

1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to complete testing on the Zurn Boiler (EU27-ZURNBOILER-S1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), sulfuric acid mist (H₂SO₄), and volatile organic compound (VOC) testing to demonstrate compliance with the Michigan Department of Environmental Quality (DEQ) Permit No. MI-ROP-A9831-2012c;
- Perform a relative accuracy test audit (RATA) on the facility continuous emissions monitoring system (CEMS) for oxygen (O₂), nitrogen oxides (NO_x), and carbon monoxide (CO).

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis.

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

Source Constituent	Sampling Method (USEPA)	Average Emission	Permit Limit ¹
<u>Zurn Boiler</u>			
PM (lb/MMBtu)	5	0.0007	0.0019
H ₂ SO ₄ (lb/MMBtu)	CTM-013 (mod)	0.00004	N/A
VOC (lb/MMBtu)	25A / 18	< 0.0007	0.0055

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

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

Source Constituent	Reference Method	Relative Accuracy (%)	Applicable Specification	Specification Limit ¹
<u>Zurn Boiler</u>				
O ₂ (% dv)	EPA 3A	0.02	PS3	± 1.0% dv
NO _x (lb/MMBtu)	EPA 7E	1.34	PS2	20% of RM
CO (lb/MMBtu)	EPA 10	0.43	PS4A	5% of Standard ²

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

² Standard = 0.1 lb/MMBtu

Test Program Details

Parameters

The test program included the following emissions measurements:

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

Schedule

Testing was performed on September 23, 2020. The on-site schedule followed during the test program is outlined in Table 1-3 and Table 1-4.

**Table 1-3:
Test Schedule - Compliance**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Zurn Boiler	USEPA Method 5	FPM	09/23/20	11:40	12:49
2	Zurn Boiler	USEPA Method 5	FPM	09/23/20	13:19	14:29
3	Zurn Boiler	USEPA Method 5	FPM	09/23/20	14:58	16:10
4	Zurn Boiler	USEPA Method 5	FPM	09/23/20	16:28	17:40
1	Zurn Boiler	CTM-013 (mod)	H ₂ SO ₄	09/23/20	11:40	12:40
2	Zurn Boiler	CTM-013 (mod)	H ₂ SO ₄	09/23/20	13:19	14:19
3	Zurn Boiler	CTM-013 (mod)	H ₂ SO ₄	09/23/20	14:58	15:58
4	Zurn Boiler	CTM-013 (mod)	H ₂ SO ₄	09/23/20	16:28	17:28
1	Zurn Boiler	USEPA Method 25A / 18	VOC	09/23/20	11:21	12:29
2	Zurn Boiler	USEPA Method 25A / 18	VOC	09/23/20	12:54	14:04
3	Zurn Boiler	USEPA Method 25A / 18	VOC	09/23/20	14:25	15:40

**Table 1-4:
Test Schedule - RATA**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	11:21	11:42
2	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	11:47	12:08
3	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	12:08	12:29
4	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	12:54	13:15
5	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	13:18	13:39
6	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	13:43	14:04
7	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	14:25	14:46
8	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	14:50	15:11
9	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	15:19	15:40
10	Zurn Boiler	USEPA 3A/7E/10	O ₂ /CO ₂ /NO _x /CO	09/23/20	15:58	16:19

Discussion

PM Testing

A total of four (4) 60-minute EPA Method 5 test runs were performed. PM emission results were calculated in units of pounds per million Btu (lb/MMBtu). All runs were deemed valid. The final result was expressed as the average of the three (3) highest valid runs.

H₂SO₄ Testing – Modified CTM-013

H₂SO₄ emissions were determined referencing a modified Conditional Test Method 013 (CTM-013 (Mod.)). Four (4) 60-minute CTM-013 (Mod.) runs were performed. H₂SO₄ emission results were calculated in units of lb/MMBtu. The H₂SO₄ final results were expressed as the average of four (4) runs.

VOC Testing – USEPA Methods 25A and 18

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 63-minute test runs with each run coinciding with three (3) 21-minute RATA runs. Method 25A Run 1 coincided with RATA Runs 1 through 3, Method 25A Run 2 coincided with RATA Runs 4 through 6, and Method 25A Run 3 coincided with RATA Runs 7 through 9. The Method 25A test runs were performed concurrently with three (3) 63-minute Method 18 bag collections. The final result for each VOC run was expressed as the average of three (3) runs.

