samples were extracted from the DCU as isokinetically as possible. The principal components of the combined U.S. EPA Method 5 sampling train include a heated out-of-stack quartz-fiber filter, and a series of dry impingers. The modified procedures by which total PM results were obtained on the vent gas stream is described in detail in the Test Plan, and any deviations from those modified procedures are discussed in this section.

3.5.1 Sampling Train Design

The U.S. EPA Method 5 sampling train consisted of the following components:

- Stainless steel nozzle;
- Sampling probe with glass liner;
- Heated out-of-stack quartz-fiber filter;
- Teflon transfer line;
- Glass coiled condenser;
- One large glass impinger (3-liter), with knockout stem, empty;
- One large glass impinger (3-liter), with modified Greenburg-Smith stem, containing 200 ml 10% zinc acetate solution;
- One large glass impinger, with Greenburg-Smith stems, each containing 200 ml 10% zinc acetate solution. Note: a second (optional) impinger may be added if necessary for H_2S removal;
- One standard glass impinger, with knockout stem, empty;
- One standard glass impinger, with modified Greenburg-Smith stem, containing approximately 300 g of silica gel desiccant;
- Air-tight sample pump;
- Dry gas meter; and
- Orifice.

3.5.2 Sampling Train Operation

Modified U.S. EPA Methods 2 and 4 (see Section 3.2) were performed concurrently with the modified U.S. EPA Method 5 sampling train during all test runs. The vent gas differential pressure, static pressure, temperature, and moisture concentration data obtained with each modified U.S. EPA Method 5 sampling train were used to calculate the isokinetic sampling rate.

3.5.3 Sample Recovery and Analysis

Following each sampling run, the PM samples were recovered separately into the following components:

- Front-half (nozzle, probe liner and front-half of the filter holder) rinse with acetone; and
- Quartz-fiber filter.

In addition, the moisture content of the gas stream was determined from the total weight gain of the impingers utilized in the modified U.S. EPA Method 5 sampling train.

PM determinations were performed according to U.S. EPA Method 5. After delivery to the laboratory, the PM sample fractions were dried to constant weight. Total PM concentrations are reported (see Section 2.6) in the units of grains per dry standard cubic foot (gr/dscf).

The full laboratory report is presented in Appendix 2-4. Appendix 3-2 includes calibration data for sampling equipment used with modified U.S. EPA Method 5 sampling trains. Appendix 3-4 includes sampling data sheets used for the modified U.S. EPA Method 5 sampling train.

One deviation from the Test Plan occurred in the collection of samples for determination of particulate matter.

- The Test Plan describes a single PM sampling train per vent cycle. During the 2014 Source Test, two PM sampling trains (Train A and Train B for each run) were collected simultaneously in order to minimize the potential for collecting an incomplete set of data for a given vent cycle. For Run 2, PM sample train B had a higher post-leak check rate, due to a hairline crack in the filter assembly glass bell. Although, it passed a standard leak rate of <0.02 cfm, PM sample train A was chosen for analysis. For Runs 3 and 4, the replicate sample that resulted in the greater sample volume was chosen for analysis, and the other sample was archived by the laboratory. As a result, the reported PM results from Runs 2, 3, and 4 were derived using samples 2A, 3B, and 4B, respectively.

4.0 Calculations

4.1 Data Reduction Approach

The goal of the 2014 Source Test was to quantify the mass emission rates of the target compounds released to atmosphere during the DCU venting cycles. Mass emission rates are typically expressed using an industry standard of mass per unit time, such as pounds per hour (lbs/hr), by relating the concentration of a target compound to the average volumetric flow rate of a gas stream. The data reduction approach used in this report integrates target compound mass emission rates as pounds per minute (lbs/min) throughout the complete venting cycle, starting at the point of vent activation and ending at the point of optimal depressurization of the coke drum. Total mass emission rates are expressed in this report as mass per batch cycle (lbs/cycle).

4.2 Calculations

The following sub-sections present the equations that were applied to data collected during the 2014 Source Test.

