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

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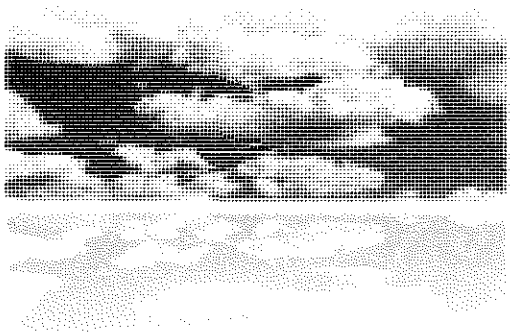

REPORT ON H_2S CEMS RATA TESTING

Detroit Refinery

Alky Flare

Crude Flare

Marathon Petroleum Company LP

1300 South Fort Street

Detroit, MI 48217

Client Reference No. 4101004604

CleanAir Project No. 13420-2

STAC Certificate No. 2007.002.0113.1217

Revision 0, Final Report

January 8, 2018

1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir 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.

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 below Table 1-1.

Table 1-1:
Summary of Results

Source Constituent (Units)	Reference Method	Applicable Specification	Relative Accuracy	Specification Limit[1]
Alky Flare				
H_2S (ppmdv)	USEPA 11	PS7	1.4%	10% of Standard[2]
Crude Flare				
H_2S (ppmdv)	USEPA 11	PS7	8.1%	10% of Standard[2]

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

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Test Program Details

Parameters

The testing was performed at the Crude Flare H_2S analyzer on November 28, 2017, and at the Alky Flare H_2S analyzer on November 29, 2017.

Reference method (RM) testing performed by CleanAir included emissions measurements for 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 the facility CEMS results over concurrent time intervals per Performance Specification (PS) 7.

Schedule

The on-site schedule followed during the test program is outlined in Table 1-2.

Table 1-2:
Test Schedule

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Crude Flare	USEPA Method 11	H_2S	11/28/17	10:23	10:43
2	Crude Flare	USEPA Method 11	H_2S	11/28/17	10:55	11:15
3	Crude Flare	USEPA Method 11	H_2S	11/28/17	11:37	11:57
4	Crude Flare	USEPA Method 11	H_2S	11/28/17	12:17	12:37
5	Crude Flare	USEPA Method 11	H_2S	11/28/17	12:44	13:04
6	Crude Flare	USEPA Method 11	H_2S	11/28/17	13:08	13:28
7	Crude Flare	USEPA Method 11	H_2S	11/28/17	13:43	14:03
8	Crude Flare	USEPA Method 11	H_2S	11/28/17	14:25	14:45
9	Crude Flare	USEPA Method 11	H_2S	11/28/17	14:51	15:11
10	Crude Flare	USEPA Method 11	H_2S	11/28/17	15:44	16:04
1	Alky Flare	USEPA Method 11	H_2S	11/29/17	10:06	10:26
2	Alky Flare	USEPA Method 11	H_2S	11/29/17	10:31	10:51
3	Alky Flare	USEPA Method 11	H_2S	11/29/17	11:01	11:21
4	Alky Flare	USEPA Method 11	H_2S	11/29/17	11:23	11:43
5	Alky Flare	USEPA Method 11	H_2S	11/29/17	11:46	12:06
6	Alky Flare	USEPA Method 11	H_2S	11/29/17	12:18	12:38
7	Alky Flare	USEPA Method 11	H_2S	11/29/17	12:52	13:12
8	Alky Flare	USEPA Method 11	H_2S	11/29/17	13:14	13:34
9	Alky Flare	USEPA Method 11	H_2S	11/29/17	13:37	13:57
10	Alky Flare	USEPA Method 11	H_2S	11/29/17	14:09	14:29

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Discussion

Project Synopsis

Each RATA consisted of 10 test runs. Final results were calculated based on nine (9) best-fit test runs and compared to the limit outlined in PS 7.

Modifications to Test Methodology

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 should significantly affect the quality of the data.

Sample Train Operation

EPA 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 D of this report.

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

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 Flare – H_2S RATA Results

Run No.	Start Time	Date (2017)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)
1	10:23	Nov 28	32.45	20.57	11.88
2	10:55	Nov 28	30.78	20.28	10.50
3	11:37	Nov 28	38.95	24.44	14.51
4	12:17	Nov 28	35.78	26.10	9.68
5	12:44	Nov 28	38.42	25.15	13.27
6 *	13:08	Nov 28	41.12	24.00	17.12
7	13:43	Nov 28	37.82	29.27	8.55
8	14:25	Nov 28	40.83	27.65	13.18
9	14:51	Nov 28	42.65	34.53	8.12
10	15:44	Nov 28	45.15	32.97	12.18
Average			**38.09**	**26.77**	**11.32**

Relative Accuracy Test Audit Results

Standard Deviation of Differences	2.231	
Confidence Coefficient (CC)	1.715	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of Appl. Std.)	**8.1%**	**10.0%**
Appl. Std. = 160 ppmdv		

RM = Reference Method (CleanAir Data) 122217 102242
CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data)
RATA calculations are based on 9 of 10 runs. * indicates the excluded run.