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

VOC emission results were calculated in units of lb/MMBtu as propane. O₂ concentrations from concurrent EPA Method 3A runs were utilized to convert VOC results to lb/MMBtu. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from nearly concurrent Method 5 runs.

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

Minute-average data points for O₂, NO_x, and CO (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A, 7E, and 10. Relative accuracy was determined based on nine (9) of 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

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

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of lb/MMBtu by utilizing an O₂-based fuel factor (F_d) for natural gas as presented in EPA Method 19, Table 19-2.

Test Conditions

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

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:
Zurn Boiler – PM Emissions**

Run No.		1	2	3	4	Average
Date (2020)		Sep 23	Sep 23	Sep 23	Sep 23	
Start Time (approx.)		11:40	13:19	14:58	16:28	
Stop Time (approx.)		12:49	14:29	16:10	17:40	
Process Conditions						
R _p	Steam Production (mlb/hr)	141	140	141	140	141
P ₁	Natural Gas Flow (MSCFD)	4,051	4,055	4,055	3,996	4,039
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710	8,710
H _i	Actual heat input (MMBtu/hr)	162.5	161.1	162.8	161.6	162.0
Gas Conditions						
O ₂	Oxygen (dry volume %)	3.5	3.5	3.7	3.6	3.5
CO ₂	Carbon dioxide (dry volume %)	9.7	9.5	9.5	9.6	9.6
T _s	Stack temperature (°F)	309	309	309	308	308
B _w	Actual water vapor in gas (% by volume)	15.8	17.6	17.2	17.2	16.9
Gas Flow Rate						
Q _a	Volumetric flow rate, actual (acfm)	52,100	52,400	51,500	50,800	51,800
Q _s	Volumetric flow rate, standard (scfm)	35,000	35,200	34,600	34,200	34,800
Q _{std}	Volumetric flow rate, dry standard (dscfm)	29,500	29,000	28,700	28,300	28,900
Sampling Data						
V _{mstd}	Volume metered, standard (dscf)	41.06	41.50	41.37	40.41	40.99
%I	Isokinetic sampling (%)	102.0	104.7	105.6	104.5	103.8
Laboratory Data¹						
m _{filter}	Matter collected on filter(s) (g)	0.00029	0.00029	0.00029	0.00029	
m _s	Matter collected in solvent rinse(s) (g)	0.00140	0.00072	0.00049	0.00048	
m _n	Total FPM (g)	0.00169	0.00101	0.00078	0.00077	
FPM Results¹						
C _{sd}	Particulate Concentration (lb/dscf)	9.06E-08	5.39E-08	4.16E-08	4.19E-08	6.21E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.160	0.0938	0.0717	0.0712	0.108
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.000947	0.000564	0.000441	0.000441	0.000651

¹ Final results are the average of the three (3) highest valid runs.

**Table 2-2:
Zurn Boiler – H₂SO₄ Emissions**

Run No.	1	2	3	4	Average
Date (2020)	Sep 23	Sep 23	Sep 23	Sep 23	
Start Time (approx.)	11:40	13:19	14:58	16:28	
Stop Time (approx.)	12:40	14:19	15:58	17:28	
Process Conditions					
P ₁ Steam Production Rate (mlb/hr)	141	140	141	140	141
P ₂ Natural Gas Flow (MSCFD)	4,050	4,055	4,055	3,993	4,038
F _d Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	8,710	
H _i Firing Rate (MMBtu/hr)	163	161	163	161	162
Gas Conditions					
O ₂ Oxygen (dry volume %)	3.6	3.6	3.6	3.7	3.6
CO ₂ Carbon dioxide (dry volume %)	9.6	9.6	9.6	9.5	9.6
T _s Sample temperature (°F)	315	314	315	313	314
B _w Actual water vapor in gas (% by volume)	16.1	18.2	16.0	17.5	17.0
Sampling Data					
V _{mstd} Volume metered, standard (dscf)	25.49	25.53	27.32	25.42	25.94
Laboratory Data (Ion Chromatography)					
m _n Total H ₂ SO ₄ collected (mg)	0.0272	0.0502	0.0560	0.0508	
Sulfuric Acid Vapor (H₂SO₄) Results					
C _{sd} H ₂ SO ₄ Concentration (lb/dscf)	2.35E-09	4.34E-09	4.52E-09	4.41E-09	3.90E-09
C _{sd} H ₂ SO ₄ Concentration (ppmdv)	0.00925	0.0171	0.0178	0.0173	0.0153
E _{Fd} H ₂ SO ₄ Rate - Fd-based (lb/MMBtu)	2.48E-05	4.57E-05	4.75E-05	4.66E-05	4.11E-05