4.2.1 Vent Gas Velocity

The average velocity of the gas released from the vents during the venting cycle will be calculated according to U.S. EPA Equation 2-7:

$$V_S = 85.49 \times C_P \times \sqrt{\Delta P} \times \sqrt{\frac{T_S}{P_S \times M_W}}$$

Where:

V_S	=	Average velocity of the vent gas, ft/sec;
85.49	=	Conversion constant, per Equation 2-7 of U.S. EPA Method 2;
C_p	=	Type-S Pitot correction factor, 0.84;
ΔP	=	Average of the square roots of the differential pressures measured by Type-S Pitot tube, in. H_2O;
T_s	=	Average vent gas temperature, °R;
P_s	=	Average absolute pressure, in. Hg; and
M_w	=	Average wet gas molecular weight, lb/lb-mol.

4.2.2 Vent Gas Volumetric Flow Rate – Standard Conditions

The average volumetric flow rate of the gas released from the vents during the venting cycle, corrected to standard conditions, was calculated according to U.S. EPA Method 2:

$$Q_s = 60 \times V_s \times A \times \left(\frac{528}{T_S} \right) \times \left(\frac{P_S}{29.92} \right)$$

Where:

Q_s = Average volumetric flow rate of the vent gas, corrected to standard conditions, scfm;
60 = Conversion from seconds to minutes;
V_s = Average velocity of the vent gas, ft/sec;
A = Cross-sectional area of the #1 or #5 Drum Vent, ft^2;
528 = Standard temperature, °R;
T_s = Average vent gas temperature, °R;
29.92 = Standard pressure, in. Hg; and
P_s = Average absolute vent pressure, in. Hg.

The total gas volume (scf) released to atmosphere during the venting cycle was calculated by multiplying the average volumetric flow rate (scfm) by the duration of the venting cycle (minutes).

4.2.3 Vent Gas Volumetric Flow Rate – Dry Standard Conditions

The average volumetric flow rate of the gas released from the vents, corrected to dry standard conditions, was calculated according to U.S. EPA Method 2. The average venting cycle moisture concentration, developed from moisture concentrations quantified by each individual sampling train operated during a given venting cycle, and the average volumetric flow rate (corrected to standard conditions) was used to calculate average dry gas volumetric flow rates (dscfm) as:

$$Q_{sd} = Q_s \times (1 - B_{ws})$$

Where:

Q_{sd} = Average vent gas dry volumetric flow rate, standard conditions, dscfm;
Q_s = Average vent gas volumetric flow rate, standard conditions, scfm; and
B_{ws} = Average proportion of water vapor, by volume.

The total dry gas volume (dscf) released to atmosphere during the venting cycle was calculated by multiplying the average volumetric flow rate (dscfm) by the duration of the venting cycle (minutes).

4.2.4 Concentration of PM in the Vent Gas

The concentration of PM was calculated as:

$$C_{g/dscf} = \frac{M}{V_{sd}}$$

Where:

$C_{g/dscf}$ = Concentration of target compound, g/dscf;

M = Mass of analyte collected in the modified isokinetic sampling train, g; and

V_{sd} = Dry gas meter volume collected with the sampling train, at standard conditions, dscf.

4.2.5 Concentrations of Methane, Ethane, NMNE VOC, and Hydrogen Sulfide in the Vent Gas

The concentration of THC (as propane) in the vent gas was measured continuously throughout the venting cycle in units of parts per million on a wet basis (ppmvw). The NMNE VOC concentration was calculated by subtracting the average concentrations of methane and ethane (as determined using modified U.S. EPA Method 18) from the average concentration of THC (using modified U.S. EPA Method 25A). The average concentration of NMNE VOC during each test period was calculated as:

$$C_{VOC} = C_{THC} - \left(\frac{C_M \times 1}{3}\right) - \left(\frac{C_E \times 2}{3}\right)$$

Where:

1/3 = Methane/propane equivalence factor, unit-less;

2/3 = Ethane/propane equivalence factor, unit-less;

C_{VOC} = Average concentration of NMNE VOC, as propane, ppmvw;

C_{THC} = Average concentration of THC, as propane, ppmvw;

C_M = Average concentration of methane, ppmvw; and

C_E = Average concentration of ethane, ppmvw.

Conversion of average methane, ethane, NMNE VOC, and hydrogen sulfide concentration results from ppmvw to mole fraction was performed using this equation:

$$MF = \frac{C}{10^6}$$

Where:

MF = Average mole fraction of target compound, unit-less;
C = Average concentration of target compound, ppmvw; and
10^6 = Conversion factor from ppmvw to mol/mol, unit-less.

