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AIR QUALITY DIV.

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REPORT ON COMPLIANCE TESTING

Performed for:
**MARATHON PETROLEUM COMPANY
DETROIT REFINERY**

ZURN BOILER STACK (SV27-BR7)

Client Reference No: 4100048779
CleanAir Project No: 12469-1
Revision 0: July 2, 2014

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.

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PROJECT OVERVIEW

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INTRODUCTION

Marathon Petroleum Company (MPC) contracted Clean Air Engineering (CleanAir) to perform emission measurements 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 (USEPA) and the Michigan Department of Environmental Quality (DEQ). The permit limits are referenced in Michigan Department of Environmental Quality, Air Quality Division Permit to Install No. 63-08C, issued January 11, 2012.

Key Project Participants

Individuals responsible for coordinating and conducting the test program were:

Crystal Davis – MPC
Joe Reidy – MPC
Thomas Gasloli – DEQ
Jaci Amundsen – CleanAir

Test Program Parameters

The testing was performed at the Zurn Boiler Stack (Emission Unit ID No. EG27-ZURNBOILER; Stack ID No. SV27BR7) on May 6 and 7, 2014, and included the following emissions measurements:

- particulate matter (PM), assumed equivalent to filterable particulate matter (FPM) only
- sulfuric acid (H₂SO₄)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
 - methane (CH₄)
 - ethane (C₂H₆)
- nitrogen oxides (NO_x)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas flow rate

PROJECT OVERVIEW

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	Zurn Boiler Stack	USEPA 5	FPM	05/06/14	10:08	12:15
2	Zurn Boiler Stack	USEPA 5	FPM	05/06/14	13:00	15:12
3	Zurn Boiler Stack	USEPA 5	FPM	05/06/14	15:50	18:32
1	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	10:10	10:31
2	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	10:49	11:10
3	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	11:21	11:42
4	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	11:54	12:15
5	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	12:26	12:47
6	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	12:59	13:20
7	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	13:32	13:53
8	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	14:05	14:26
9	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	14:39	15:00
10	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	15:11	15:32
11	Zurn Boiler Stack	USEPA 3A/7E	O ₂ /CO ₂ /NO _x	05/06/14	15:44	16:05
1	Zurn Boiler Stack	USEPA 3A/18/25A	O ₂ /CO ₂ /CH ₄ /C ₂ H ₆ /THC	05/06/14	10:10	11:42
2	Zurn Boiler Stack	USEPA 3A/18/25A	O ₂ /CO ₂ /CH ₄ /C ₂ H ₆ /THC	05/06/14	12:59	14:26
3	Zurn Boiler Stack	USEPA 3A/18/25A	O ₂ /CO ₂ /CH ₄ /C ₂ H ₆ /THC	05/06/14	14:39	16:05
4	Zurn Boiler Stack	USEPA 3A/18/25A	O ₂ /CO ₂ /CH ₄ /C ₂ H ₆ /THC	05/06/14	16:18	17:18
0	Zurn Boiler Stack	Draft ASTM CCM	H ₂ SO ₄	05/07/14	09:40	10:40
1	Zurn Boiler Stack	Draft ASTM CCM	H ₂ SO ₄	05/07/14	11:27	12:27
2	Zurn Boiler Stack	Draft ASTM CCM	H ₂ SO ₄	05/07/14	13:04	14:04
3	Zurn Boiler Stack	Draft ASTM CCM	H ₂ SO ₄	05/07/14	14:38	16:37

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PROJECT OVERVIEW

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Results Summary

Tables 1-2 and 1-3 summarize the results of the test program. A more detailed presentation of the test conditions and results of analysis are shown on pages 2-1 through 2-10.

**Table 1-2:
Summary of Emission Compliance Test Results**

<u>Source</u>			Average Emission	Permit Limit ¹
Constituent	(Units)	Sampling Method		
<u>Zurn Boiler Stack</u>				
PM	(lb/MMBtu)	USEPA 5	0.0009	0.0019
H ₂ SO ₄	(ppmdv)	Draft ASTM CCM	0.024	N/A
	(lb/MMBtu)		8.2E-05	N/A
VOC	(lb/MMBtu)	USEPA 18/25A	< 0.0007	0.0055
NO _x	(lb/MMBtu)	USEPA 7E	0.14	0.20

¹ Permit limits obtained from MDEQ Permit To Install No. 63-08C.

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**Table 1-3:
Summary of RATA Results**

<u>Source</u>	Reference Method	Applicable Specification	Relative Accuracy (%)	Specification Limit ¹
Constituent (Units)				
<u>Zurn Boiler Stack</u>				
O ₂ (% dv)	USEPA 3A	PS3	0.30	±1.0% dv
NO _x (ppmdv)	USEPA 7E	PS2	5.8	20% of RM
NO _x (ppmdv @ 0%O ₂)	USEPA 7E	PS2	7.9	20% of RM
NO _x (lb/MMBtu)	USEPA 7E	PS2	8.9	20% of RM

¹ Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

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PROJECT OVERVIEW

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Discussion of Test Program

FPM Testing - EPA Method 5

For this test program, PM emission rate is assumed equivalent to FPM emission rate. Three (3) 120-minute Method 5 test runs were performed on May 6.

Upon analysis, the laboratory discovered that the front half acetone rinse from Run 1 contained a foreign object in the sample. The object was magnetic and is not believed to be representative of the actual stack gas sampled. It is CleanAir's opinion that this foreign object is a port scraping.

The laboratory first obtained a weight with the foreign object inside the sample. The object was then removed, rinsed, then reanalyzed. While both analytical results are presented in the laboratory report, the reanalyzed Run1 result with the foreign piece removed was used to calculate the final results.

The final result was expressed as the average of three valid runs and was below the permit limit for PM.

H₂SO₄ Testing - Draft ASTM Controlled Condensation Method

Three (3) 60-minute test runs were performed on May 7. The final result was expressed as the average of three valid runs.

Run 3 was paused approximately 40 minutes in because of a stoppage of work due to lightning in the area. The run was resumed approximately 60 minutes later following the all clear signal.

O₂ and NO_x Emissions / RATA Testing - EPA Methods 3A and 7E; Performance Specifications 2 and 3

Minute-average data points for O₂, CO₂ and NO_x (dry basis) were collected over a period of 21 minutes for each RATA Reference Method (RM) run. The average result for each RM run was calculated and compared to the average result from the facility CEMS over an identical time interval in order to calculate relative accuracy (RA).

