

# 1. Introduction

AECOM Technical Services Inc (AECOM) was contracted by Corteva Agriscience to conduct methanol and total hydrocarbon emission testing for two Thermal Treatment Units that control emissions from EUPROCESS. The purpose of testing was to establish allowable operating envelopes of the TTUs. Each TTU was tested at multiple fuel-to-air ratios. This report presents the results of that emission testing. Testing was performed using various instrumental monitors including a Fourier Transform Infrared (FTIR) system optimized for the analysis of the requested species and a Total Hydrocarbon analyzer. The sampling systems provided near real-time measurements. Representatives from the Michigan Department of Environment, Great Lakes & Energy (EGLE) were present during the test.

Initial testing was conducted March 3-4, 2021. The results indicated that formaldehyde is emitted from catalytic treatment units TTU-850 and TTU-865 at the Harbor Beach site. Corteva does not believe formaldehyde is generated during their manufacturing process and is therefore generated by the catalytic treatment units. Formaldehyde emissions were measured in the April test campaign from each of the four catalytic treatment units (TTU-850, TTU-855, TTU860, TTU-865) and the regenerative thermal oxidizer (RTO-870). Results are summarized in Table 1-1 and Table 1-3 both as concentration and mass emission rate.

The TTU's are used for controlling emissions of Organic HAP from EUPROCESS; the regulatory limit (40 CFR Part 63, Subpart MMM (PAI MACT)) is less than 20 ppmv. PAI MACT defines Organic HAP as those HAP listed in Section 112(b) of the Clean Air Act. Corteva believes the primary Organic HAP of concern for EUPROCESS is methanol. The 112(b) list also includes formaldehyde. Emissions of organic HAP generated in a catalytic incinerator are not explicitly regulated by Subpart MMM and should not be included in the outlet concentration measurements used for determining compliance with the 20 ppmv limit. Therefore, to determine compliance with the 20 ppmv in the future, Corteva intends to directly measure methanol and exclude formaldehyde from the Organic HAP concentration total. To justify this approach, Corteva demonstrated that formaldehyde is not generated by EUPROCESS by collecting inlet samples for determination of formaldehyde.

During a second test campaign in April 2021, AECOM measured methanol and formaldehyde in the TTU emissions. In addition, EPA Methods 1, 2, 3A and the FTIR were used to determine gas characteristics (velocity, molecular weight, and moisture). The use of the FTIR for determination of moisture was approved by EGLE. The emission testing was conducted under the following conditions to support expanded operating range of the limits currently mandated by Condition IV.3.a.iv in MI-ROP-B4942-2020a.:

- TTU-850 – three different fuel:air ratios
- TTU-855 – three different fuel:air ratios, and in the firebox
- TTU-860 – two different temperatures in the exhaust; and in the firebox
- TTU-865 – two different temperatures
- RTO-870 – at a single (“normal”) fuel-to-air ratio approximately 22:1 , as the RTO does not have the capability for adjusting the parameter.
- Inlet Header

Results from this testing are summarized in Table 1-2.

During the April testing event, the emissions of formaldehyde and methanol were measured from TTU 860 under furnace operating temperatures of both 675°F and 950°F. Increasing the furnace operation reduced the formaldehyde concentration by approximately half. Testing also indicated that formaldehyde was present in the inlet, although at low concentrations (<1 ppmv). Formaldehyde was also measured at the firebox before the catalyst. The firebox of TTU-855 indicated formaldehyde levels of 19.42 ppm and 9.78 ppm in TTU-860. This suggests that the formaldehyde is partially being generated in the burner as well as across the catalyst.

AECOM collected formaldehyde measurements using FTIR and flow measurements using EPA Methods 1, 2, 3, & moisture by FTIR. Emission rates for formaldehyde from each of the sources was calculated. This is developed in the Formaldehyde Toxic Assessment report, attached as Appendix C. The total emission rate of formaldehyde was approximately 13.6 lb/hr from all thermal treatment units. This rate represents the maximum

cumulative emission rate as each unit was operating at the maximum condition per the test plan. To annualize emission rates, we assumed B4942 operates at maximum rates for 90% of the year. Based on this assumption, annual average emission rate is 12.2 lb/hr. For the AERMOD model, natural gas combustion emission factors were used to estimate emissions from the boilers and turbines. AERMOD results were above the 0.08 ug/m<sup>3</sup> IRSL (Initial Risk Screening Level) and below the 0.8 ug/m<sup>3</sup> SRSL (Secondary Risk Screening Level) for formaldehyde. As a conservative measure, no attempt was made to estimate an annual average from TTU-860. TTU-860 formaldehyde mass emission rate is greater than the sum of the other sources as shown in Table 1-3.

AECOM used the preliminary results of this measurement effort to model emissions from this facility, using AERMOD. Based on this assessment, AECOM and Corteva believes the screening level was acceptable at the time of the testing. This belief is based on the AERMOD value being less than the SRSL. Current screening levels are significantly lower.

**Table 1-1 Summary of Methanol and Total Hydrocarbons Concentrations – March Testing**

Source	Fuel:Air Ratio	Analyte(ppmv)	
		Methanol	Total Hydrocarbons
TTU-850 at 675°F	7.5 to 1	4.73	2.70
	15 to 1	1.52	15.93
TTU-865 at 675°F	7.5 to 1	9.65	4.77
	15 to 1	3.75	3.60

**Table 1-2 Summary of Methane, Formaldehyde and Methanol concentrations – April Testing**

Source	Fuel:Air Ratio	Analyte (ppmv)		
		Methane	Formaldehyde	Methanol
Inlet Header	NA	4.00	0.70	346
TTU-850 at 675°F	10 to 1	5.32	20.4	9.84
	14 to 1	31.9	11.4	4.55
	7.5 to 1	2.25	20.1	9.41
TTU-855 at 675°F	10 to 1	4.77	3.72	2.74
	7.5 to 1	6.23	4.38	2.68
	14 to 1	14.1	1.66	2.11
TTU-855 Fire Box	NA	8.37	19.4	3.70
TTU-860 at 675°F	10 to 1	2.93	57.4	29.9
TTU-860 at 950°F	10 to 1	4.39	35.83	13.53
TTU-860 Fire Box	NA	3.38	9.78	3.83
TTU-865 at 675°F	10 to 1	3.99	31.1	11.2
TTU-865 at 875°F	10 to 1	4.25	21.35	7.34
RTO-870	22 to 1	0.25	0.55	4.83