4.2.6 Mass Emission Rate of PM

The mass emission rate of total PM was calculated during the venting cycle using this equation:

$$\mathrm{MER}_P = C_{g/dscf} \times \left(\frac{\mathrm{Q_{sdt}}}{453.59}\right) \times \left(\frac{1}{cycle}\right)$$

Where:

$\mathrm{MER_P}$ = Mass emission rate of target compound, per venting cycle (lbs/cycle);
$\mathrm{C_{g/dscf}}$ = Concentration of target compound (g/dscf);
$\mathrm{Q_{sdt}}$ = Total volume of dry gas released to atmosphere, at standard conditions (dscf);
453.59 = Conversion from grams to pounds (g/lb); and
cycle = One venting cycle.

4.2.7 Mass Emission Rate of Methane, Ethane, NMNE VOC, and Hydrogen Sulfide

The mass emission rates of methane, ethane, NMNE VOC, and hydrogen sulfide were calculated during each venting cycle interval using an equation based upon U.S. EPA Equation Y-19 of the Greenhouse Gas Reporting Rule (40 CFR §98.253[i][2]):

$$MER_V = MF \times Q_{st} \times \left(\frac{MW}{385}\right) \times \left(\frac{1}{interval}\right)$$

Where:

$\mathrm{MER_V}$ = Mass emission rate of target compound, per venting cycle interval, lbs/interval;
MF = Average mole fraction of target compound per sampling interval, unit-less;

Q_{st} = Total volume of wet gas released to atmosphere during the venting cycle interval, at standard conditions, scf;

MW = Molecular weight of the target compound, lb/lb-mol;

385 = Ideal gas law constant, scf/lb-mol;

interval = One venting cycle interval.

5.0 Quality Assurance Objectives for Measurement Data

The test was conducted in accordance with the Test Plan, and any deviations are presented in Sections 1.4 and 3.0 and summarized in Table 1-3 of this document. The potential impact of these deviations on the test results is discussed in this section.

The primary objectives of the QA/QC effort were to control, assess, and document data quality. To accomplish these objectives, the QA/QC approach consisted of the following key elements:

- Definition of data quality objectives that reflect the overall technical objectives of the measurement program;
- Design of a sampling, analytical, QA/QC, and data analysis system to meet those objectives;
- Evaluation of the performance of the measurement system; and
- Initiation of corrective action when measurement system performance does not meet the specifications.

The QA procedures described in the Test Plan include the use of sampling and analytical procedures, along with specified calibration requirements, QC checks, data reduction, and validation procedures and sample tracking. A review of analytical results for QA/QC samples and assessment of overall data quality is presented in this section. Detailed QC information is presented in Appendix 5-1 of this report.

A review of the data quality associated with this test program indicates that these data are supportable and usable for the purpose intended.

5.1 Collection and Analysis of Vent Gas Samples for Determination of Methane and Ethane

QA/QC activities associated with the collection of the vent gas samples for the determination of methane and ethane, using the modified U.S. EPA Methods 18/25A/OTM 12 sampling system include:

- Use of calibrated sampling equipment;
- Use of calibration and dilution gas of appropriate and documented quality;
- Collection of samples at appropriate operating conditions;

- Proper operation of the dilution sampling system; and
- Collection of samples per the Test Plan and applicable U.S. EPA reference methods.

QA/QC activities associated with the analysis of vent gas samples for methane and ethane include:

- Calibration of the analytical instrumentation;
- Use of documented calibration standards;
- Replicate analyses;
- Incorporation of appropriate holding-time criteria; and
- Analyses of samples per the Test Plan and applicable U.S. EPA reference methods.

A review of the data quality associated with these measurements indicates that the data collected during all test runs are supportable and usable for the purpose intended. Refer to the detailed quality assessment in Appendix 5-1. No issues were identified during this data quality review.

5.2 Collection and Analysis of Vent Gas Samples for Determination of Hydrogen Sulfide

QA/QC activities associated with the collection of the vent gas samples for the determination of hydrogen sulfide using the modified U.S. EPA Methods 18/25A/OTM 12 sampling system include:

- Use of calibrated sampling equipment;
- Use of calibration and dilution gas of appropriate and documented quality;
- Collection of samples at appropriate operating conditions;
- Proper operation of the dilution sampling system; and
- Collection of samples per the Test Plan and applicable U.S. EPA reference methods.