- For O₂, RA is expressed as the average absolute difference between the RM and facility CEMs runs. The final result was below the limit of $\pm 1.0\%$ dv set by PS3.
- For NO_x (ppmdv, ppmdv @ 0% O₂, and lb/MMBtu), RA is expressed as the percent difference between RM and facility CEMs runs. The final results were below the limit of 20% of the RM set by PS2.
- CO₂ data was collected only as supplemental information.

PROJECT OVERVIEW

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NO_x results from the RATA were converted from units of dry volume-based concentration (ppmdv) to mass-based emission rate units (lb/MMBtu) to demonstrate compliance with permit limits. The final result was expressed as the average of all 11 RATA runs. The final result was below the permit limit.

VOC Testing - EPA Methods 25A and 18

Three VOC test runs were performed concurrently with the RATA testing. Nine (9) 21-minute Method 25 test runs for THC were performed concurrently with three Method 18 bag collections for CH₄ and C₂H₆, with each Method 18 sample collected over a period of about 60 minutes. Method 18 samples were collected as follows:

- Method 18 Run 1: Collected during RATA Runs 1, 2 and 3
- Method 18 Run 2: Collected during RATA Runs 6, 7 and 8
- Method 18 Run 3: Collected during RATA Runs 9, 10 and 11

Following Method 18 Run 2, the CEMS operator failed to close the inlet valve to the CH₄ and C₂H₆ collection bag. This resulted in the sample bag being subjected to foreign calibration gas. This run was not used in the calculation of the final results. An additional 60-minute Method 18 test run was performed following the completion of the RATA.

VOC emission rate is normally equivalent to THC emission rate, minus CH₄ and C₂H₆ emission rate. The calculated emission rate of CH₄ and C₂H₆ detected through analysis of each Method 18 sample bag exceeded the amount of THC measured by the on-line THC analyzer.

This is likely due to variations in the calibration standards, measurement and analytical technique. Therefore, VOC emissions are reported as a value "less than" 1% of the calibration span of THC instrument. The final results were calculated using the average of three valid test runs, all using a concentration of 1% of the instrument span and reported as "less than" the amount.

Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted to units of pounds per million Btu (lb/MMBtu) using the oxygen-based fuel factor (F_d) for natural gas in EPA Method 19, Table 19-2.

End of Section 1 – Project Overview

RESULTS

2-1

**Table 2-1:
Zurn Boiler Stack – FPM Emissions (M-5)**

Run No.		1	2	3	Average
Date (2014)		May 6	May 6	May 6	
Start Time (approx.)		10:08	13:00	15:50	
Stop Time (approx.)		12:15	15:12	18:32	
Process Conditions					
P ₁	Natural gas flow rate (Mscf/day)	2,499	2,848	3,264	2,871
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760
Gas Conditions					
O ₂	Oxygen (dry volume %)	7.8	7.4	7.2	7.5
CO ₂	Carbon dioxide (dry volume %)	7.0	7.2	7.4	7.2
T _s	Sample temperature (°F)	330	338	344	337
B _w	Actual water vapor in gas (% by volume)	11.4	13.4	13.9	12.9
Gas Flow Rate					
Q _a	Volumetric flow rate, actual (acfm)	44,600	47,300	52,200	48,000
Q _s	Volumetric flow rate, standard (scfm)	28,900	30,300	33,200	30,800
Q _{std}	Volumetric flow rate, dry standard (dscfm)	25,600	26,200	28,600	26,800
Q _a	Volumetric flow rate, actual (acf/hr)	2,680,000	2,840,000	3,130,000	2,880,000
Q _s	Volumetric flow rate, standard (scf/hr)	1,730,000	1,820,000	1,990,000	1,850,000
Q _{std}	Volumetric flow rate, dry standard (dscf/hr)	1,530,000	1,570,000	1,710,000	1,610,000
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	68.24	72.96	78.49	73.23
%I	Isokinetic sampling (%)	97.7	101.8	100.6	100.0
Laboratory Data					
m _n	Total FPM (g)	0.00180	0.00163	0.00304	
m _{Part}	Total filterable particulate matter (g)	0.00180	0.00163	0.00304	
n _{MDL}	Number of non-detectable fractions	N/A	N/A	N/A	
DLC	Detection level classification	ADL	ADL	ADL	
FPM Results					
C _{sd}	Particulate Concentration (lb/dscf)	5.82E-08	4.93E-08	8.54E-08	6.43E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.089	0.078	0.146	0.104
E _{T/yr}	Particulate Rate (Ton/yr)	0.391	0.339	0.641	0.457
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.0008	0.0007	0.0011	0.0009

Average includes 3 runs.

Detection level classifications are defined as follows:

ADL = Above Detection Level - all fractions are above detection limit

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RESULTS

**Table 2-2:
Uncertainty Analysis – FPM (M-5)**

	FPM Results (lb/MMBtu)		FPM Results (lb/hr)		FPM Results (Ton/yr)	
Method	5		5		5	
Run No.	1	0.0008	1	0.0892	1	0.3909
	2	0.0007	2	0.0775	2	0.3395
	3	0.0011	3	0.1464	3	0.6410
SD	0.0002		0.0368		0.1613	
AVG	0.0009		0.1044		0.4571	
RSD	27.7%		35.3%		35.3%	
N	3		3		3	
SE	0.0001		0.0213		0.0931	
RSE	16.0%		20.4%		20.4%	
P	95.0%		95.0%		95.0%	
TINV	4.303		4.303		4.303	
CI +	0.0015		0.1959		0.8579	
AVG	0.0009		0.1044		0.4571	
CI -	0.0003		0.0129		0.0564	
TB +	0.0027		0.3864		1.6923	

AVG (average) is the mean value of the runs; N is the number of individual runs.

SD (standard deviation) and RSD (relative standard deviation) are measures of the variability of individual runs.

SE (standard error) and RSE (relative standard error) are measures of the variability of the average of the runs.

P (probability) is the confidence level associated with the two-tailed Student's t-distribution.

TINV (t-value) is the value of the Student's t-distribution as a function of P (probability) and N-1 (degrees of freedom).

