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**EU1200 RTO PERFORMANCE TEST REPORT and SUPPLEMENTAL NOTIFICATION OF COMPLIANCE STATUS REPORT FOR SUBPART FFFF (MON NOCS) (SRN P1028)**

Corteva Agriscience LLC (Corteva) is submitting this letter and report of results from a performance test conducted on 10/25/22 and 10/26/22 on EU1200's RTO-1870 and RTO-1875 (regenerative thermal oxidizer). These RTOs are used for control of organic HAP emissions from Group 1 process vents of the EU1200 process. The test was used to demonstrate compliance with the Subpart FFFF (MON MACT).

The test demonstrated compliance with the below MON MACT emission control standard for process vents:

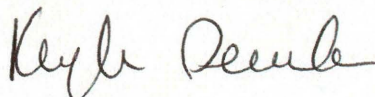
- Reduce uncontrolled organic HAP emissions from one or more batch process vents within the process by venting through one or more closed-vent systems to any combination of control devices (excluding a flare) that reduce organic HAP to an outlet concentration  $\leq 20$  ppm TOC or total organic HAP [§63.2450(e)(2), Table 2 to Subpart FFFF],

Corteva is also submitting the required supplemental Subpart FFFF Notification of Compliance Status (NOCS) report which has been updated to reflect the revised operating limits based on the performance test. The associated MACT Notification of Process Change reports will be included in the next semi-annual report which is due 3/15/23.

Test report copies are being sent to Michigan EGLE Saginaw Bay District Office, EGLE Technical Programs Unit in Lansing, and EPA Region V. The test report was also submitted via EPA's electronic reporting tool (ERT) as required by Subpart FFFF.

If you have questions regarding this submittal, please contact Patty Worden at or 989-898-5129 or at [patricia.worden@corteva.com](mailto:patricia.worden@corteva.com).

**CERTIFICATION STATEMENT** - *I certify that, based on information and belief formed after reasonable inquiry, the statements and information in this submittal and supporting enclosures are true, accurate, and complete.*



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Attachment

P1028-test-20221025



# MON MACT Compliance Test Report for 1200 Building (EU1200) RTO-1870 and RTO-1875

Corteva Agriscience LLC (SRN P1028)  
Midland, Michigan

Project Number: 60677135

October 31, 2022

### Quality information

<u>Prepared by</u>	<u>Checked by</u>	<u>Approved by</u>
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### Revision History

Revision	Revision date	Details	Authorized	Name	Position

### Distribution List

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Corteva Agriscience  
(EU1200) RTO-1870 and RTO-1875

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# 1. Introduction

AECOM Technical Services, Inc. (AECOM) of Midland, Michigan was retained by Corteva Agriscience, LLC (Corteva), which owns and operates an agricultural chemicals manufacturing facility located in Midland, Michigan, to perform MON MACT emissions testing on regenerative thermal oxidizers (RTOs), RTO-1870 and RTO-1875, which control emissions from the 1200 Building process.

1200 Building (EU1200) is a new Corteva production facility in Midland, Michigan (SRN P1028) that was constructed under Michigan EGLE Permit to Install PTI No. 37-20 (dated June 2, 2020). The EU1200 emissions (fermentation, crystallization, and packaging process vents) are collected in a vent header and routed to two RTOs: RTO-1870 and RTO-1875. The process can send process vents to both RTOs at the same time or just one of them, depending on the on-line status of the RTOs.

The MON MACT requires test completion and submittal of results within 150 days of startup operation. Day 1 of operation was June 9, 2022 so the test must be completed and submitted by November 6, 2022.

In accordance with the MON MACT, the RTO emission limits are as follows:

- VOC (NMHC) – Reduce emissions of total organic HAP to an outlet process concentration  $\leq 20$  ppmv as total organic HAP or TOC.