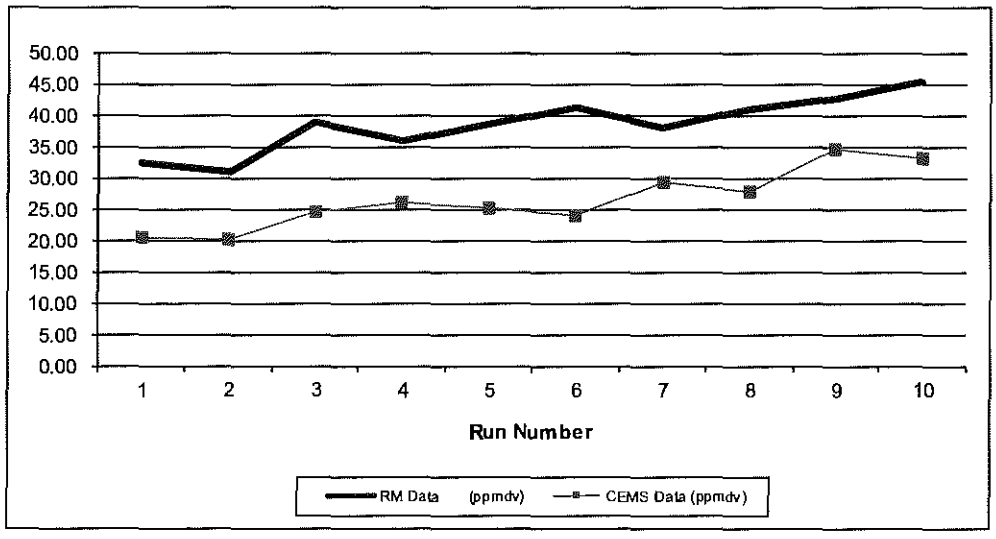


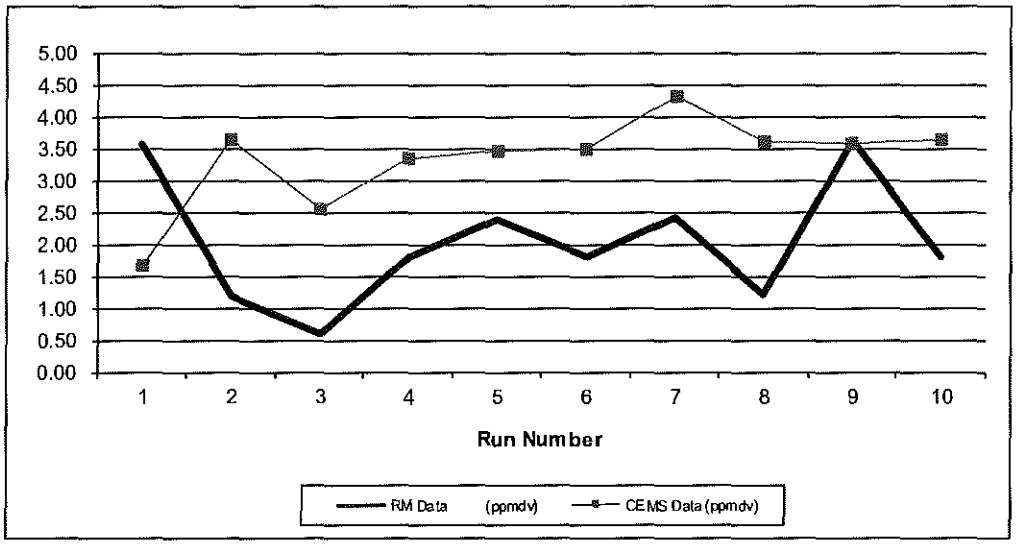
Table 2-2:
Alky Flare – H_2S RATA Results

Run No.	Start Time	Date (2017)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)
1	10:06	Nov 29	3.56	1.65	1.91
2 *	10:31	Nov 29	1.19	3.62	-2.43
3	11:01	Nov 29	0.60	2.54	-1.94
4	11:23	Nov 29	1.80	3.34	-1.54
5	11:46	Nov 29	2.39	3.46	-1.07
6	12:18	Nov 29	1.80	3.48	-1.68
7	12:52	Nov 29	2.41	4.30	-1.89
8	13:14	Nov 29	1.20	3.61	-2.41
9	13:37	Nov 29	3.61	3.56	0.05
10	14:09	Nov 29	1.81	3.64	-1.83
	Average		**2.13**	**3.29**	**-1.16**

Relative Accuracy Test Audit Results

Standard Deviation of Differences	1.346	
Confidence Coefficient (CC)	1.034	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of Appl. Std.)	**1.4%**	**10.0%**
Appl. Std. = 160 ppmdv		

RM = Reference Method (CleanAir Data) 122217 102242
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

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 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

4. METHODOLOGY

Procedures and Regulations

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.

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 11 "Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries"

Title 40 CFR Part 60, Appendix B Performance Specifications

PS 7 "Specifications and Test Procedures for Hydrogen Sulfide Continuous Emission Monitoring Systems in Stationary Sources"

Methodology Discussion

Reference Method H_2S Testing – EPA Method 11

RM H_2S concentration was determined using EPA 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 to two minutes.

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