CI (confidence interval) indicates that if the test is conducted again under the same conditions, the average would be expected to fall within the interval (CI- to CI+) about 95% of the time.

TB+ (upper tolerance bound) is the value below which 95% of future runs are expected to fall (assuming testing at the same conditions).

RESULTS

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**Table 2-3:
Zurn Boiler Stack – H₂SO₄ Emissions (Draft ASTM CCM)**

Run No.		1	2	3	Average
Date (2014)		May 7	May 7	May 7	
Start Time (approx.)		11:27	13:04	14:38	
Stop Time (approx.)		12:27	14:04	16:37	
Process Conditions					
P ₁	Fuel gas flow rate (Mscf/day)	3,170	3,401	3,266	3,279
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710
Gas Conditions					
O ₂	Oxygen (dry volume %)	7.0	6.8	7.6	7.1
CO ₂	Carbon dioxide (dry volume %)	7.6	7.6	7.3	7.5
T _s	Sample temperature (°F)	358	361	367	362
B _w	Actual water vapor in gas (% by volume)	13.7	14.4	13.7	13.9
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	27.83	27.46	27.20	27.50
Laboratory Data (Ion Chromatography)					
m _n	Total H ₂ SO ₄ collected (mg)	0.0750	0.0924	0.0651	
Sulfuric Acid Vapor (H₂SO₄) Results					
C _{sd}	H ₂ SO ₄ Concentration (lb/dscf)	5.94E-09	7.42E-09	5.28E-09	6.21E-09
C _{sd}	H ₂ SO ₄ Concentration (ppmdv)	0.0233	0.0292	0.0208	0.0244
E _{Fd}	H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	7.78E-05	9.58E-05	7.23E-05	8.20E-05

Average includes 3 runs.

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RESULTS

**Table 2-4:
Uncertainty Analysis – H₂SO₄ (Draft ASTM CCM)**

Method	H2SO4 Results (ppmdv)		H2SO4 Results (lb/MMBtu)	
	Run No.	CCM	Run No.	CCM
	1	0.0233	1	7.78E-05
	2	0.0292	2	9.58E-05
	3	0.0208	3	7.23E-05
SD		0.0043		1.23E-05
AVG		0.0244		8.20E-05
RSD		17.6%		15.0%
N		3		3
SE		0.0025		7.10E-06
RSE		10.2%		8.7%
P		95.0%		95.0%
TINV		4.303		4.303
CI +		0.0351		1.13E-04
AVG		0.0244		8.20E-05
CI -		0.0137		5.14E-05
TB +		0.057		1.76E-04

AVG (average) is the mean value of the runs; N is the number of individual runs.

SD (standard deviation) and RSD (relative standard deviation) are measures of the variability of individual runs.

SE (standard error) and RSE (relative standard error) are measures of the variability of the average of the runs.

P (probability) is the confidence level associated with the two-tailed Student's t-distribution.

TINV (t-value) is the value of the Student's t-distribution as a function of P (probability) and N-1 (degrees of freedom).

CI (confidence interval) indicates that if the test is conducted again under the same conditions, the average would be expected to fall within the interval (CI- to CI+) about 95% of the time.

TB+ (upper tolerance bound) is the value below which 95% of future runs are expected to fall (assuming testing at the same conditions).

RESULTS

**Table 2-5:
Zurn Boiler Stack – THC, CH₄, C₂H₆ and VOC Emissions (M-25A / 18)**

Run No.		1	2*	3	4	Average
Date (2014)		May 6	May 6	May 6	May 6	
Start Time (approx.)		10:10	12:59	14:39	16:18	
Stop Time (approx.)		11:42	14:26	16:05	17:18	
Process Conditions						
P ₁	Natural gas flow rate (Mscf/day)	2,472	2,847	2,852	3,505	2,943
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710	8,710
Gas Conditions						
O ₂	Oxygen (dry volume %)	7.4	7.4	7.4	6.8	7.2
CO ₂	Carbon dioxide (dry volume %)	7.5	7.5	7.5	7.8	7.6
B _w	Actual water vapor in gas (% by volume) [†]	11.4	13.4	13.4	13.9	12.9
THC Results						
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	28.3	36.1	35.6	33.7	32.5
C _{sd}	Concentration (lb/dscf)	3.23E-06	4.13E-06	4.07E-06	3.85E-06	3.72E-06
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0436	0.0555	0.0547	0.0497	0.0493
Methane Results						
C _{sd}	Concentration (ppmdv)	94.5	116.5	115.1	109.0	106.2
C _{sd}	Concentration (lb/dscf)	3.94E-06	4.85E-06	4.79E-06	4.54E-06	4.42E-06
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0531	0.0652	0.0644	0.0585	0.0587
Ethane Results						
C _{sd}	Concentration (ppmdv)	3.09	4.24	3.98	3.81	3.63
C _{sd}	Concentration (lb/dscf)	2.41E-07	3.31E-07	3.11E-07	2.97E-07	2.83E-07
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.0033	0.0044	0.0042	0.0038	0.0038
VOC Results						
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007

Average includes 3 Runs. * indicates a run not included in the average.

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[†] Moisture data used for ppmwv to ppmdv correction obtained from nearly-concurrent Method 5 runs.

For VOCs, '<' indicates a measured/calculated response below the detection limit (assumed to be 1% of the instrument calibration span).

RESULTS

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**Table 2-6:
Zurn Boiler Stack – NO_x Emissions (M-7E)**

Run No.		1	2	3	4	5	6
Date (2014)		May 6	May 6	May 6	May 6	May 6	May 6
Start Time (approx.)		10:10	10:49	11:21	11:54	12:26	12:59
Stop Time (approx.)		10:31	11:10	11:42	12:15	12:47	13:20
Process Conditions							
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710	8,710	8,710
Gas Conditions							
O ₂	Oxygen (dry volume %)	7.4	7.4	7.4	7.4	7.6	7.2
CO ₂	Carbon dioxide (dry volume %)	7.5	7.5	7.5	7.5	7.4	7.6
Nitrogen Oxides Results							
C _{sd}	Concentration (ppmdv)	87.0	86.6	86.3	87.3	85.0	88.9
C _{sd}	Concentration (lb/dscf)	1.04E-05	1.03E-05	1.03E-05	1.04E-05	1.02E-05	1.06E-05
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.140	0.140	0.139	0.140	0.139	0.142