**Table 1-3 – Emission Rates of Sitewide Formaldehyde Sources**

Emission Unit ID	Model ID	Source Description	CH2O_S (Max) (lb/hr)	CH2O_L (Annual Average) (lb/hr)
SV00007	SV00007	EU_N_Turbine	0.00533	0.00533
SV00009	SV00009	EU_S_Turbine	0.00533	0.00533
SV00003	SV00003	TTU850	2.15	1.93
SV00004	SV00004	TTU855	0.42	0.38
SV00005	SV00005	TTU860	7.68	6.92
SV00006	SV00006	TTU865	3.26	2.93
SV00017	SV00017	TTU870	0.10	0.09

**Note:**

1. Emission rate of the TTUs were developed using the measurement data.
2. CH2O\_S emission rate represents the maximum rates as all assets were operating per testing plan. The maximum hourly emission rate was used to predict the 24-hour impact against ITSL.
3. CH2O\_L emission rate represents the annual average emission rate assuming that the plant would be operated at the max rate for 90% of the year. This annual average hourly emission rate was used to predict the annual average impact against IRSL and SRSL.

## 1.1 Responsible Parties

AECOM personnel from the Midland, MI and Austin, TX offices conducted the sampling and analysis during this field effort. The primary responsibility of AECOM personnel was the analysis of the stack effluent for the requested compounds during the one-hour runs.

**AECOM CONTACTS:**

- James Edmister served as the Project Manager. In this role, he had the overall responsibility for the success and quality of the project. Mr. Edmister had primary authority for all decisions concerning sampling and analysis.
- Randy Reinke was the local representative from AECOM at the Corteva facility, and served as the Technical Lead for CEMS. Mr. Reinke also coordinated with plant operations for the success of the test.
- Ignacio Gallardo was the FTIR Senior Scientist and was responsible for the FTIR preparation, performing and overseeing FTIR testing, FTIR data analysis, and report generation.
- Mark Modrak provided support as a technical review of the test data.

**CORTEVA CONTACTS:**

- Jim McGee provided support as the Environmental Focal Point for this test. The Environmental Focal Point is responsible for ensuring that all regulatory requirements and citations are reviewed and considered for the testing. All agency communication will be completed through this role. Contact information is 989-479-5283.
- Scott Grekowicz provided support as the Process Focal Point. The Process Focal Point is responsible for coordinating the plant operation during the test and ensuring the unit is operating at the agreed-upon conditions in the test plan. They also serve as the key contact for collecting any process data required and providing all technical support related to process operation.

## 1.2 Test Chronology

**Table 1-4 March Summary of Sample Collection Times**

Stack	Fuel:Air Ratio	Run	Date/Time		
			Date	Run Start	Run End
TTU-850	7.5 to 1	Run 1	3/3/2021	8:45	9:44
		Run 2		10:45	11:44
		Run 3		12:25	13:24
	15 to 1	Run 1b	3/3/2021	15:00	15:59
		Run 2b		16:45	17:44
		Run 3b		18:10	19:10
TTU-865	7.5 to 1	Run 1	3/4/2021	9:10	10:09
		Run 2		10:34	11:33
		Run 3		12:00	12:59
	15 to 1	Run 1b	3/4/2021	14:03	15:02
		Run 2b		15:23	16:22
		Run 3b		16:50	17:49

**Table 1-5 April Summary of Sample Collection Times**

Stack	Fuel:Air Ratio	Run	Date/Time		
			Date	Run Start	Run End
Inlet	NA	Run 1	4/14/2021	11:29	12:28
		Run 2		12:40	13:35
		Run 3		13:55	14:54
TTU-850 at 675°F	10 to 1	Run 1a	4/12/2021	08:56	09:55
		Run 2a		10:38	11:37
		Run 3a		12:10	13:09:
	14 to 1	Run 1b	4/12/2021	14:31	15:30
		Run 2b		16:25	17:24
		Run 3b		18:26	19:25
	7.5 to 1	Run 1c	4/13/2021	07:20	08:19
		Run 2c		08:55	09:54
		Run 3c		10:28	11:27
TTU-855 at 675°F	10 to 1	Run 1a	4/12/2021	09:02	10:01
		Run 2a		10:36	11:35
		Run 3a		12:03	13:02
	7.5 to 1	Run 1b	4/12/2021	14:21	15:20
		Run 2b		16:03	17:02
		Run 3b		17:45	18:44
	c 14 to 1	Run 1c	4/13/2021	07:15	08:14
		Run 2c		08:50	09:49
		Run 3c		10:25	11:24
TTU-860 at 675°F	10 to 1	Run 1	4/13/2021	16:08	17:07
		Run 2		17:35	18:34
		Run 3		19:02	20:01
TTU-860 at 950°F	10 to 1	Run 1	4/15/2021	08:23	09:22
		Run 2		09:39	10:38
		Run 3		10:52	11:51
TTU-855 Fire Box	NA	Run 1 855	4/14/2021	17:35	18:34
TTU-860 Fire Box	NA	Run 1 860	4/14/2021	16:16	17:07
TTU-865 at 675°F	10 to 1	Run 1	4/13/2021	15:41	16:40
		Run 2		17:23	18:22
		Run 3		18:51	19:51
TTU-865 at 875°F	10 to 1	Run 1a	4/15/2021	08:50	09:48
		Run 2a		10:00	10:59
		Run 3a		11:13	12:12
TTU-870	22 to 1	Run 1	4/14/2021	09:37	10:36
		Run 2		11:05	12:04
		Run 3		12:30	13:29

## 2. Results Summary

The results of the engineering support testing are summarized in the table 2-1 below.

