CleanAir

CleanAir Engineering
500 W. Wood Street
Palatine, IL 60067-4975
cleanair.com

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

REPORT ON H_2S CEMS RATA TESTING

Performed for:
MARATHON PETROLEUM COMPANY LP
DETROIT REFINERY

ALKY FLARE
CRUDE FLARE

Client Reference No: 4100665755
CleanAir Project No: 13125
Revision 0: December 27, 2016

To the best of our knowledge, the data presented in this report are accurate, complete, error free, legible and representative of the actual emissions during the test program. Clean Air Engineering operates in conformance with the requirements of ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies.

Submitted by,

Andy Obuchowski
Midwest Engineering Group
Business Leader
aobuchowski@cleanair.com
(800) 627-0033 ext. 4537

Reviewed by,

Ken Sullivan
Project Manager
ksullivan@cleanair.com
(800) 627-0033 ext. 4527

REVISION HISTORY

REPORT ON H2S CEMS RATA TESTING

DRAFT REPORT REVISION HISTORY

Revision:	Date	Pages	Comments
D0a	12/21/16	All	Draft version of original document.

FINAL REPORT REVISION HISTORY

Revision:	Date	Pages	Comments
0	12/27/16	All	Final version of original document.

PROJECT OVERVIEW

INTRODUCTION

Marathon Petroleum Company LP (MPC) contracted Clean Air Engineering (CleanAir) to perform a relative accuracy test audit (RATA) on two (2) hydrogen sulfide (H_2S) continuous emissions monitoring systems (CEMS) installed at the Detroit Refinery for compliance purposes.

All testing was conducted in accordance with the regulations set-forth by the United States Environmental Protection Agency (EPA) and the Michigan Department of Environmental Quality (DEQ). These regulations are referenced in Michigan Department of Environmental Quality, Air Quality Division Renewable Operating Permit No. MI-ROP-A9831-2012c, issued September 12, 2016.

Key Project Participants

Individuals responsible for coordinating and conducting the test program were:

Crystal Davis – MPC
Joe Reidy – MPC
Chad Eilering – CleanAir

Test Program Parameters

The testing was performed at the Crude Flare H_2S Analyzer on November 29, 2016, and at the Alky Flare H_2S Analyzer on November 30, 2016. All testing was performed at a point along the flare gas line at each location.

Reference method (RM) testing performed by CleanAir included emissions measurements for hydrogen sulfide (H_2S) in units of parts per million on a dry volume basis (ppmdv).

The relative accuracy of the facility H_2S analyzers were calculated by comparing RM H_2S results to facility CEMS results over concurrent time intervals per Performance Specification (PS) 7.

TEST PROGRAM SYNOPSIS

Test Schedule

The on-site schedule followed during the test program is outlined in Table 1-1.

Table 1-1:
Schedule of Activities

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Crude Flare	USEPA Method 11	H_2S	11/29/16	10:32	10:52
2	Crude Flare	USEPA Method 11	H_2S	11/29/16	11:08	11:28
3	Crude Flare	USEPA Method 11	H_2S	11/29/16	11:38	11:58
4	Crude Flare	USEPA Method 11	H_2S	11/29/16	12:08	12:28
5	Crude Flare	USEPA Method 11	H_2S	11/29/16	12:42	13:02
6	Crude Flare	USEPA Method 11	H_2S	11/29/16	13:07	13:27
7	Crude Flare	USEPA Method 11	H_2S	11/29/16	13:35	13:55
8	Crude Flare	USEPA Method 11	H_2S	11/29/16	14:00	14:20
9	Crude Flare	USEPA Method 11	H_2S	11/29/16	14:25	14:45
10	Crude Flare	USEPA Method 11	H_2S	11/29/16	14:51	15:11
11	Crude Flare	USEPA Method 11	H_2S	11/29/16	15:16	15:36
1	Alky Flare	USEPA Method 11	H_2S	11/30/16	09:00	09:20
2	Alky Flare	USEPA Method 11	H_2S	11/30/16	09:24	09:44
3	Alky Flare	USEPA Method 11	H_2S	11/30/16	09:49	10:09
4	Alky Flare	USEPA Method 11	H_2S	11/30/16	10:12	10:32
5	Alky Flare	USEPA Method 11	H_2S	11/30/16	10:37	10:57
6	Alky Flare	USEPA Method 11	H_2S	11/30/16	11:02	11:22
7	Alky Flare	USEPA Method 11	H_2S	11/30/16	11:25	11:45
8	Alky Flare	USEPA Method 11	H_2S	11/30/16	11:49	12:09
9	Alky Flare	USEPA Method 11	H_2S	11/30/16	12:12	12:32
10	Alky Flare	USEPA Method 11	H_2S	11/30/16	12:36	12:56

121416 170407

Results Summary

Table 1-2 summarizes the results of the test program. A more detailed presentation of the test conditions and results of analysis are shown in Tables 2-1 and 2-2 (on pages 2-1 and 2-2).