Formaldehyde was measured during this test since it is generated as a result of incomplete combustion in the RTO firebox; however, formaldehyde is not generated by the EU1200 process. As a result of previous discussions between EGLE and Corteva regarding a similar PAIP MACT subject process that measured formaldehyde emissions as a result of incomplete combustion, Corteva included formaldehyde testing in this compliance demonstration. Although Corteva does not agree with EGLE that formaldehyde generated in the RTO firebox is regulated by the PAIP MACT (and because MON MACT is written similarly, we do not believe it to be regulated under MON MACT either), Corteva demonstrated compliance with the  $\leq 20$  ppmv outlet concentration limit as TOC or Total OHAP, including the formaldehyde emissions. In addition, AECOM tested for formaldehyde in the outlet vent for informational purposes and planning of the subsequent comprehensive compliance emissions test to satisfy air permit emission limits.

The 1200 Building has both batch and continuous process vents that are manifolded into a common header; therefore, the hierarchy will be followed, and the process vents will be treated as designated Group 1 batch process vents under the MON MACT [[63.2450(c)]. As required, the test was conducted under hypothetical worst-case conditions and the emission profile was based on capture and control system limitations for designated Group 1 batch process vents in accordance with 63.2460(b)(5)(ii). There are no other Group 1 emission points venting to these control devices.

**Worst case conditions:** The testing occurred when sending all process vents to only one RTO, therefore maximizing the organic HAP load to the RTO being tested. This is the worst-case operating scenario for demonstrating  $\leq 20$  ppm TOC at each individual RTO stack outlet because, generally, the organic HAP loading from process vents will normally be split between the two RTOs. RTO testing was also completed while  $\geq 50\%$  of all fermentors were at  $\geq 50\%$  of the batch cycle time. Methanol is the only organic HAP with an emission profile of any significance, and it is generated by the fermentation process. The methanol generation increases over the batch cycle time. Only one fermentor batch can be started per day so each fermentor will be in a different day of the batch cycle time. The previously described condition for fermentor batch status results in a normal worst-case scenario of maximum methanol generation rate.

RTO-1870 was tested first on October 25, 2022. The combustion chamber temperature control setpoint was set to 1500 F and Runs 1-3 were completed. The total TOC plus formaldehyde ppm levels were at or above 20 ppmv, so the temperature control setpoint was increased to 1550 F. Runs 4-6 were completed at the 1550 F setpoint, and these are the runs that are being used for compliance purposes. Data for Runs 1-3 is also being included in the report appendices.

RTO-1875 was tested on October 26, 2022, with a combustion chamber temperature control setpoint of 1550 F.



This test report addressed the need to test for emissions and control efficiency of volatile organic compounds (VOC) defined as hazardous air pollutants (HAP) specified by the United States Environmental Protection Agency (US EPA) regulations in the National Emissions Standards for Hazardous Air Pollutants (NESHAP) under "Subpart FFFF - Miscellaneous Organic Chemical Manufacturing (MON)" Maximum Achievable Control Technology (MACT) standards. The MON MACT specifies an emissions limit for total organic HAPs (measured as TOC) of 20 parts per million by volume (ppmv). Additionally, this test report established formaldehyde (HCHO) emissions for informational purposes related to VOC emissions in advance of the final overall EU1200 air permit Compliance Performance Test.

This test report presents results for TOC emission concentrations as the sum of total hydrocarbons (THC) plus formaldehyde (HCHO) concentrations. THC was measured using a flame ionization analyzer calibrated with methane standards and expressed as ppmv carbon (C<sub>1</sub>) at actual exhaust gas conditions including moisture, wet (ppmvw C<sub>1</sub>). HCHO is a molecule having one carbon atom and was measured using an FTIR analyzer and expressed as ppmv at actual exhaust gas conditions including moisture (ppmvw C<sub>1</sub>).

Testing was performed using various instrumental analyzers including a Fourier Transform Infrared (FTIR) system optimized for the analysis of the requested species and a total hydrocarbons (THC) 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.

During testing, each RTO was operated under worst-case conditions with all fermentors venting only to the tested RTO while operating the tested RTO at the minimum operating temperature of 1,550 degrees F. RTO testing was also completed while ≥50% of all fermentors were at ≥50% of the batch cycle time.