Run No.		7	8	9	10	11	Average
Date (2014)		May 6	May 6	May 6	May 6	May 6	
Start Time (approx.)		13:32	14:05	14:39	15:11	15:44	
Stop Time (approx.)		13:53	14:26	15:00	15:32	16:05	
Process Conditions							
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710	8,710	8,710
Gas Conditions							
O ₂	Oxygen (dry volume %)	7.4	7.4	7.4	7.3	7.3	7.4
CO ₂	Carbon dioxide (dry volume %)	7.5	7.4	7.5	7.5	7.5	7.6
Nitrogen Oxides Results							
C _{sd}	Concentration (ppmdv)	86.8	86.5	87.1	89.4	88.2	87.2
C _{sd}	Concentration (lb/dscf)	1.04E-05	1.03E-05	1.04E-05	1.07E-05	1.05E-05	1.04E-05
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	0.140	0.139	0.140	0.143	0.141	0.140

Average includes 11 runs.

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RESULTS

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**Table 2-7:
Zurn Boiler Stack – O₂ Relative Accuracy (M-3A / PS3)**

Run No.	Start Time	Date (2014)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	10:10	May 6	7.37	7.06	0.31	4.2%
2	10:49	May 6	7.44	7.15	0.29	3.9%
3	11:21	May 6	7.43	7.13	0.30	4.0%
4	11:54	May 6	7.35	7.06	0.29	3.9%
5 *	12:26	May 6	7.59	7.20	0.39	5.1%
6 *	12:59	May 6	7.25	6.91	0.34	4.7%
7	13:32	May 6	7.42	7.10	0.32	4.3%
8	14:05	May 6	7.42	7.15	0.27	3.6%
9	14:39	May 6	7.40	7.14	0.26	3.5%
10	15:11	May 6	7.32	7.00	0.32	4.4%
11	15:44	May 6	7.33	6.99	0.34	4.6%
Average			7.39	7.09	0.30	4.1%

Relative Accuracy Test Audit Results

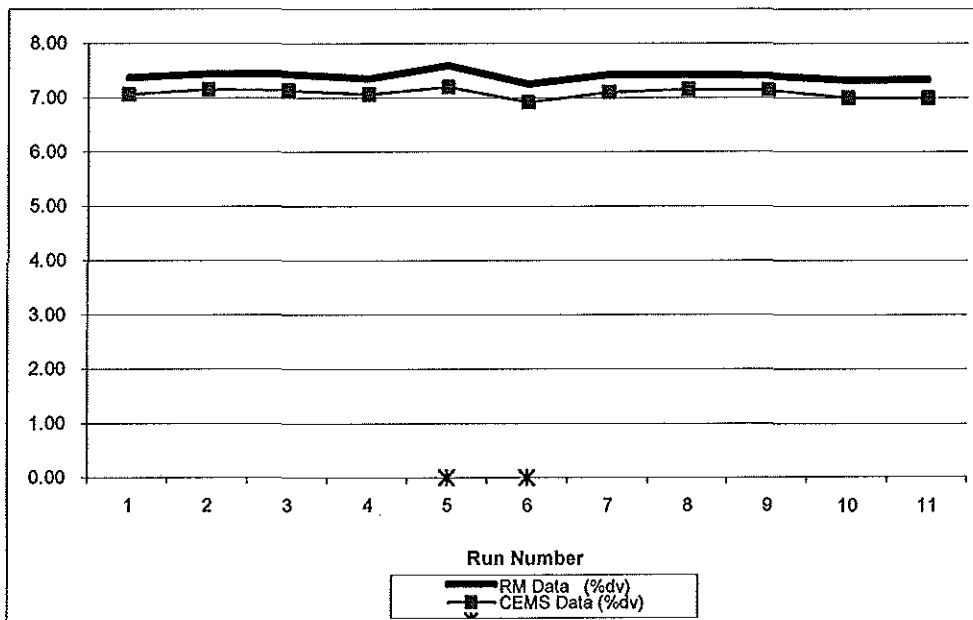
Standard Deviation of Differences	0.025	
Confidence Coefficient (CC)	0.020	
t-Value for 9 Data Sets	2.306	
Avg. Abs. Diff. (%dv)	0.30	Limit 1.0

RM = Reference Method (CleanAir Data)

061314 105817

CEMS = Continuous Emissions Monitoring System (Marathon Data)

RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.



RESULTS

**Table 2-8:
Zurn Boiler Stack – NO_x (ppmdv) Relative Accuracy (M-7E / PS2)**

Run No.	Start Time	Date (2014)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	10:10	May 6	86.98	82.06	4.92	5.7%
2 *	10:49	May 6	86.56	81.26	5.30	6.1%
3	11:21	May 6	86.33	81.61	4.72	5.5%
4	11:54	May 6	87.26	82.29	4.97	5.7%
5	12:26	May 6	85.02	81.02	4.00	4.7%
6	12:59	May 6	88.91	83.89	5.02	5.6%
7	13:32	May 6	86.81	81.77	5.04	5.8%
8	14:05	May 6	86.50	81.85	4.65	5.4%
9 *	14:39	May 6	87.10	81.32	5.78	6.6%
10	15:11	May 6	89.40	84.31	5.09	5.7%
11	15:44	May 6	88.20	83.38	4.82	5.5%
Average			87.27	82.46	4.80	5.5%