**Table 2-1 March Results Summary**

Source	Fuel:Air Ratio	Run #	Analyte(ppmv)		Exhaust Gas Conditions	
			Methanol	Total Hydrocarbons	Oxygen (Dry Volume %)	Carbon Dioxide (Dry Volume %)
TTU-850	7.5 to 1	1	4.09	2.5	18.35	2.05
		2	5.3	2.5	18.48	1.78
		3	4.8	3.1	18.58	1.70
	15 to 1	1b	2.03	19.8	18.66	1.70
		2b	1.15	15.6	18.66	1.78
		3b	1.37	12.4	18.74	1.70
TTU-865	7.5 to 1	1	11.07	4.8	17.73	2.55
		2	9.15	4.7	17.7	2.58
		3	8.74	4.8	17.77	2.52
	15 to 1	1b	3.53	3.5	17.7	2.52
		2b	3.58	3.7	17.69	2.54
		3b	4.15	3.6	17.63	2.56

**Table 2-2 April FTIR Results Summary (units in ppmv)**

Source	Fuel:Air Ratio	Run	Analyte			
			Methane	Formaldehyde	Water	Methanol
Inlet	NA	1	4.14	0.72	2.41	338.63
		2	3.92	0.76	2.24	327.39
		3	3.94	0.63	2.79	371
TTU-850 at 675°F	10 to 1	1a	5.82	20.8	6.10	10.3
		2a	5.21	19.8	4.18	9.71
		3a	4.92	20.5	4.26	9.53
	14 to 1	1b	32.5	11.5	5.39	4.76
		2b	31.5	11.1	4.02	4.41
		3b	31.7	11.6	4.34	4.47
	7.5 to 1	1c	2.32	20.8	5.90	8.64
		2c	2.05	20.5	7.09	10.7
		3c	2.37	18.9	4.58	8.86
TTU-855 at 675°F	10 to 1	1a	4.78	3.80	5.17	2.80
		2a	4.75	3.58	4.13	2.70
		3a	4.79	3.78	4.28	2.72
	7.5 to 1	1b	6.16	4.37	5.23	2.72
		2b	6.28	4.30	4.22	2.60
		3b	6.24	4.48	4.24	2.73
	14 to 1	1c	14.8	1.71	4.91	2.01
		2c	14.8	1.68	6.07	2.24
		3c	12.7	1.60	4.37	2.08
TTU-860 at 675°F	10 to 1	1	2.99	59.9	5.03	33.09
		2	2.82	56.0	4.07	28.10
		3	2.99	56.2	4.12	28.60
TTU-860 at 950°F	10 to 1	1	4.31	38.6	4.24	15.18
		2	4.78	35.8	4.21	13.3
		3	4.09	33.1	4.26	12.12
TTU-855 Fire Box	NA	1 FB	8.37	19.4	3.70	273
TTU-860 Fire Box	NA	1 FB	3.38	9.78	3.83	277
TTU-865 at 675°F	10 to 1	1	4.11	31.4	5.13	11.2
		2	3.84	30.6	4.39	11.0
		3	4.01	31.1	4.43	11.3
TTU-865 at 875 F	10 to 1	1a	4.43	22.0	4.28	7.60
		2a	4.25	21.3	4.28	7.35
		3a	4.07	20.7	4.31	7.08
TTU-870	22 to 1	1	0.34	0.61	3.23	4.64
		2	0.27	0.53	3.35	4.81
		3	0.14	0.51	4.53	5.03

**Table 2-3 April Non-FTIR Results Summary**

<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 850 (7.5:1)</b>				
<b>Run Identification</b>	<b>TTU 850 7.5:1 Run 1</b>	<b>TTU 850 7.5:1 Run 2</b>	<b>TTU 850 7.5:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/13/21	4/13/21	4/13/21	
<b>Run Time</b>	09:44-10:44	10:55-11:55	12:05-13:05	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.20	18.23	18.30	18.22
Carbon Dioxide (dry volume %)	2.33	2.33	2.31	2.33
Average Stack Temperature (°F) (TS)	338.4	333.6	332.5	334.8
Barometric Pressure ("Hg) (Pbar)	29.4	29.1	29.4	
Static Pressure ("wc) (Pg)	-0.4	-0.4	-0.3	
Flue Gas Moisture (%) (BWS)	5.9	7.1	4.6	5.9
Avg Flow Rate (acfm)	30,735	31,177	32,165	31,359
<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 850 (10:1)</b>				
<b>Run Identification</b>	<b>TTU 850 10:1 Run 1</b>	<b>TTU 850 10:1 Run 2</b>	<b>TTU 850 10:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/12/21	4/12/21	4/12/21	
<b>Run Time</b>	08:56-09:56	10:38-11:38	12:10-13:10	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.36	18.42	18.40	18.39
Carbon Dioxide (dry volume %)	2.23	2.23	2.23	2.23
Average Stack Temperature (°F) (TS)	338.8	326.1	335.5	333.5
Barometric Pressure ("Hg) (Pbar)	29.0	29.1	29.1	
Static Pressure ("wc) (Pg)	-0.4	-0.4	-0.5	
Flue Gas Moisture (%) (BWS)	6.1	4.2	4.3	4.8
Avg Flow Rate (acfm)	34,028	34,304	33,795	34,042
<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 850 (14:1)</b>				
<b>Run Identification</b>	<b>TTU 850 14:1 Run 1</b>	<b>TTU 850 14:1 Run 2</b>	<b>TTU 850 14:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/12/21	4/12/21	4/12/21	
<b>Run Time</b>	14:31-15:31	16:25-17:25	18:26-19:26	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.49	18.45	18.43	18.46
Carbon Dioxide (dry volume %)	2.19	2.17	2.18	2.18
Average Stack Temperature (°F) (TS)	323.4	303.9	317.4	314.9
Barometric Pressure ("Hg) (Pbar)	29.10	29.10	29.19	
Static Pressure ("wc) (Pg)	-0.27	-0.27	-0.27	
Flue Gas Moisture (%) (BWS)	5.4	4.0	4.3	4.6
Avg Flow Rate (acfm)	21,230	20,554	21,358	21,047