Testing was conducted on October 25-26, 2022, for RTOs 1870 and 1875, respectively. During testing of RTO 1870, testing was first performed at an RTO temperature setpoint of 1,500 degrees F where emissions were very close to the MON MACT 20 ppmv TOC limit. A decision was then made to increase the setpoint to 1,550 to achieve a greater margin of emissions below the limit. The text of this report focuses on results of emissions when operating both RTOs at a temperature setpoint of 1,550 degrees F. Results for emissions from RTO 1870 at a setpoint of 1,500 degrees F is provided in Appendix E for informational purposes only.

**Capture and control system information:** The RTOs were operated at a minimum firebox temperature of 1550 F based on the manufacturer's recommendation. Each RTO has a maximum rated heat input of 5.78 MMBtu/hr and an average rated heat input of 3.83 MMBtu/hr. Process airflow to the RTOs ranges between 30,000- 38,000 scfm.

A maximum allowable organic HAP emission rate out the RTO vent of 4.2 lb/hr was calculated using 20 ppmv as an upper limit based on the max organic HAP emission concentration allowed by a Subpart FFFF process vent control device.

$$\begin{aligned}
 R &= 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \\
 V/n &= RT/P = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 360\text{K} / 1\text{atm} = 29.54 \frac{\text{L}}{\text{mol}} \\
 \text{Maximum RTO Flowrate} &= 38,000 \frac{\text{ft}^3}{\text{min}} \\
 \text{Molar Flowrate} &= \frac{38,000 \frac{\text{ft}^3}{\text{min}} \times 28.317 \frac{\text{L}}{\text{ft}^3}}{29.54 \frac{\text{L}}{\text{mol}}} = 36,400 \frac{\text{mol ideal gas}}{\text{min}} \\
 \frac{20 \frac{\text{mol propane}}{\text{mol}^6 \text{ ideal gas}} \cdot 36,400 \frac{\text{mol ideal gas}}{\text{min}} \cdot 44.1 \frac{\text{g}}{\text{mol propane}} \cdot 60 \frac{\text{min}}{\text{hr}}}{453.59 \frac{\text{g}}{\text{lb}}} &= 4.2 \frac{\text{lb}}{\text{hr}}
 \end{aligned}$$

The worst-case emission rate based on the results from this test was 2.3 lb/hour (10.9 ppm).

EGLE inquired about the potential cause of increased moisture during Run 2 on each day of testing. Corteva and EGLE staff discussed the high moisture with the RTO Manufacturer (DURR) representative and Corteva production staff. Corteva process activity that may have generated moisture during stack testing period included steam sterilization of a vessel from 10:14 -12:25 each day that vented a significant amount of steam to the RTOs.

**Table 1-1 Summary of TOC Emission Concentrations**

Source	RTO Minimum Operating Temperature	Average Analyte Concentration (ppmvw C <sub>1</sub> )		
		THC	Formaldehyde (HCHO)	Total TOC (THC plus HCHO)
RTO 1870	1554 F	8.3	2.4	10.7
RTO 1875	1552 F	6.4	1.1	7.5

## 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 sampling duration test 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.
- Wayne Washburn, QSTI was the local representative from AECOM at the Corteva facility and served as the Technical Lead for the field program as well as operating the O<sub>2</sub>, CO<sub>2</sub>, and THC analyzers. Mr. Washburn 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.

### CORTEVA CONTACTS:

- Patty Worden 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 communications were completed through this role. Contact information is 989-395-1724.
- Jason Nelson 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.