QA/QC activities associated with the analysis of vent gas samples for methane, ethane, and hydrogen sulfide concentrations include:

- Calibration of the analytical instrumentation;
- Use of documented calibration standards;
- Replicate analyses;
- Incorporation of appropriate holding-time criteria; and

- Analyses of samples per the Test Plan and applicable U.S. EPA reference methods.

A review of the data quality associated with these measurements indicates that the data collected during all test runs are supportable and usable for the purpose intended. Refer to the detailed quality assessment in Appendix 5-1. No issues were identified during this data quality review.

5.3 Collection and Analysis of Vent Gas Samples for THC Concentration

QA/QC activities associated with the collection of vent gas samples using the modified U.S. EPA Methods 18/25A/OTM12 sampling system include:

- Use of pre-printed data sheets;
- Use of dilution gas of appropriate and documented quality;
- Collection of samples at appropriate operating conditions;
- Proper operation of the dilution sampling system; and
- Collection of samples per the Test Plan and applicable U.S. EPA reference methods.

QA/QC activities associated with the analysis of vent gas samples for THC concentrations include:

- Use of calibrated sampling equipment;
- Performance of Calibration Error Tests;
- Performance of Drift Tests;
- Use of documented calibration standards; and
- Analyses of samples per the Test Plan and applicable U.S. EPA reference methods.

A review of the data quality associated with these measurements indicates that the data collected during all test runs are supportable and usable for the purpose intended. Refer to the detailed quality assessment in Appendix 5-1. The only issue identified during the data quality assessment follows:

- During Run 1, the signal output of the high level THC analyzer was lost. As hydrocarbon readings entered this range, this run was not used in emissions calculations, and Run 4 performed to replace it.
- The THC2 analyzer response to the mid-level calibration gas at the conclusion of Runs 1 and 4 were outside of the 3.0% drift check criteria (-3.6 and -4.7% respectively). The Run 1 data was not used, and has no effect on data quality.

Following Run 4, a 4-point post test calibration was performed as per U.S. EPA Method 25A. The data was evaluated against the resulting curve. The data was then corrected to the new calibration curve as this provided the more conservative emissions measurement. The use of the revised, bias corrected data may provide a positive bias to the data.

- The THC1 analyzer response to the mid-level calibration gas at the conclusion of Run 4 was outside of the 3.0% drift check criteria (-8.7%). Following Run 4, a 4-point post test calibration was performed as per U.S. EPA Method 25A. The data was evaluated against the resulting curve. The data was then corrected to the new calibration curve as this provided the more conservative emissions measurement. The use of the revised, bias corrected data may provide a positive bias to the data.

5.4 Collection of Vent Gas Samples for Determination of Total Particulate Matter

QA/QC activities associated with the collection of vent gas samples for Total PM sampling trains include:

- Use of pre-printed sampling data sheets;
- Use of calibrated sampling equipment;
- Collection of samples at appropriate operating conditions;
- Collection of acceptable sample volumes;
- Performance of sampling system leak checks; and
- Collection of samples per the Test Plan and applicable U.S. EPA reference methods.

A review of the data quality associated with these measurements indicates that the data collected during all test runs are supportable and usable for the purpose intended. Refer to the detailed quality assessment in Appendix 5-1. The issues identified during the data quality review are:

- The Test Plan specified that sample will be collected for 30-45 minutes. In Runs 1 and 3, the vent durations were 24 and 22 minutes. The data are considered representative of the emission event. No data are qualified or invalidated based on sample volume.
- One point during Run 3 had a probe temperature above the specification. This was resolved and all other points met the specification. The excursion has no impact on the interpretation of the results. No data are qualified or invalidated based on probe or filter temperature.

5.5 Analysis of Vent Gas Samples for Total Particulate Matter

QA/QC activities associated with the analysis of vent gas samples for particulate matter concentration include:

- Sample handling and preservation;
- Preparation and analysis of samples within appropriate holding times;
- Collection and analysis of field blanks; and
- Analyses of samples per the applicable U.S. EPA methods.

A review of the data quality associated with these analyses indicates the data from all test runs are supportable and usable for the purpose intended. Refer to the detailed quality assessment in Appendix 5-1. The only issue identified during the data quality review is:

- The field blank result for probe and nozzle rinse is similar to the results for the actual vent samples. The field blank results suggest that the results for the vent samples may have a high bias. As the results represent conservative estimates of the emissions, no data are qualified or invalidated based on the field blank results.