**Table 2-3:
 Zurn Boiler – VOC Emissions**

Run No.		1	2	3	Average
Date (2020)		Sep 23	Sep 23	Sep 23	
Start Time (approx.)		11:21	12:54	14:25	
Stop Time (approx.)		12:29	14:04	15:40	
Process Conditions					
P ₁	Steam Production Rate (mlb/hr)	141	140	141	141
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,710	8,710	8,710	
H _i	Firing Rate (MMBtu/hr)	162	162	162	162
Gas Conditions					
O ₂	Oxygen (dry volume %)	3.4	3.4	3.4	3.4
CO ₂	Carbon dioxide (dry volume %)	10.3	10.3	10.3	10.3
B _w	Actual water vapor in gas (% by volume) ¹	15.8	17.6	17.3	16.9
THC Results²					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.546	<0.558	<0.556	<0.554
C _{sd}	Concentration (lb/dscf)	<6.25E-08	<6.39E-08	<6.37E-08	<6.34E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000652	< 0.000666	< 0.000663	< 0.000660
VOC Results³					
C _{sd}	Concentration (ppmdv as C ₃ H ₈)	< 0.546	< 0.558	< 0.556	< 0.554
C _{sd}	Concentration (lb/dscf)	<6.25E-08	<6.39E-08	<6.37E-08	<6.34E-08
E _{Fd}	Emission Rate - F _d -based (lb/MMBtu)	< 0.000652	< 0.000666	< 0.000663	< 0.000660

¹ Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent EPA M5 runs.

² For THC, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

³ VOC is reported as THC since all THC results were less than VOC limit.

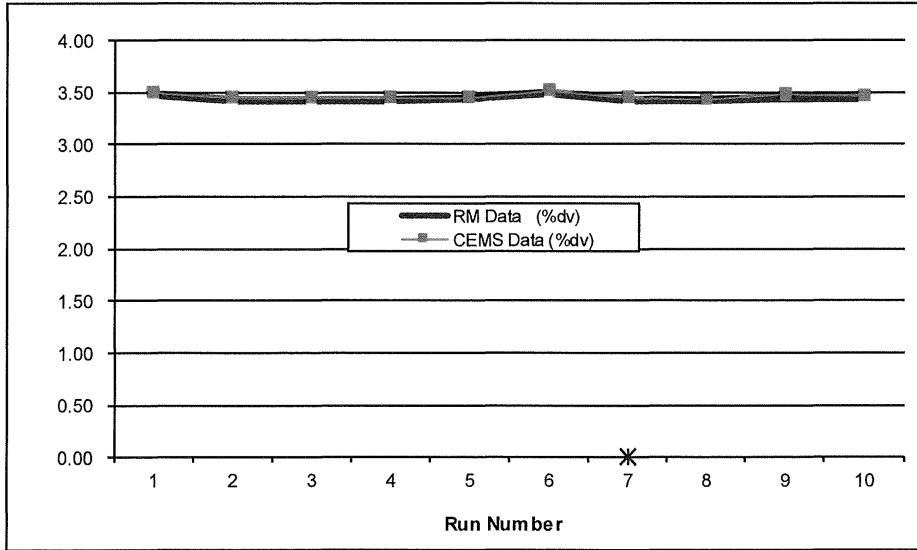
**Table 2-4:
 Zurn Boiler – O₂ (%dv) Relative Accuracy**

Run No.	Start Time	Date (2020)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	11:21	Sep 23	3.46	3.49	-0.03	-0.9%
2	11:47	Sep 23	3.42	3.45	-0.03	-0.9%
3	12:08	Sep 23	3.41	3.44	-0.03	-0.9%
4	12:54	Sep 23	3.42	3.44	-0.02	-0.6%
5	13:18	Sep 23	3.43	3.45	-0.02	-0.6%
6	13:43	Sep 23	3.49	3.51	-0.02	-0.6%
7 *	14:25	Sep 23	3.41	3.45	-0.04	-1.2%
8	14:50	Sep 23	3.41	3.43	-0.02	-0.6%
9	15:19	Sep 23	3.44	3.47	-0.03	-0.9%
10	15:58	Sep 23	3.44	3.46	-0.02	-0.6%
Average			3.44	3.46	-0.02	-0.7%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.00527	
Confidence Coefficient (CC)	0.00405	
t-Value for 9 Data Sets	2.306	
		Limit
Avg. Abs. Diff. (%dv)	0.02	1.0