## Compliance Program Summary

<b>Responsible Groups</b>	<ul style="list-style-type: none"> <li>• Corteva Agriscience, LLC 1200 Building</li> <li>• Michigan Department of Environment, Great Lakes, and Energy (EGLE)</li> <li>• United States Environmental Protection Agency (US EPA)</li> </ul>
<b>Applicable Regulations</b>	<ul style="list-style-type: none"> <li>• "40CFR 63, Subpart FFFF - Miscellaneous Organic Chemical Manufacturing (MON)" Maximum Achievable Control Technology (MACT) standards</li> <li>• 40 CFR Part 60, Appendix A; 40 CFR Part 63, Appendix A</li> </ul>
<b>Industry/Plant</b>	• Fermentation, 1200 Building
<b>Plant Location</b>	• Midland, Michigan I-Park Facilities 48667
<b>Unit Initial Start-up</b>	• 2022
<b>Emission Points</b>	<ul style="list-style-type: none"> <li>• RTO-1870</li> <li>• RTO-1875</li> </ul>
<b>Pollutants/Diluent Measure</b>	<ul style="list-style-type: none"> <li>• VOC (NMHC)</li> <li>• Formaldehyde (HCHO)</li> </ul>
<b>Test Dates</b>	• October 25 & 26, 2022

<b>Facility Information</b>	
Facility Name:	Corteva Agriscience™
Facility Address:	1200 Building, Midland, Michigan 48667
Facility Contact:	Patty Worden
Title:	Senior Environmental Specialist
Phone:	(989) 898-5129
<b>Source Information</b>	
Equipment:	RTO-1870 & RTO-1875 (Regenerative Thermal Oxidizers) Serving 1200 Building (EU1200)
Permit No:	Permit to Install (PTI No. 37-20, dated June 2, 2020)
Measurement Parameters:	VOC and Formaldehyde (HCHO)
Test Conditions:	Maximum Achievable Capacity under Normal Operations
<b>Agency Information</b>	
State Agency:	Michigan Department of Environment, Great Lakes, and Energy (EGLE) Air Quality Division
Agency Contact:	Lindsey Wells
Phone:	(517)-282-2345
<b>Test Firm Information</b>	
Test Organization:	AECOM
Address:	3700 James Savage Road, Building 1602, Midland, MI 46842
Contact:	James Edmister
Title:	Project Manager
Phone:	(585)-721-9128

## 1.2 Test Chronology

Table 1-2 Summary of Sample Collection Times

Stack	Run	Operating Setpoint (degrees F)	Date/Time		
			Date	Run Start	Run End
RTO 1870	1	1,500	25-Oct-2022	08:53	09:53
	2			10:17	11:17
	3			11:43	12:43
	4	1,550	25-Oct-2022	15:07	16:07
	5			16:31	17:31
	6			17:50	18:50
RTO 1875	1	1,550	26-Oct-2022	09:12	10:12
	2			10:34	11:34
	3			12:18	13:18

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## 2. Results Summary

The results of the MON MACT VOC emissions compliance testing are summarized in Tables 2-1 and 2-2 below.

**Table 2-1**  
**RTO 1870 TOC Emissions Results Summary**

Run Identification	Run 4	Run 5	Run 6	Average
Run Date	10/25/22	10/25/22	10/25/22	-----
Run Time	15:07-16:07	16:31-17:31	17:50-18:50	-----
<u>Operating Conditions</u>				
RTO Temperature Setpoint (°F)	1,550	1,550	1,550	-----
RTO Temperature #1 (°F)	1,554	1,554	1,554	1,554
<u>Exhaust Gas Conditions</u>				
Oxygen (% dry)	18.31	18.30	18.24	-----
Carbon Dioxide (% dry)	2.13	2.14	2.20	-----
Flue Gas Moisture (%)	3.67	3.67	3.68	3.68
<u>Formaldehyde (HCHO)</u>				
Concentration (ppmvw) via FTIR	2.43	2.46	2.44	2.44
<u>Total Hydrocarbons (as Methane)</u>				
Concentration (ppmvw C <sub>1</sub> )	8.21	8.27	8.37	8.28
<u>Total TOCs (THC plus HCHO)</u>				
Concentration (ppmvw C <sub>1</sub> )	10.64	10.73	10.81	10.73