Relative Accuracy Test Audit Results

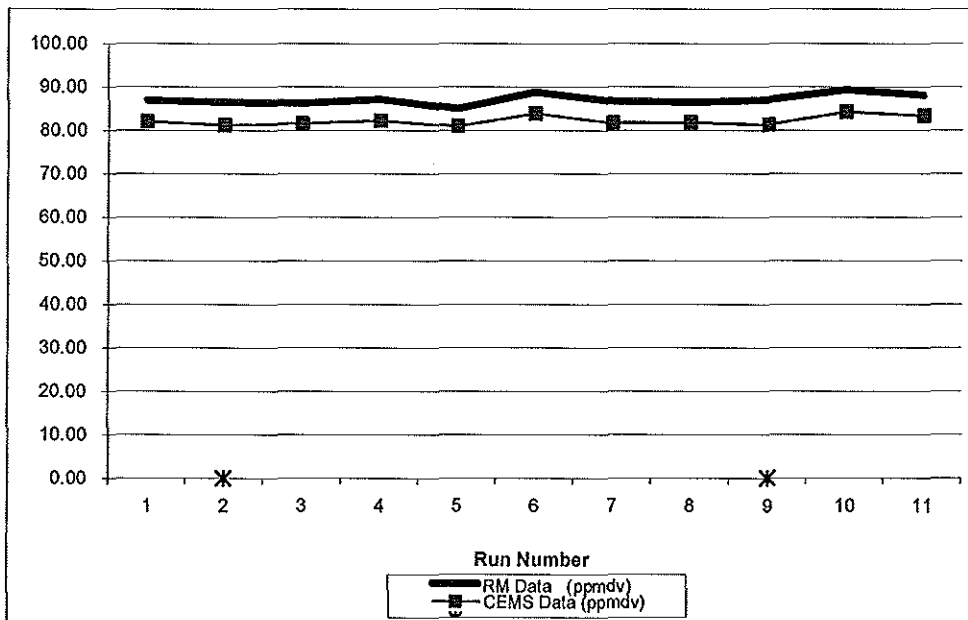
Standard Deviation of Differences	0.336	
Confidence Coefficient (CC)	0.258	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	5.8%	Limit 20.0%

RM = Reference Method (CleanAir Data)

081314 105817

CEMS = Continuous Emissions Monitoring System (Marathon Data)

RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.



RESULTS

**Table 2-9:
Zurn Boiler Stack – NO_x (ppmdv @ 0% O₂) Relative Accuracy (M-7E / PS2)**

Run No.	Start Time	Date (2014)	RM Data (ppm@0%O2)	CEMS Data (ppm@0%O2)	Difference (ppm@0%O2)	Difference Percent
1	10:10	May 6	134.37	123.57	10.80	8.0%
2 *	10:49	May 6	134.39	123.46	10.93	8.1%
3	11:21	May 6	133.95	123.95	10.00	7.5%
4	11:54	May 6	134.64	124.25	10.39	7.7%
5	12:26	May 6	133.52	123.51	10.01	7.5%
6	12:59	May 6	136.10	126.10	10.00	7.3%
7	13:32	May 6	134.61	124.24	10.37	7.7%
8	14:05	May 6	134.12	124.06	10.06	7.5%
9 *	14:39	May 6	134.84	123.69	11.15	8.3%
10	15:11	May 6	137.63	126.63	11.00	8.0%
11	15:44	May 6	135.86	125.37	10.49	7.7%
Average			134.98	124.63	10.35	7.7%

Relative Accuracy Test Audit Results

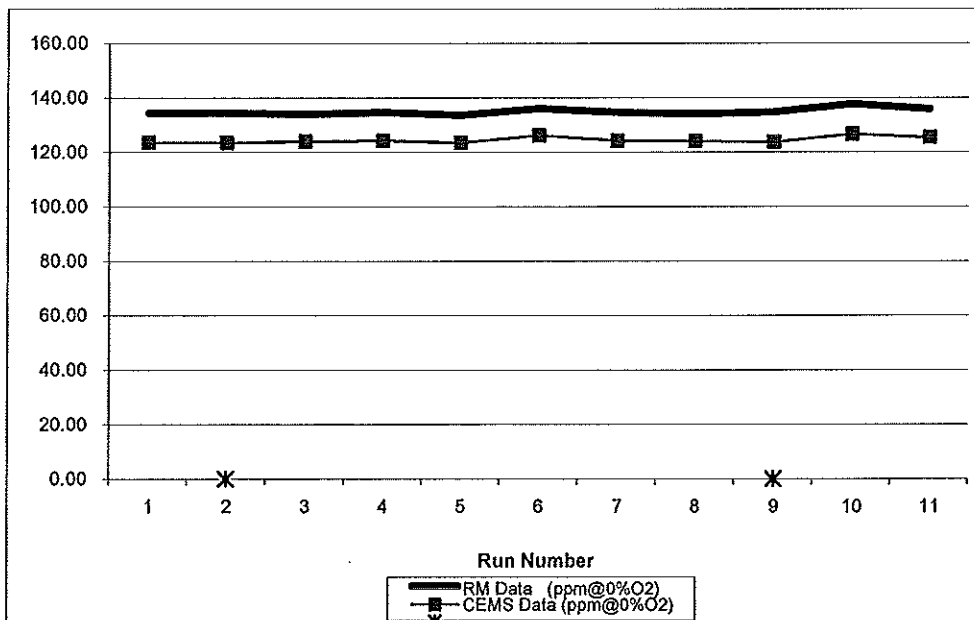
Standard Deviation of Differences	0.369	
Confidence Coefficient (CC)	0.284	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	7.9%	Limit 20.0%

RM = Reference Method (CleanAir Data)

061314 105817

CEMS = Continuous Emissions Monitoring System (Marathon Data)

RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.



RESULTS

2-10

**Table 2-10:
Zurn Boiler Stack – NO_x (lb/MMBtu) Relative Accuracy (M-7E / PS2)**

Run No.	Start Time	Date (2014)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1 *	10:10	May 6	0.1397	0.1231	0.0166	11.9%
2 *	10:49	May 6	0.1398	0.1261	0.0137	9.8%
3	11:21	May 6	0.1393	0.1276	0.0117	8.4%
4	11:54	May 6	0.1400	0.1280	0.0120	8.6%
5	12:26	May 6	0.1389	0.1284	0.0105	7.6%
6	12:59	May 6	0.1415	0.1288	0.0127	9.0%
7	13:32	May 6	0.1400	0.1291	0.0109	7.8%
8	14:05	May 6	0.1395	0.1292	0.0103	7.4%
9	14:39	May 6	0.1402	0.1292	0.0110	7.8%
10	15:11	May 6	0.1431	0.1294	0.0137	9.6%
11	15:44	May 6	0.1413	0.1298	0.0115	8.1%
Average			0.1404	0.1288	0.0116	8.3%