**Table 2-3 April Non-FTIR Results Summary**

<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 855 (7.5:1)</b>				
<b>Run Identification</b>	<b>TTU 855 7.5:1 Run 1</b>	<b>TTU 855 7.5:1 Run 2</b>	<b>TTU 855 7.5:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/12/21	4/12/21	4/12/21	
<b>Run Time</b>	14:21-15:21	16:03-17:03	17:45-18:45	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.11	18.10	18.11	18.11
Carbon Dioxide (dry volume %)	2.32	2.32	2.32	2.32
Average Stack Temperature (°F) (TS)	338.3	333.6	332.5	334.8
Barometric Pressure ("Hg) (Pbar)	29.4	29.4	29.4	
Static Pressure ("wc) (Pg)	-0.39	-0.45	-0.27	
Flue Gas Moisture (%) (BWS)	5.2	4.2	4.2	4.6
Avg Flow Rate (acfm)	30,698	30,812	32,147	31,219
<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 855 (10:1)</b>				
<b>Run Identification</b>	<b>TTU 855 10:1 Run 1</b>	<b>TTU 855 10:1 Run 2</b>	<b>TTU 855 10:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/12/21	4/12/21	4/12/21	
<b>Run Time</b>	09:02-10:02	10:36-11:36	12:03-13:03	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.06	18.02	18.02	18.03
Carbon Dioxide (dry volume %)	2.36	2.40	2.39	2.38
Average Stack Temperature (°F) (TS)	348.6	351.8	346.9	349.1
Barometric Pressure ("Hg) (Pbar)	29.0	29.1	29.1	
Static Pressure ("wc) (Pg)	-0.47	-0.49	-0.60	
Flue Gas Moisture (%) (BWS)	5.2	4.1	4.3	4.53
Avg Flow Rate (acfm)	37,755	37,546	36,713	37,338
<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 855 (14:1)</b>				
<b>Run Identification</b>	<b>TTU 855 14:1 Run 1</b>	<b>TTU 855 14:1 Run 2</b>	<b>TTU 855 14:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/13/21	4/13/21	4/13/21	
<b>Run Time</b>	07:15-08:15	08:50-09:50	10:25-11:25	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.15	18.12	18.13	18.13
Carbon Dioxide (dry volume %)	2.27	2.30	2.28	2.28
Average Stack Temperature (°F) (TS)	339.1	335.4	338.5	337.7
Barometric Pressure ("Hg) (Pbar)	29.40	29.42	29.42	
Static Pressure ("wc) (Pg)	-0.32	-0.40	-0.33	
Flue Gas Moisture (%) (BWS)	4.9	6.1	4.4	5.1
Avg Flow Rate (acfm)	23,478	26,175	24,987	24,880

**Table 2-3 April Non-FTIR Results Summary**

<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 865 (10:1)</b>				
<b>Run Identification</b>	<b>TTU 865 10:1 Run 1</b>	<b>TTU 865 10:1 Run 2</b>	<b>TTU 865 10:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/13/21	4/13/21	4/13/21	
<b>Run Time</b>	15:42-16:42	17:23-18:23	18:52-19:52	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	17.52	17.62	17.62	17.59
Carbon Dioxide (dry volume %)	2.79	2.63	2.63	2.68
Average Stack Temperature (°F) (TS)	403.6	393.4	398.4	398.5
Barometric Pressure ("Hg) (Pbar)	29.4	29.4	29.4	
Static Pressure ("wc) (Pg)	-0.53	-0.56	-0.35	
Flue Gas Moisture (%) (BWS)	5.1	4.4	4.4	4.7
Avg Flow Rate (acfm)	37,427	35,529	36,693	36,550
<b>Emission Summary Table Harbor Beach TTU Testing Harbor Beach - Corteva 870 (22:1)</b>				
<b>Run Identification</b>	<b>TTU 870 22:1 Run 1</b>	<b>TTU 870 22:1 Run 2</b>	<b>TTU 870 22:1 Run 3</b>	<b>Average</b>
<b>Flow Run Number</b>	Flow Run 1	Flow Run 2	Flow Run 3	
<b>Run Date</b>	4/14/21	4/14/21	4/14/21	
<b>Run Time</b>	09:38-10:38	11:05-12:05	12:30-13:30	
<b>Exhaust Gas Conditions</b>				
Oxygen (dry volume %)	18.34	18.30	18.32	18.32
Carbon Dioxide (dry volume %)	2.38	2.40	2.44	2.41
Average Stack Temperature (°F) (TS)	161.8	160.2	164.0	162.0
Barometric Pressure ("Hg) (Pbar)	29.4	29.4	29.4	
Static Pressure ("wc) (Pg)	-0.15	-0.14	-0.33	
Flue Gas Moisture (%) (BWS)	3.2	3.4	4.5	3.7
Avg Flow Rate (acfm)	44,331	44,091	45,854	44,759

## 3. Sampling and Analytical Procedures

### 3.1 Sample Time

The duration of each test run was approximately sixty (minutes) for a total of 720 minutes for 12 runs for the March 2021 testing.

The duration of each test run was approximately sixty (minutes) for a total of 2,280 minutes for 38 runs for the April 2021 testing.

### 3.2 Instrumental (non-FTIR) Methods

Emission gas was withdrawn from each TTU exhaust and transported to the AECOM CEMS located at ground level. A stainless-steel sampling probe was inserted into the exhaust stacks and used to collect sample gas. A heated Teflon sample line transported the sample gas from the sampling probe to the instrumental analyzers gas conditioning system. The instrumental analyzers were kept at a stable temperature inside the AECOM mobile laboratory. At the mobile laboratory, a portion of the untreated (i.e., hot/wet) sample gas was routed to the THC analyzer for analysis on a wet basis, while the remainder of the sample gas was routed to a moisture condenser and then transported to the analyzers for analysis of O<sub>2</sub> and CO<sub>2</sub> on a dry basis.

The analyzers' electronic output signals were converted to a digital format and stored by AECOM's computerized data acquisition system. The system translated this digital signal into the proper units of measurement (e.g., percent CO<sub>2</sub> by volume on a dry basis) and stored them on a hard drive. The system stores the data as ten-second averages.

The instrumental analyzers were calibrated prior to initiating testing using appropriately certified standards as specified by EPA Methods 3A and 25A. Only EPA Traceability Protocol gases or certified pure zero nitrogen and air gases were used for calibration.