**Table 2-2**

**RTO 1875 TOC Emissions Results Summary**

Run Identification	Run 1	Run 2	Run 3	Average
Run Date	10/26/22	10/26/22	10/26/22	-----
Run Time	09:12-10:12	10:34-11:34	12:18-13:18	-----
<u>Process Operating Conditions</u>				
RTO Temperature Setpoint (°F)	1,550	1,550	1,550	-----
RTO Temperature #1 (°F)	1,550	1,548	1,558	1,552
<u>Exhaust Gas Conditions</u>				
Oxygen (% dry)	18.23	18.17	18.10	-----
Carbon Dioxide (% dry)	2.19	2.24	2.30	-----
Flue Gas Moisture (%)	3.26	4.08	4.73	4.02
<u>Formaldehyde (HCHO)</u>				
Concentration (ppmvw) via FTIR	1.10	1.23	1.13	1.15
<u>Total Hydrocarbons (as Methane)</u>				
Concentration (ppmvw C <sub>1</sub> )	6.17	6.36	6.55	6.36
<u>Total TOCs (THC plus HCHO)</u>				
Concentration (ppmvw C <sub>1</sub> )	7.27	7.58	7.68	7.51



# 3. Sampling and Analytical Procedures

## Overview

This test program was designed to quantify emissions of non-methane VOCs (NMVOC's as propane), Formaldehyde (HCHO), and fixed gases concentrations of Oxygen (O<sub>2</sub>) and Carbon Dioxide (CO<sub>2</sub>) in order to demonstrate compliance with MON MACT emission limits. All testing was completed using approved US EPA test methods as follows:

### Exhaust Stack Parameters and Matrix

Sampling Location	No. of Runs	Sample/Type Pollutant	Sampling Method	Sampling Organization	Sample Run Time (min.)	Sampling Frequency	Analytical Method	Analytical Lab
RTO 1870 outlet vent	3	Mol. Wt. (O <sub>2</sub> /CO <sub>2</sub> )	M3A	AECOM	Minimum 1 hour	Continuous	Infrared	AECOM
RTO 1875 outlet vent		Moisture	M320				Fourier Transform Infrared (FTIR) Spectroscopy	
		(NMVOC's)	M25A/ALT-096*					
		Formaldehyde (HCHO)	M320					

\*ALT-096 is a broadly approved alternative test method, Federal Register / Vol. 78, No. 32 / Friday, February 15, 2013.

### 3.1 Sample Time

The duration of each test run was approximately sixty (minutes) for a total of 180 minutes for each RTO at each tested operating temperature setpoint.

### 3.2 Instrumental (non-FTIR) Methods

Emission gas was withdrawn from each RTO 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 ±2% of span from the calibration gas value, and the system bias check for each of these gases was no more than ±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.