Relative Accuracy Test Audit Results

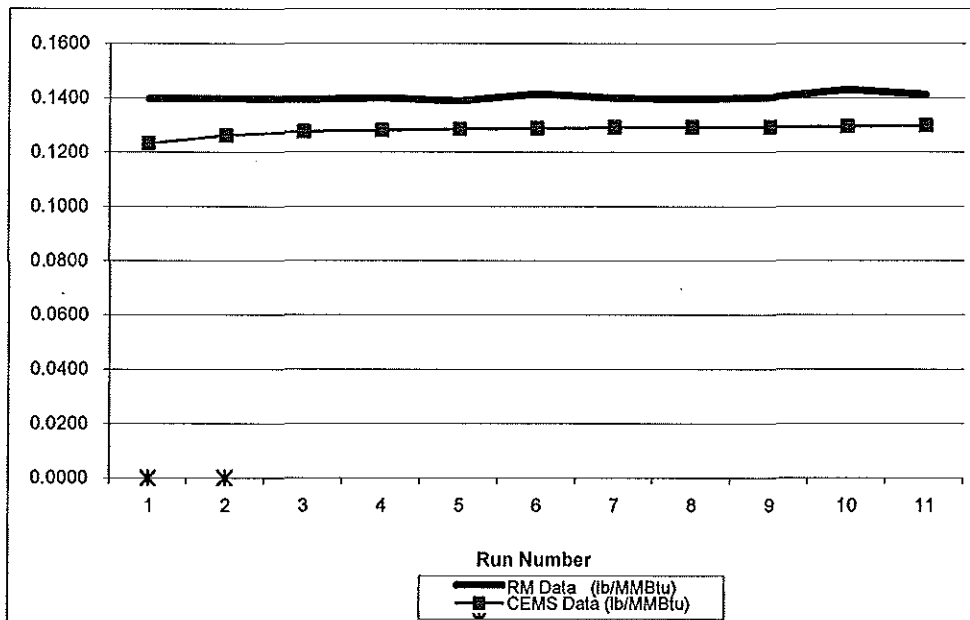
Standard Deviation of Differences	0.001	
Confidence Coefficient (CC)	0.001	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	8.9%	Limit 20.0%

RM = Reference Method (CleanAir Data)

061314 105817

CEMS = Continuous Emissions Monitoring System (Marathon Data)

RATA calculations are based on 9 of 11 runs. * indicates the excluded runs.



End of Section 2 – Results

DESCRIPTION OF INSTALLATION

PROCESS DESCRIPTION

MPC's facility in Detroit, Michigan produces refined petroleum products from crude oil. As part of the Detroit Heavy Oil Upgrade Project (DHOUP), new equipment has been installed to process heavy crude oil from Canada. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Zurn Boiler (EG27-ZURNBOILER) generates steam required by other refinery process components. The unit is fired by natural gas. Emissions are vented to the atmosphere via the Zurn Boiler Stack (SV27-BR7).

The testing reported in this document was performed at the Zurn Boiler Stack.

DESCRIPTION OF SAMPLING LOCATIONS

Sampling point locations were determined according to EPA Methods 1 and 7E, and Performance Specification 2.

Table 3-1 outlines the sampling point configurations. The figures shown on pages 3-2 and 3-3 illustrate the sampling points and orientation of sampling ports.

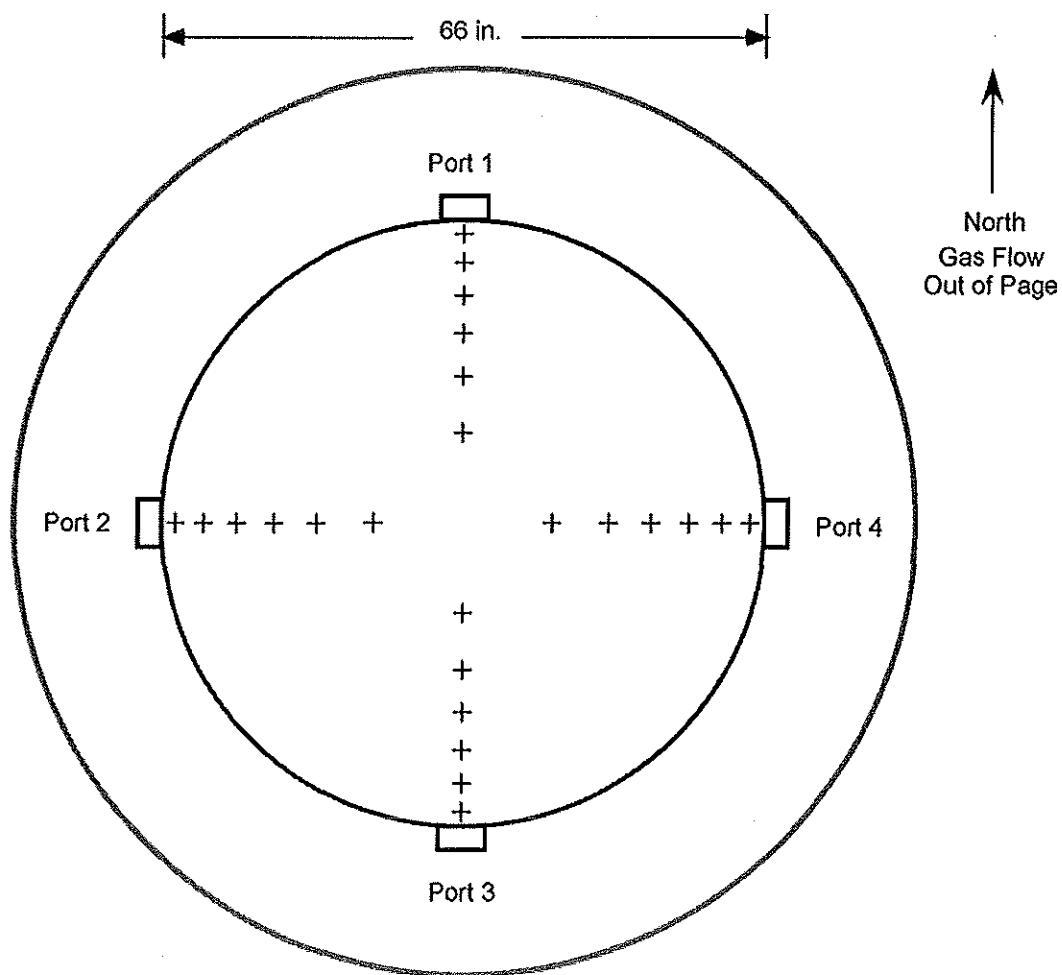
**Table 3-1:
Sampling Points**

<u>Source</u>		Run	Points per	Minutes per	Total		
Constituent	Method (USEPA)	No.	Port	Point	Minutes	Figure	
<u>Zurn Boiler Stack</u>							
FPM	5	1-3	4	6	5	120	3-1
H ₂ SO ₄	Draft ASTM CCM	1-3	1	1	60	60	N/A ¹
O ₂ / CO ₂ / CH ₄ / C ₂ H ₆ / THC	3A / 18 / 25A	1-4	1	3	21/20	63/60	3-2
O ₂ / NO _x (RATAs)	3A+PS3 / 7E+PS2	1-11	1	3	7	21	3-2

¹ Sampling occurred at a single point near the center of duct.