For the O<sub>2</sub> and CO<sub>2</sub> samples, a three-point direct calibration error test was performed on the instrumental analyzers prior to testing. Zero, mid-range, and span gases were introduced directly to the instruments to establish calibration error, or linearity. Then, the zero and mid-range gases were introduced through the entire sample acquisition system as a QC system bias check. The instrument direct response for each of these gases was no more than  $\pm 2\%$  of span from the calibration gas value, and the system bias check for each of these gases was no more than  $\pm 5\%$  of span from the direct response value.

For the THC sample, a four-point system calibration error test was performed on the instrumental analyzer prior to testing by passing calibration gas through the entire sample acquisition system. Zero and span gases were introduced through the entire sampling system to establish calibration set points. Then, the low and mid-range gases were introduced through the entire system as a QC calibration error check. The instrument system response for each of these gases was no more than  $\pm 5\%$  of span from the calibration gas certified value.

The AECOM sampling system response time was checked. The total system, which includes the probe, sample line, sample pump, and condenser, were incorporated into the system response time test.

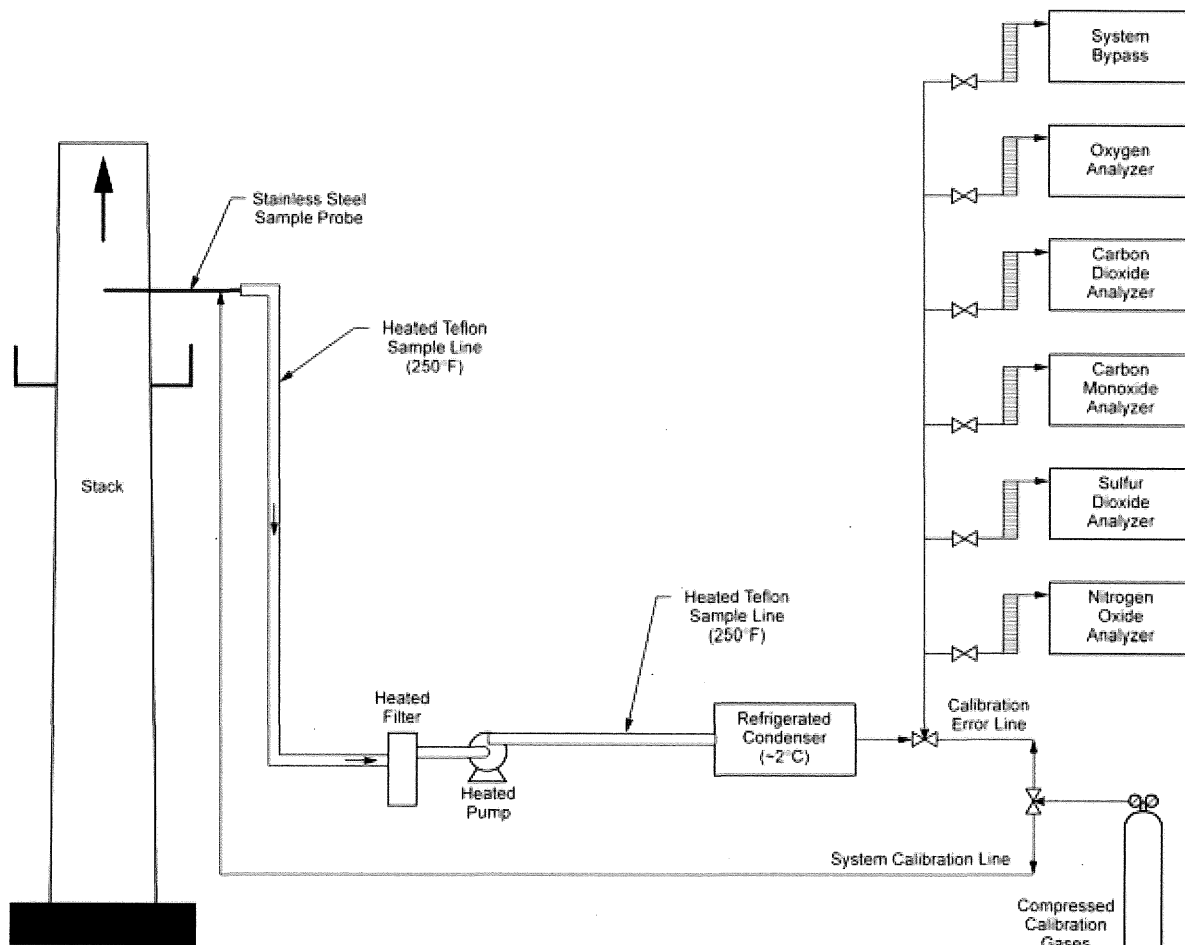
A system response time test for each parameter was performed and documented.

A schematic of the instrumental sampling system is shown in Figure 4.

#### 3.2.1 EPA Method 3A (O<sub>2</sub>/CO<sub>2</sub>)

AECOM used a Servomex Model 1440 analyzer to measure O<sub>2</sub> and CO<sub>2</sub> concentrations, on a dry volume basis, according to EPA Method 3A. The analyzer employs paramagnetic detection.

**Figure 3-1 non-FTIR Instrumental Sampling System**



L:\MBSA\1008\PHCS1\_Figures\CEMS System\_G Youngeman\_CEMS System\_Schematic\_Full System

### 3.3 FTIR Sample System Description

The FTIR extractive system was comprised of:

- stainless steel probe (~4 foot)
- stainless steel spiking "T"
- 100-ft heated (150°C) PFA-grade Teflon line
- MKS 2030 FTIR spectrometer

March testing and April testing on the inlet source, TTU-855, TTU-860, TTU-860 Model 2030DBG2EZKS13T S/N: 18631631. April sources TTU-850, TTU-865, RTO-870 and two Fire Boxes were measured with Model 2030DBG2EZKS13T SN: 017758935) completed with a heated (191°C) fixed-path (5.11m) sample cell, a flow regulating valve, a rotameter and a sample pump. A schematic of the sampling system similar to the one used for this testing is depicted in Figure 3-2. Analyte monitoring consisted of continuously pulling a gas stream from the sample port through the sample probe, spiking tee, and heated extraction line, into the heated FTIR sample cell and out through the pump and exhaust line. Sample flow was continuous and maintained at approximately 4 standard liters per minute, by a diaphragm pump connected to the outlet of the FTIR cell. Since the pump provided samples slightly below ambient pressure to the FTIR cell, cell pressure was continuously recorded during measurement periods using a pressure sensor calibrated over the 0 – 900 torr range. These pressures were then used in the quantification of each spectrum.