Table 1-2:
Summary of RATA Results

Source Constituent (Units)	Reference Method	Applicable Specification	Relative Accuracy	Specification Limit[1]
Alky Flare				
H_2S (ppmdv)	USEPA 11	PS7	0.2%	10% of Standard[2]
Crude Flare				
H_2S (ppmdv)	USEPA 11	PS7	3.6%	10% of Standard[2]

[1] Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.
[2] Emission standard = 160 ppmdv.

122016 163416

Discussion of Test Program

Crude Flare
The RATA on the Crude Flare consisted of eleven (11) test runs.

Run 1 was considered invalid because following the recovery of the sample train there remained a small amount of yellow residual in the impingers. This occurrence means that the absorbing solution in the impingers may have become spent, failing to capture all of the H_2S present. All consecutive test runs were performed with an additional absorbing solution impinger in the sample system which resolved this potential sample bias.

Final results were calculated based on nine (9) valid and best-fit test runs and were found to be below the limit of 10% of the emission standard set by PS7.

Alky Flare
The RATA on the Alky Flare consisted of ten (10) test runs.

Final results were calculated based on nine (9) best-fit test runs and were found to be below the limit of 10% of the emission standard set by PS7.

The following is a summary of the slight deviations from EPA Method 11 test methodology that were noted during RM sampling. None of these deviations are expected to significantly affect the quality of the data.

Sample Train Operation

Method 11, §7.1.2 and §7.1.4 outlines a procedure for operating and leak-checking the sample train under positive pressure. CleanAir opted for an alternative set-up in which the sample train was operated under slightly negative pressure. The sample system pulled flare gas from a port (isolated with a main on-off valve) along the flare gas and supplied pressurized gas to a single sample tee. One leg of the tee was open to atmosphere and the other leg was connected to the Method 11 sample train via a TFE sample line (isolated with a secondary on-off valve when not in use).

A leak-free sample pump was used to draw a slipstream of the pressurized flare gas from the tee. Excess gas was continuously verified to be flowing out of the open end of the tee using a rotameter. The sample train was leak-checked under negative pressure before and after each test run, at a vacuum greater than or equal to the vacuum measured during the test run.

Titrant Standardization

Method 11, §10.2.2 outlines a procedure for standardizing the 0.1 N sodium thiosulfate reagent used for titrating the samples. The method specifies performing the standardization on a weekly basis or once per test series, whichever is shorter. The standardized 0.1 N sodium thiosulfate reagent is then diluted by a factor of 10 using a pipette and a volumetric flask to 0.01 N, assuming perfect dilution (no further standardization is performed).

Instead of standardizing the 0.1 N sodium thiosulfate in the field, CleanAir utilized a certified 0.1 N sodium thiosulfate standard prepared by a chemical supplier. A certification sheet, including the exact reagent concentration and any applicable expiration date is included in Appendix G.

As required by the method, CleanAir performed a daily standardization of the 0.01 N iodine solution used for titrating the samples.

End of Section 1 – Project Overview

RESULTS

Table 2-1:
Crude Flare – H_2S RATA Results

Run No.	Start Time	Date (2016)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)
1 *	10:32	Nov 29	68.6	76.8	-8.2
2	11:08	Nov 29	76.8	80.9	-4.1
3	11:38	Nov 29	74.7	81.0	-6.3
4	12:08	Nov 29	74.3	80.4	-6.1
5	12:42	Nov 29	74.9	68.2	6.8
6	13:07	Nov 29	75.6	77.1	-1.5
7	13:35	Nov 29	81.9	83.1	-1.2
8	14:00	Nov 29	90.1	96.9	-6.7
9	14:25	Nov 29	93.0	91.8	1.2
10 *	14:51	Nov 29	91.3	105.0	-13.7
11	15:16	Nov 29	99.2	103.3	-4.0
Average			**82.3**	**84.7**	**-2.4**

Relative Accuracy Test Audit Results

Standard Deviation of Differences	4.367	
Confidence Coefficient (CC)	3.357	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of Appl. Std.)	**3.6%**	**10.0%**
Appl. Std. = 160 ppmdv		

RM = Reference Method (CleanAir Data) 122016 163550
CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.