RM = Reference Method (CleanAir Data) 10 1520 102258
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Co. Data)
 RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



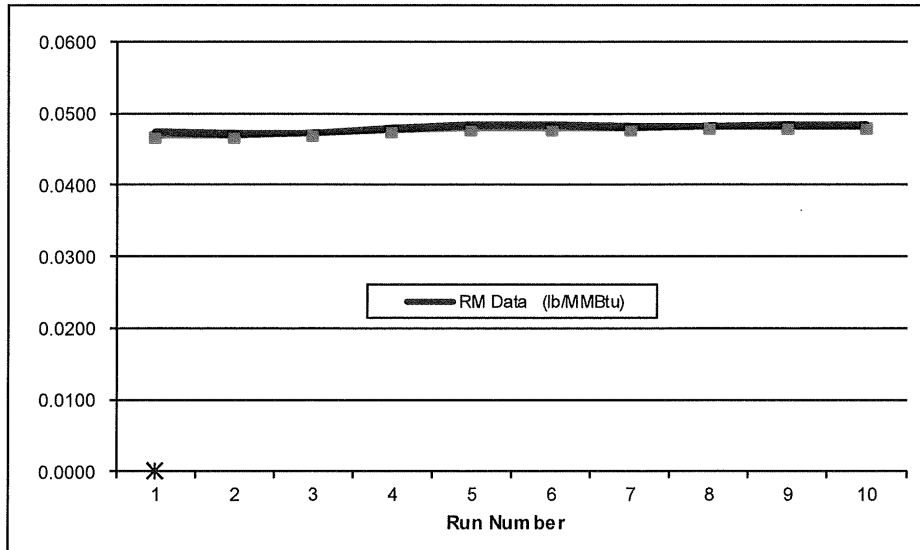
**Table 2-5:
 Zurn Boiler – NO_x (lb/MMBtu) Relative Accuracy**

Run No.	Start Time	Date (2020)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1 *	11:21	Sep 23	0.0474	0.0466	0.0008	1.7%
2	11:47	Sep 23	0.0471	0.0466	0.0005	1.1%
3	12:08	Sep 23	0.0471	0.0467	0.0004	0.8%
4	12:54	Sep 23	0.0479	0.0472	0.0007	1.5%
5	13:18	Sep 23	0.0482	0.0475	0.0007	1.5%
6	13:43	Sep 23	0.0482	0.0475	0.0007	1.5%
7	14:25	Sep 23	0.0480	0.0475	0.0005	1.0%
8	14:50	Sep 23	0.0481	0.0476	0.0005	1.0%
9	15:19	Sep 23	0.0483	0.0478	0.0005	1.0%
10	15:58	Sep 23	0.0482	0.0477	0.0005	1.0%
Average			0.0479	0.0473	0.0006	1.2%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.000113	
Confidence Coefficient (CC)	0.0000869	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of RM)	1.34%	Limit 20.0%

RM = Reference Method (CleanAir Data) 10 152.0 1022.58
 CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Co. Data)
 RATA calculations are based on 9 of 10 runs. * indicates the excluded run.



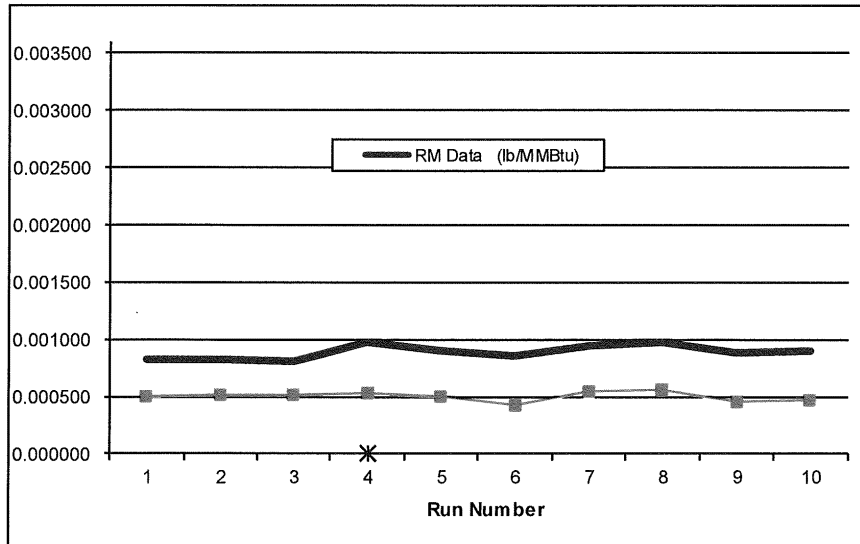
**Table 2-6:
 Zurn Boiler – CO (lb/MMBtu) Relative Accuracy**