### 3.3.1 Analyte Spiking System

Per EPA Method 320, analyte spiking must be performed to determine the effectiveness of the sampling and analytical systems in transporting and quantifying analytes. The aforementioned spiking "T", placed between the probe and the extraction line (as specified in the EPA Method 320), enabled injection of the analyte gas standards directly into the extracted sample gas stream.

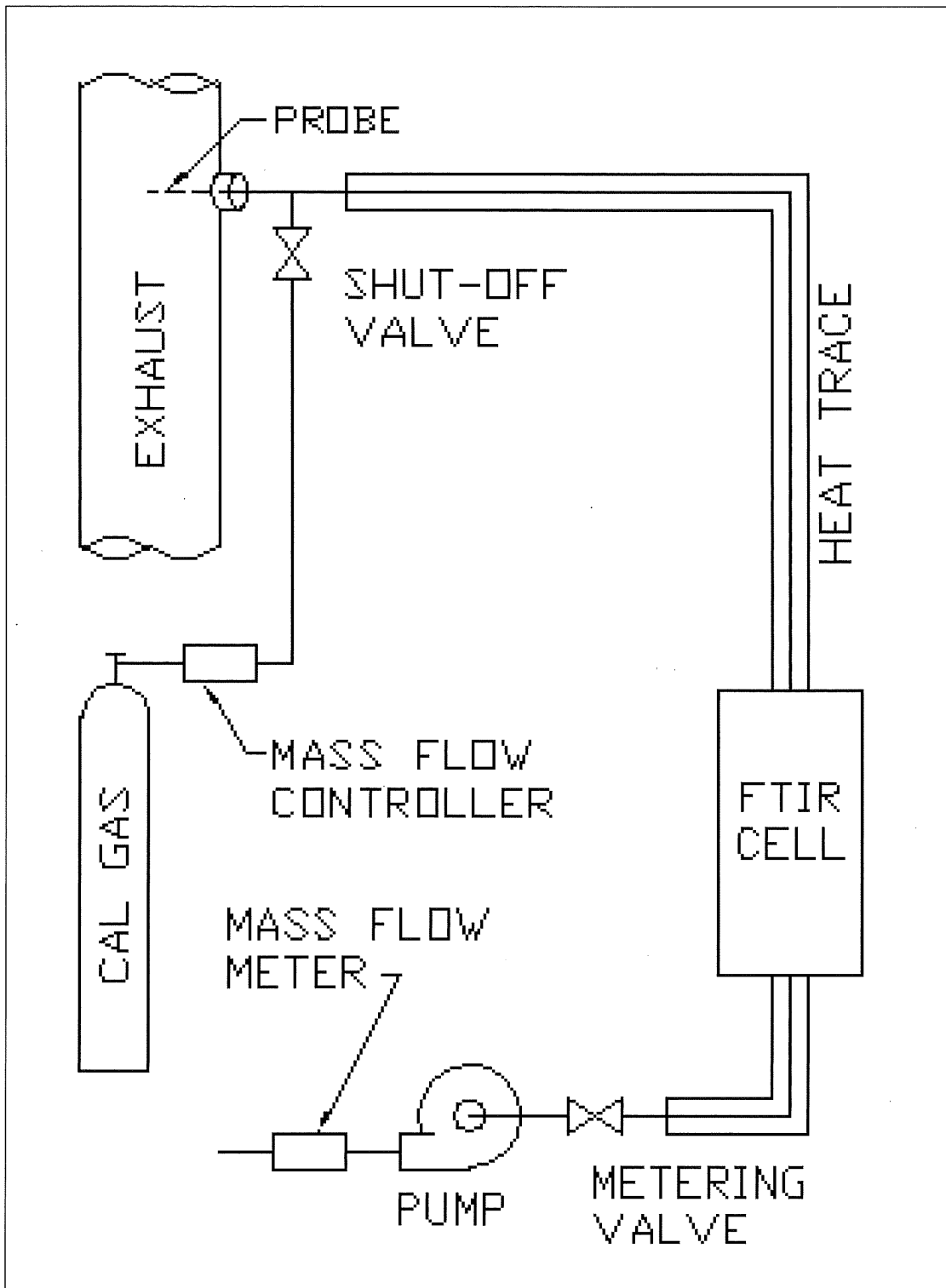
The EPA Method 320 stipulates an analyte spike equal to the native concentration at no more than 10% of the total flow be delivered through the entire sampling system. Spikes were performed using three cylinders.

The cylinder contained a calibration standard:

- 30.04 ppm methanol
- 10.02 ppm SF<sub>6</sub> as a tracer gas.

Precise volumes of the analyte gas standards were delivered into the extracted stack gas (system recovery checks). Since the injected standard flow was low compared to the extracted sample flow (maximum of 10% of total extracted flow), the sample gas matrix (including interferences) was not significantly changed.

Figure 3-2 FTIR Sample System



Note: This figure shows the configuration for the March test. For the April test, the heated pump was placed between the source and the FTIR, inducing positive pressure inside the FTIR. No statistically significant difference was seen during the calibrations between these two configurations. Change in configuration suggested by EGLE

### 3.3.2 FTIR Spectrum Analyses Method

An infrared spectrum can be collected and analyzed in approximately one second, but data are typically averaged over one- to five-minute integration periods to produce adequate signal-to-noise and ppb-level detection limits. For this testing, all run data and most QA data were signal- averaged for one minute. Shorter scan durations (10-second) were used for the spikes and mechanical response tests to better characterize system retention/response times and interpolations were made to get sub-second estimation or minute averages.

An infrared spectrum analysis is performed by matching the features of an observed spectrum to those of reference standards. If more than one feature is present in the same region, a linear combination of references is used to match the compound features. The standards are scaled to match the observed band intensities; this scaling also matches the unknown concentrations.

The scaled references are added together to produce a composite that represents the best match with the sample. A classical least squares mathematical technique is used to match the reference standards' absorption profiles with those of the observed sample spectrum in specified spectral analysis regions. Compounds of interest and any known compounds expected to present spectral interference (water and carbon dioxide for this data set) are included in the analyte regions. The analysis method for this sampling was optimized for the analyte analysis during sampling and later refined to best fit the interferences within the analytes analysis regions.