RESULTS

Table 2-2:
Alky Flare – H_2S RATA Results

Run No.	Start Time	Date (2016)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)
1 *	09:00	Nov 30	0.0	0.4	-0.4
2	09:24	Nov 30	0.0	0.4	-0.4
3	09:49	Nov 30	0.0	0.2	-0.2
4	10:12	Nov 30	0.0	0.2	-0.2
5	10:37	Nov 30	0.0	0.2	-0.2
6	11:02	Nov 30	0.0	0.2	-0.2
7	11:25	Nov 30	0.0	0.2	-0.2
8	11:49	Nov 30	0.0	0.2	-0.2
9	12:12	Nov 30	0.0	0.2	-0.2
10	12:36	Nov 30	0.0	0.2	-0.2
	Average		**0.0**	**0.2**	**-0.2**

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.059	
Confidence Coefficient (CC)	0.045	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of Appl. Std.)	**0.2%**	**10.0%**
Appl. Std. = 160 ppmdv		

RM = Reference Method (CleanAir Data) 122016 163646
CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
RATA calculations are based on 9 of 10 runs. * indicates the excluded run.

End of Section 2 – Results

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 facility has five flares that are tied into the process at various points and used to combust the flammable materials in process gas emitted as waste or released from pressure relief valves. The gas stream to be combusted in each flare must be continually monitored for H_2S by MPC. As part of the annual compliance testing, a RATA must be conducted on the H_2S CEMS installed on the Alky and Crude flare lines.

The flare gas analyzers are capable of measuring H_2S, carbonyl sulfide (COS) and carbon disulfide (CS_2). H_2S concentrations are measured by gas chromatographic (GC) separation and flame photometric detection (FPD). H_2S concentration data is recorded and logged by MPC's distributive control system.

The testing described in this document was performed at the Alky Flare and Crude Flare, at a point along the flare line.

End of Section 3 – Description of Installation

METHODOLOGY

Clean Air Engineering followed procedures as detailed in EPA Method 11 and Performance Specification 7. The following table summarizes the methods and their respective sources.

Table 4-1:
Summary of Sampling Procedures

Title 40 CFR Part 60 Appendix A	
Method 11	"Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries"
Title 40 CFR Part 60 Appendix B (Performance Specifications (PS))	
PS7	"Specifications and Test Procedures for Hydrogen Sulfide Continuous Emission Monitoring Systems in Stationary Sources"

These methods appear in detail in Title 40 of the Code of Federal Regulations (CFR) and are located on the internet at http://ecfr.gpoaccess.gov.

Diagrams of the sampling apparatus and major specifications of the sampling, recovery and analytical procedures are summarized for each method in Appendix A.

CleanAir followed specific quality assurance and quality control (QA/QC) procedures as outlined in the individual methods and as prescribed in CleanAir's internal Quality Manual. Results of all QA/QC activities performed by CleanAir are summarized in Appendix G.

METHODOLOGY

Reference Method H_2S Testing - EPA Method 11

Reference Method (RM) H_2S concentration was determined using Method 11. An integrated sample was extracted from the flare line using a TFE sample line and connected to the Method 11 sample train. During test runs, a leak-free sample pump was used to draw a slipstream of the flare gas.

After passing through the TFE sample line, the gas sample passed through a series of midget impingers. The first impinger contained hydrogen peroxide (H_2O_2) for sulfur dioxide (SO_2) collection. The second impinger was empty to prevent carryover. The third, fourth and fifth impingers contained cadmium sulfate for H_2S collection. The gas sample then passed through a drying tube for residual moisture collection and was drawn into a dry gas meter by the pump for dry volume measurement.

Prior to the start of each test run, the midget impinger train was leak-checked under negative pressure. The sample line was then purged by allowing process gas to flow through the line and vent to atmosphere for one (1) to two (2) minutes.

Sample time for each RM test run was 20 minutes. Sampling was performed at a constant rate (±10%), targeting approximately one (1) liter per minute (LPM).

At the conclusion of each test run, the midget impinger train was leak-checked under negative pressure. The impinger train was then purged with clean ambient air for 15 minutes at a rate of one (1) LPM to ensure that all H_2S was removed from the H_2O_2 in Impinger 1.

Impingers 3, 4, 5 and 6 (when applicable) were recovered into a 500 mL flask containing acidified iodine (I_2) solution, allowed to stand about 30 minutes in the dark for absorption of the H_2S into the I_2, then titrated per Method 11 specifications.

End of Section 4 – Methodology