Run No.	Start Time	Date (2020)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)
1	11:21	Sep 23	0.000826	0.000500	0.000326
2	11:47	Sep 23	0.000827	0.000515	0.000312
3	12:08	Sep 23	0.000812	0.000509	0.000303
4 *	12:54	Sep 23	0.000967	0.000520	0.000447
5	13:18	Sep 23	0.000892	0.000498	0.000394
6	13:43	Sep 23	0.000850	0.000415	0.000435
7	14:25	Sep 23	0.000948	0.000539	0.000409
8	14:50	Sep 23	0.000970	0.000553	0.000417
9	15:19	Sep 23	0.000886	0.000442	0.000444
10	15:58	Sep 23	0.000895	0.000469	0.000426
Average			0.000878	0.000493	0.000385

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0000558	
Confidence Coefficient (CC)	0.0000429	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of Appl. Std.)	0.43%	Limit
Appl. Std. = 0.1 lb/MMBtu		5.0%

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



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 Zurn Boiler (EU27-ZURNBOILER-S1) was retrofitted with a new package boiler utilizing low NO_x burners last year, as required in the Tier 3 Gasoline Project Permit (PTI 118-15). This boiler 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 (SV22-BR7) (the same stack used for the original boiler), where testing was performed.

The Zurn Boiler CEMS analyzer datum is presented in Table 3-1.

**Table 3-1:
 Zurn Boiler Stack – CEMS Analyzer Datum**

Emission Unit	Parameter	Install Date	Manufacturer	Model	Serial #
Zurn Boiler	CO	2005	ABB	Uras 26	3.341671.1
Zurn Boiler	O ₂	2008	ABB	Magnos 206	3.341670.1
Zurn Boiler	NO _x	2005	ABB	Limas 11	3.341196.1

Test Location

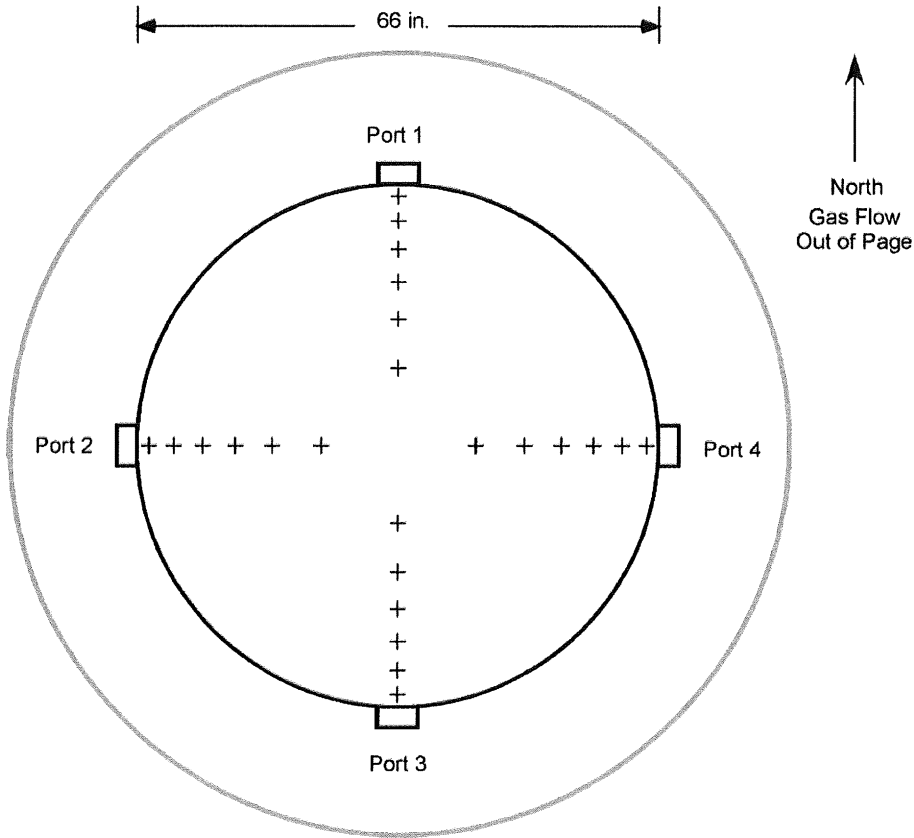
The sample point locations were determined by EPA Methods 1 and 7E. Table 3-22 presents the sampling information for the test location described in this report. The figures shown on pages 12 and 13 represent the layout of the test location.