### 3.3.3 Analyte Measurements

Analyte measurements and spiking were performed in accordance with the FTIR EPA Method 320. To meet these objectives, each stack gas was monitored over one-hour runs. The following paragraphs discuss and present the sampling locations, pre- and post-test QA requirements and collection methods used in this performance test.

The FTIR measured, methanol on a hot wet basis. Table 3-1 correlates the component and its corresponding analysis method.

**Table 3-1 FTIR Test Methods**

Compound Monitored	Test Methodology
Methanol*	EPA Method 320
Formaldehyde	EPA Method 320**
Methane	EPA Method 320***
Moisture	FTIR

\*single compound measured by FTIR in March

\*\* At least one spike as agreed with EGLE

\*\*\* no spikes as agreed with EGLE, CTS had Methane

The FTIR and QA spiking systems are described in previous sections. Gas was continuously extracted from the center of the Stack exhaust pipe and delivered to the FTIR sample cell. A data point was obtained every minute during the runs and reflected the average of 60 individual spectra. Ten-second averages (11 averaged spectra) were collected during QA spiking. All analytes were observed above their minimum detection limit (MDL) during the runs. The results are presented in Table 2-1 and the QA spiking results are presented and discussed in Section 4.2.4

## 4. QAQC

### 4.1 Instrumental Methods (non-FTIR)

To ensure accurate and defensible results, strict quality assurance and quality control measures were followed. All testing was performed following standard protocols as referenced above. All performance testing was performed while the process was operating at normal conditions, or as near thereto as practicable.

All test criteria were thoroughly documented and checked for completeness. EPA Protocol gas certification documentation for compressed gas cylinders used as reference standards during this testing can be supplied upon request. The O<sub>2</sub>/CO<sub>2</sub> and THC monitors used by AECOM Corporation were operated and calibrated in accordance with EPA Methods 3A and 25A respectively. Calibration results can be provided upon request.

**Table 4-1 Instrumental Method Performance Checks**

Activity	Method	Criterion
Span Selection	3A	Emissions between 20% and 100% of calibration span
Calibration Gas Selection	3A	Protocol gas, Calibration span, 40-60% of calibration span, and <20% of calibration span (or zero gas)
Calibration Error	3A	Span gas within $\pm 2.0\%$ of calibration span (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
		Mid-range gas within $\pm 2.0\%$ of calibration span (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
		Zero gas within $\pm 2.0\%$ of calibration span (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
System Bias Check	3A	Gas through system agrees with calibration error value for that gas within $\pm 5.0\%$ of calibration span (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
Post-Test Calibration Drift Check	3A	Selected gas reading within $\pm 3.0\%$ of calibration span of pre-test reading (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
		Zero gas within $\pm 3.0\%$ of calibration span of pre-test reading (or $\pm 0.5\%$ for O <sub>2</sub> or CO <sub>2</sub> )
	3A	Selected gas reading within $\pm 3\%$ of span of pre-test reading
		Zero gas within $\pm 3\%$ of span of previous reading
Response Time	3A	No criteria, evaluated to determine duration at sample points
Sample Flow Rate	3A	Stable sample flow rate within 10% of flow rate established during system response time check and bias check

### 4.2 FTIR

As per EPA Method 320, a significant amount of QA/QC activity had to be performed in order to demonstrate the effectiveness of the FTIR and sampling system to accurately monitor and transport analyte containing gas samples. These pre-test and post-test QC/QA checks verify that the FTIR was capable of monitoring analytes at acceptable (low enough) concentrations, and that the system operated in a stable fashion throughout each run as well as the entire testing period. Similarly, EPA Method 3A and the AECOM internal QA/QC procedures call for rigorous checks and calibrations to ensure a high degree of data quality.

The sections below present detailed discussions of the QA/QC activities associated with sampling and analysis, as well as a data quality assessment. The overall conclusion of the QA/QC assessment is that the results of this test are of high quality and are appropriate for their intended use.

#### 4.2.1 FTIR QA/QC Results



This section describes the EPA Method 320 QA/QC requirements and presents the results. The pre-test QC EPA Method 320 requirements were done on site immediately before/after the testing and compared to the post-test results to ensure the FTIR system operated in a stable fashion throughout the entire sampling duration. These QA tests demonstrate that the FTIR and extractive system were capable of monitoring and transporting analytes at concentrations below those required to meet the test objectives. The tabulated details for these quality assessments are presented in Appendix XXX

#### 4.2.2 Pre-Test EPA Method 320 QA/QC Verifications

A series of tests were performed to demonstrate analytes quantification accuracy, system response time, etc. The results were obtained using nitrogen, a Calibration Transfer Standard (CTS) and a certified cylinder containing analytes. It should be noted that some of the EPA Method 320 required checks have passing criteria that are user-defined based upon the test objectives (i.e., path length). All the results demonstrate an acceptable performance of the FTIR and sampling system for analytes detection.

#### 4.2.3 Pre- and Post-Test Data QC Results

The EPA Method 320 requires a set of QC checks to be done prior to testing. A series of daily operational checks as well as more frequent (pre- and post-test) system accuracy and stability checks were performed per EPA Method 320 procedures, thus ensuring high quality data. The following checks were done at a minimum of once per day:

1. A system noise-equivalent-absorbance (NEA) under a nitrogen atmosphere was measured. NEA is a measure of the system noise and a good indicator that the system is properly aligned and operating optimally. NEA is also used to determine a best-case minimum detectable concentration. All the NEA checks were acceptable for quantifying analytes below the regulatory limit.
2. System background spectra were collected by purging the cell with UHP nitrogen (which does not absorb infrared radiation). This profiles the IR detector's response absent of all compound absorption. The background, once generated, is ratioed to all subsequent sample spectra.
3. Resolution Checks. The resolution was checked before the first run and after the 12-run test by measuring the field width at half maximum (FWHM) of a water band when a nitrogen purge was applied before the testing. The resolution check was compared to the lab reference and expected resolution. The spectral resolution was at or near 0.5 cm<sup>-1</sup> throughout the test and the results listed in **Error! Reference source not found.** are acceptable for this test.
4. Line Position. Since each reference in this analysis method had been normalized (shifted) to a specific frequency, it was imperative that the sample spectra were also aligned at this frequency and maintained this alignment throughout the test. This was achieved by monitoring the position of an H<sub>2</sub>O absorption peak which was injected by leaking air and N<sub>2</sub> into the system. This line position was checked before the test and it was compared to the lab reference and expected line position. The results demonstrate acceptable performance.