DESCRIPTION OF INSTALLATION

3-2



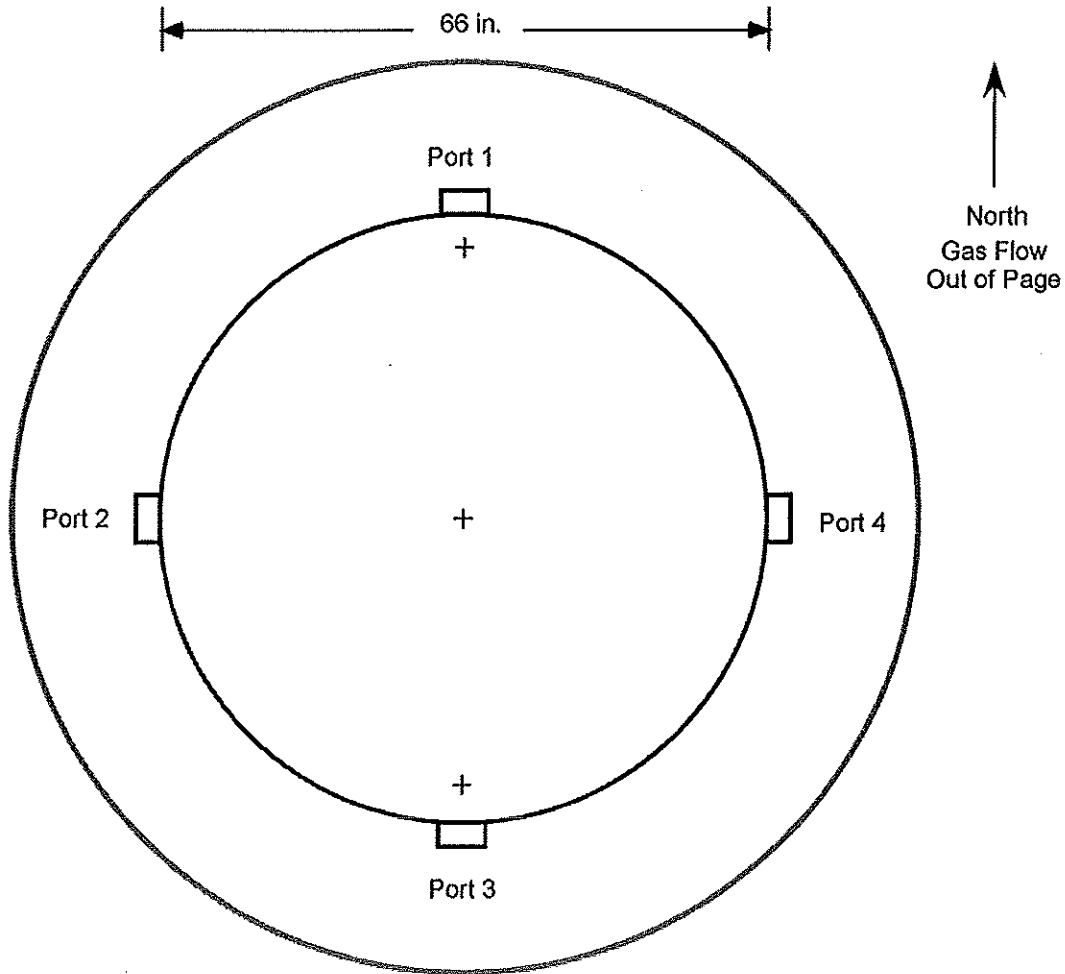
<u>Sampling Point</u>	<u>Port to Point Distance (in.)</u>
1	23.5
2	16.5
3	11.7
4	7.8
5	4.4
6	1.4

Duct diameters upstream from flow disturbance (A): 10.0 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 3.4 Limit: 2.0

Figure 3-1: EPA Method 5 Sampling Points

DESCRIPTION OF INSTALLATION

3-3



<u>Sampling Point</u>	<u>Port to Point Distance (in.)</u>
1	11.0
2	33.0
3	55.0

Duct diameters upstream from flow disturbance (A):	10.0	Limit: 0.5
Duct diameters downstream from flow disturbance (B):	3.4	Limit: 2.0

Figure 3-2: EPA Method 3A/7E/18/25A Sampling Points

End of Section 3 – Description of Installation

METHODOLOGY

4-1

Clean Air Engineering followed procedures as detailed in EPA Methods 1, 2, 3, 3A, 3B, 4, 5, 7E, 18, 19, 25A, Performance Specifications 2, 3, and the Draft ASTM Controlled Condensation Method (CCM). The following table summarizes the methods and their respective sources.

**Table 4-1:
Summary of Sampling Procedures**

<u>Title 40 CFR Part 60 Appendix A</u>	
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 Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 18	"Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"
Method 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"
<u>Title 40 CFR Part 60 Appendix B (Performance Specifications (PS))</u>	
PS2	"Specifications and Test Procedures for SO ₂ and NO _x Continuous Emission Monitoring Systems in Stationary Sources"
PS3	"Specifications and Test Procedures for O ₂ and CO ₂ Continuous Emission Monitoring Systems in Stationary Sources"
<u>Draft Methods</u>	
Draft ASTM CCM	"Standard Test Method for Determination of Sulfur Trioxide and Sulfuric Acid Vapor and Mist, from Stationary Sources Using a Controlled Condensation Sampling System"

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 D.

METHODOLOGY

4-2

FPM Testing - EPA Method 5

Particulate matter emissions were determined using EPA Method 5. For this test program, particulate matter is assumed equivalent to FPM.