**Table 3-2:
 Sampling Point Information**

Source	Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
Zurn Boiler	FPM	5	1-4	4	6	2.5	60	3-1
	H ₂ SO ₄	CTM-013 (Mod.)	1-4	1	1	60	60	N/A ¹
	O ₂ / CO ₂ / CH ₄ / C ₂ H ₆ / THC	3A / 18 / 25A	1-3	1	3	21	63	3-2
	O ₂ / CO ₂ / NO _x / CO	3A / 7E / 10	1-10	1	3	7	21	3-2

¹ CTM-013 (Mod.) and EPA M-25A sampling occurred at a single point near the center of the duct.

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

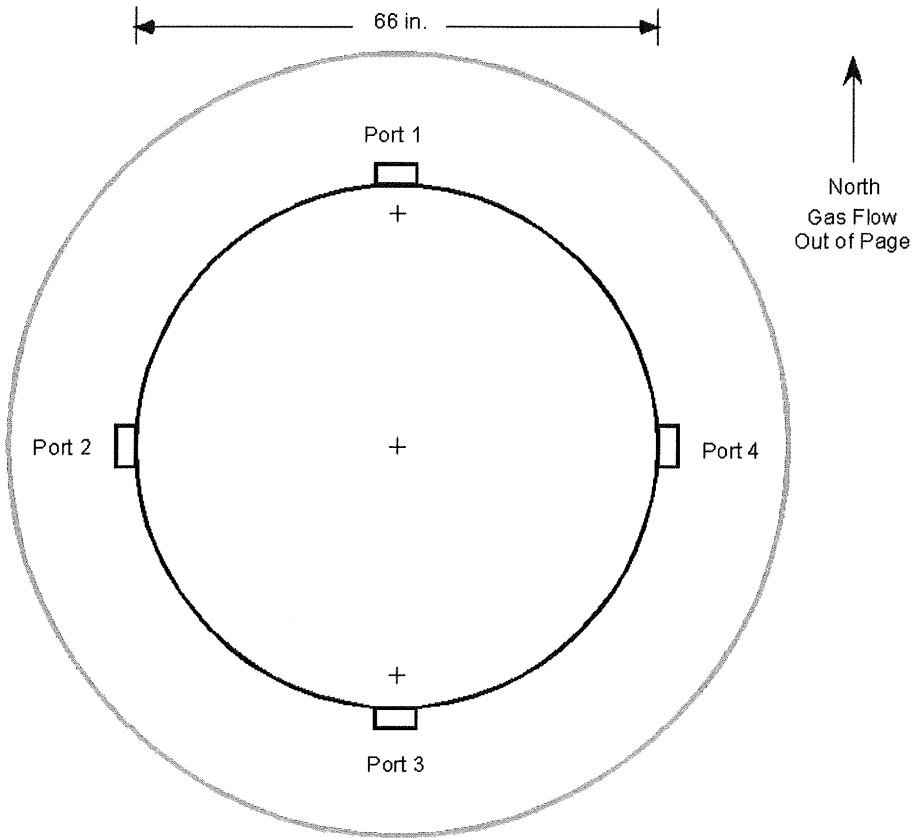


Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	23.5
2	25.0	16.5
3	17.7	11.7
4	11.8	7.8
5	6.7	4.4
6	2.1	1.4

Duct diameters upstream from flow disturbance (A): 10.0
 Duct diameters downstream from flow disturbance (B): 3.5

Limit: 0.5
 Limit: 2.0

**Figure 3-2:
 O₂, NO_x, CO, & THC Sample Point Layout**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	83.3	55.0
2	50.0	33.0
3	16.7	11.0

Duct diameters upstream from flow disturbance (A): 10.0
 Duct diameters downstream from flow disturbance (B): 3.5

Limit: 0.5
 Limit: 2.0