#### 4.2.4 QA System Recovery Spiking

As part of quality assurance procedures of the EPA Method 320, a total of 12 QA spikes of the target analyte must be performed prior and after testing, for each source. As a matter of good practice, AECOM performed spikes for each analyte before and after the performance test. These checks challenge the analysis method for accuracy of each analyte quantification while simultaneously verifying that the extractive system and analyzer are unreactive with analytes. Successful spiking is also an indication of a good analyte direct-inject measurement. The spiking procedure for the system recovery that was done separately for all analysis described in detail in the EPA Method 320 and summarized for methanol below.

A test, in which the methanol gas standard, was introduced directly into the heated sample cell (bypassing the extractive assembly), was performed. In addition to Methanol, the gas cylinder also contained a spectroscopic tracer (a broad, strong IR absorber which behaves linearly over a large range of concentrations) to calculate dilution factors. Sulfur hexafluoride (SF<sub>6</sub>) was the tracer used in the system recovery checks. After the cell was sufficiently purged

with the Methanol/SF<sub>6</sub> standard, the analysis method returned values for SF<sub>6</sub> and Methanol that were then compared to the certified cylinder values (SF<sub>6 cylinder</sub> & Methanol<sub>cylinder</sub>). Upon direct injection of the certified Methanol/ SF<sub>6</sub> standard into the FTIR sample cell, the SF<sub>6</sub> and the Methanol concentrations read from the FTIR compared within acceptable criterion for reactive gases to the cylinder certified values (9.84 to 10.02 ppm for SF<sub>6</sub>, 31.48 to 30.04 to ppm for Methanol).

The gas standard was then injected into the spiking "T" downstream of the probe as the stack effluent was drawn through the FTIR system. The Methanol/SF<sub>6</sub> gas standard injection flow was maintained at a constant rate using a flow controlling needle valve. After the FTIR cell was sufficiently purged with the gas standard/stack effluent mix (stable for ~5 minutes), the analysis method returned a value (SF<sub>6 sample</sub>) which represents the concentration of SF<sub>6</sub> diluted by the stack effluent. From the SF<sub>6</sub> concentrations the dilution factor (DF) can be determined by dividing the SF<sub>6 sample</sub> by the SF<sub>6 cylinder</sub>.

The expected concentration of Methanol (Methanol<sub>Theoretical</sub>) is the sum of diluted cylinder concentration (spiked) and the native stack concentration (also diluted by the injected spike) and was calculated as follows:

$$\text{Methanol}_{\text{Theoretical}} = \left( \frac{\text{SF}_{6\text{sample}}}{\text{SF}_{6\text{cylinder}}} \right) (\text{Methanol}_{\text{cylinder}}) + \left[ 1 - \left( \frac{\text{SF}_{6\text{sample}}}{\text{SF}_{6\text{cylinder}}} \right) \right] (\text{Methanol}_{\text{stack}})$$

Where:

Methanol <sub>Theoretical</sub>	=	Theoretical Methanol concentration (ppm);
SF <sub>6 sample</sub>	=	SF <sub>6</sub> concentration (ppm) as seen by the FTIR during QA spiking;
SF <sub>6 cylinder</sub>	=	SF <sub>6</sub> concentration observed during the direct inject;
Methanol <sub>cylinder</sub>	=	Methanol concentration observed during the direct inject; and
Methanol <sub>stack</sub>	=	The native Methanol concentration (ppm) of the stack during stable conditions.

The criterion for a successful recovery, per the EPA Method 320, is a measured concentration within 0.7-1.3 times the calculated theoretical concentration. This performance test demonstrated recoveries within the criterion, ranging from 90 – 101%.

Note: Results are on a wet basis, uncorrected for O<sub>2</sub> concentration.

A system zero analysis was also performed by injecting a sufficient flow of nitrogen through the calibration line, into the spiking "T" such that it flooded the "T" and probe assembly. The nitrogen was then pulled through the system via pump. The time required to purge the system to <5% of native stack concentrations was approximately one minute. Similarly, the time it took to achieve 95% of the native stack concentration levels once the nitrogen was turned off was approximately one minute. See Appendix XX.

#### 4.2.5 Evaluation of Completeness

Completeness is a measure of the extent to which the results from a measurement effort fulfills objectives for the amount of data required. For this program, completeness is defined in terms of the number of valid sample results collected compared with the number planned. All samples planned and all analyses planned were performed. No results were invalidated based on a data quality assessment.

#### 4.2.6 Deviations from the EPA Method 320 Method

No deviations from the EPA Method 320 were made on March. On April, no deviations from the EPA Method 320 were made other than those approved by EGLE and described on Table 3-1. Number of spikes on April were agreed to be one per source. As a good practice, AECOM performed 2 spikes at the beginning and 2 spikes at the end of each stack test. CTS were measured before and after each run for all sources and conditions.

#### 4.2.7 Sample Handling

Individual FTIR sample spectra were electronically stored in interferogram format on the system hard drive and backed-up onto various storage media. Each spectrum is time stamped and has the path length, pressure, and

temperature it was collected at stored with it. All support spectra (NEA, background, QA etc.) were also stored in various formats. Electronic copies of all spectra have been stored on USB flash drives.

#### **4.2.8 Calibration**

Calibration of the FTIR and sampling system were completed per the EPA Method 320 requirements and QA/QC procedures. The FTIR references used to build the analysis method (R3 Natural Gas Method 191 from MKS as requested by the local state agency, EGLE) were developed by the manufacturer of the FTIR and implemented by AECOM scientists. The FTIR instrument uses the above method to predict and simulate the transmission and emission of light in the atmosphere. This analysis is based on a set of analyte references generated from multiple certified gas cylinders. These analyte references have been used reliably on many occasions.