The front-half of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 250°F, and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

After exiting the filter, the flue gas passed through a Teflon line into a series of knockout jars surrounded by ice. The purpose of the knockout jars was 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.

H₂SO₄ Testing - Draft ASTM Controlled Condensation Method

H₂SO₄ emissions were determined referencing the Draft ASTM Controlled Condensation Method.

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at 650°F and a quartz fiber filter maintained at 650°F to remove particulate matter.

The sample 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) located at the condenser outlet collected any residual sulfuric acid mist that passed through the condenser. The condenser temperature was regulated by a circulating water jacket; the SAM filter temperature was regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at 140°F ±9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved SO₂ into the H₂SO₄-collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then continued through a series of four glass knock-out jars; two containing water, one empty and one containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set was maintained below 68°F. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

METHODOLOGY

4-3

The H₂SO₄-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H₂O as the recovery/extraction solvent; any H₂SO₄ disassociated into sulfate ion (SO₄²⁻) and was stabilized in the H₂O matrix until analysis.

Prior to the first official test run, a 60-minute sample conditioning run was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H₂SO₄-collecting portion of the sample train). The conditioning run was recovered in the same manner as the official test runs, but the condenser rinse and SAM filter were not analyzed.

A field train blank was assembled, transported to the location, heated, leak-checked and recovered as if it were an actual test sample. Reagent blanks were collected to quantify background contamination.

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

O₂, CO₂ and VOC Testing - EPA Methods 3A, 18 and 25A

O₂ and CO₂ emissions were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. VOC emissions were determined using EPA Method 25A to quantify total THC emissions and EPA Method 18 to quantify methane (CH₄) and ethane (C₂H₆) emissions. VOC emissions are equivalent to THC emissions, minus CH₄ and C₂H₆ emissions.

The Method 3A/18/25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate and delivered at 250°F to a tee at the end of the heated sample line.

- One leg of the tee was connected to a flame ionization analyzer (FIA), which continuously measured minute-average THC concentration expressed in terms of propane (C₃H₈) on an actual (wet) basis.
- The other leg of the tee was connected to a gas conditioner which removed moisture before delivering the gas to a flow panel, and the O₂/CO₂ analyzers which measured concentration on a dry basis (units of %_{dv} or ppm_{dv}).
- The Method 18 gas sample was collected by pulling a slipstream from the flow panel and delivered it into a Tedlar bag at a constant rate. The moisture condensate was not collected for analysis as CH₄ and C₂H₆ are insoluble in water. Each bag was filled over a period of about one hour for each test run.

THC analyzer calibration was performed by introducing zero air, high, mid- and low range C₃H₈ 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.

METHODOLOGY

4-4

O₂/CO₂ calibration error checks were performed by introducing zero nitrogen (N₂), high range 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. Per Method 3A, the average results for each run were drift-corrected.

Analysis for CH₄ and C₂H₆ was performed off-site by CleanAir Analytical Services using gas chromatography (GC). Since moisture was removed from the sample prior to collection and GC analysis, the concentration results were on a dry basis. At least five sample injections were analyzed for each run.

GC calibration was performed by generating a calibration curve from triplicate injections of three distinct CH₄ and C₂H₆ concentrations introduced directly into the GC. Upon completion of calibration, a recovery study was performed by spiking two of the bag samples with a known concentration of CH₄ and C₂H₆, storing the bags for the same period of time prior to analysis as the field samples, and analyzing the bags to determine percent recovery.

O₂, CO₂ and NO_x Emissions / RATA Testing - EPA Methods 3A and 7E, Performance Specifications 2 and 3

RM O₂ and CO₂ emissions were determined using a paramagnetic/NDIR CEMS analyzer per EPA Method 3A and Performance Specification 3. RM NO_x emissions were determined using a chemiluminescent CEMS analyzer per EPA Method 7E and Performance Specification 2. RM CO emissions were determined using an infrared CEMS analyzer per EPA Method 10 and Performance Specification 4 or 4A.

The sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate at the points specified by the stratification check or performance specification and delivered at 250°F to a gas conditioner which removed moisture. The flue gas was then delivered via a flow panel to an analyzer bank. Each analyzer measured concentration on a dry basis (units of %dv or ppm_{dv}).

Calibration error checks were performed by introducing zero nitrogen (N₂), high range 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. Per Methods 3A, 7E and 10, the average results for each run were drift-corrected. Documentation of interference checks and NO₂ converter efficiency checks are included in Appendix D.

METHODOLOGY

4-5

General Considerations

A verification of the absence of cyclonic flow was performed at the Zurn Boiler Stack on May 6, following Method 1 specifications. Documentation is included in Appendix E.

O₂ and CO₂ data for the non-instrumental (wet) sampling methods (used in molecular weight calculations and calculation of F_d-based emissions) was obtained using a modified version of EPA Method 3B:

- Multi-point, integrated gas samples (IGS) were continuously collected at a constant rate from a slipstream of the exhaust of the sample trains into a flexible vinyl bag (IGS bag), per Method 3B specifications.
- A calibrated paramagnetic/IR analyzer was used in place of a traditional Orsat analyzer to measure O₂ and CO₂ concentrations of the IGS bags, per Method 3A specifications.
- Documentation of preliminary instrument calibrations and post-analysis calibration checks are included in Appendix G.

H₂O data used for moisture correction of concentration data was obtained (when required) in the following manner during the test program:

- For Method 5, Method 4 measurements are incorporated into the sampling and recovery procedures.
- For Draft ASTM CCM, a modified Method 4 measurement is incorporated into the sampling and recovery procedures.
 - Sample gas was extracted through a heated probe at a single point at least one meter from the stack wall. Moisture stratification is not expected at test locations without free water droplets present in the flue gas.
 - Sample gas was extracted at a constant rate no greater than 0.75 cfm and at least 21 scf of flue gas was sampled.
 - After passing through the SAM condenser and filter, the sample gas was drawn through gum rubber tubing and into four iced knock-out jars for moisture collection and measurement. The knock-out jars were arranged in a series and contain identical contents as the impinger train prescribed by Method 4, but with gum rubber connections and stainless-steel internal components.
- For Methods 18 and 25A, H₂O data was obtained from nearly concurrently-operated Method 5 sample trains.

End of Section 4 – Methodology