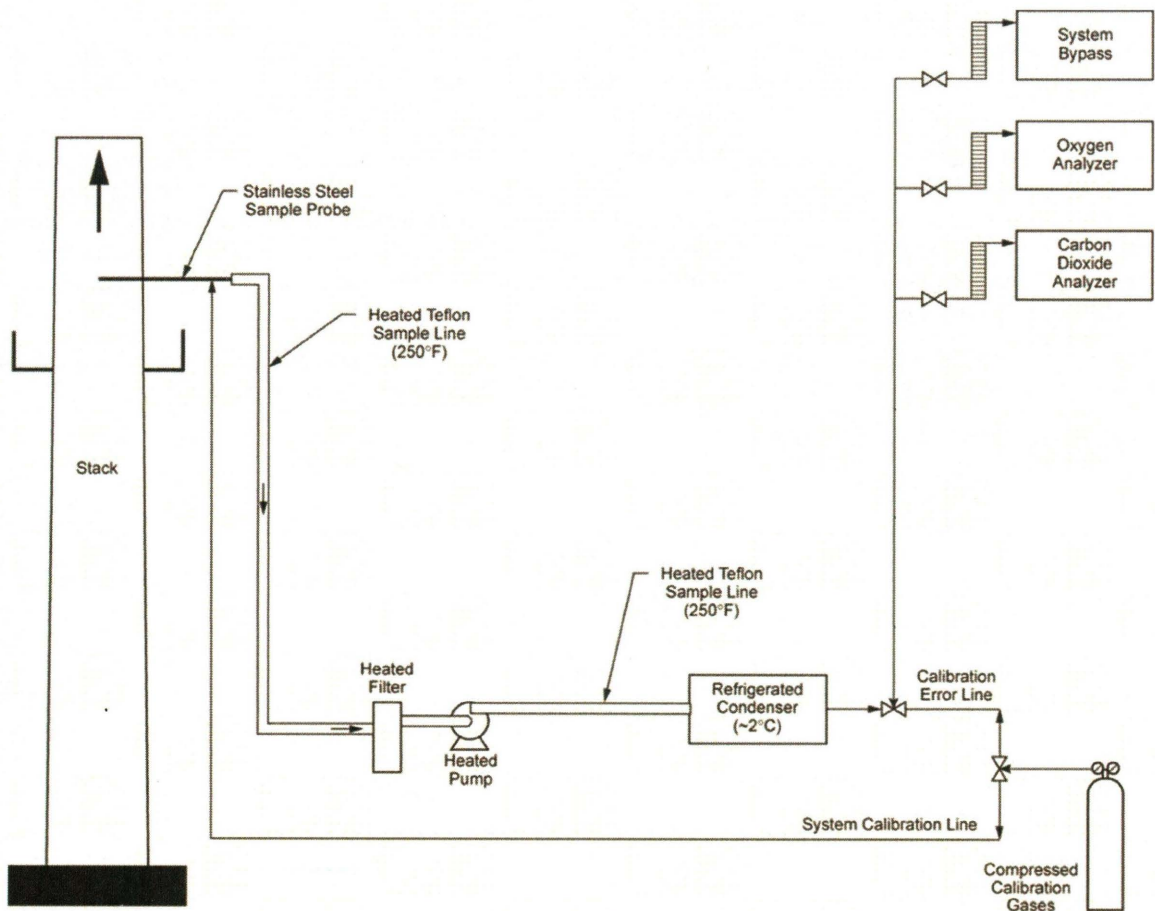
A system response time test for each parameter was performed and documented.

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-VGRAPHICS\L\_Figures\CEMS System\_G Youngman\_CEMS System\_Schematic Full System

### 3.3 FTIR Sample System Description

Formaldehyde (HCHO) and Moisture were measured in accordance with EPA320 and ASTM Method D 6348-12. Stack gas will be continuously sampled and analyzed utilizing a Fourier Transform Infrared (FTIR) Spectroscopy extractive sampling system. The FTIR instrument is a MKS MultiGas 2030. Further details of the continuous monitoring procedures for each parameter are presented in the following subsections.

The FTIR extractive system was comprised a stainless-steel probe (~2 foot), a heated filter, a stainless-steel spiking "T", a 100-ft heated (300°F) PFA-grade Teflon line, a MKS 2030 FTIR spectrometer (Model: 2030DBG2EZKS13T, SN: 018631631) complete with a heated (191 °C) fixed-path sample cell, a flow regulating valve, a rotameter, and a sample pump. A schematic of the sampling system is depicted in **Figure 3-2**. Given these components Formaldehyde and Moisture monitoring consists 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 is continuous and maintained at approximately 7 standard liters per minute (lpm) by a diaphragm pump connected to the outlet of the FTIR cell. Since the pump provides samples slightly below ambient pressure to the FTIR cell, cell pressure is continuously recorded during measurement periods using a pressure sensor calibrated over the 0 – 900 torr range. These pressures are then used in the quantification of each spectrum.

#### 3.3.1 Analyte Spiking System

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.

Per Annex 5 (A5) of the ASTM FTIR method and EPA 320 method, analyte spiking must be performed to determine the effectiveness of the sampling and analytical systems in transporting and quantifying each analyte. The aforementioned spiking "T", placed between the probe and the extraction line (as specified in the ASTM FTIR Method), enables injection of each analyte gas standard directly into the extracted sample gas stream.

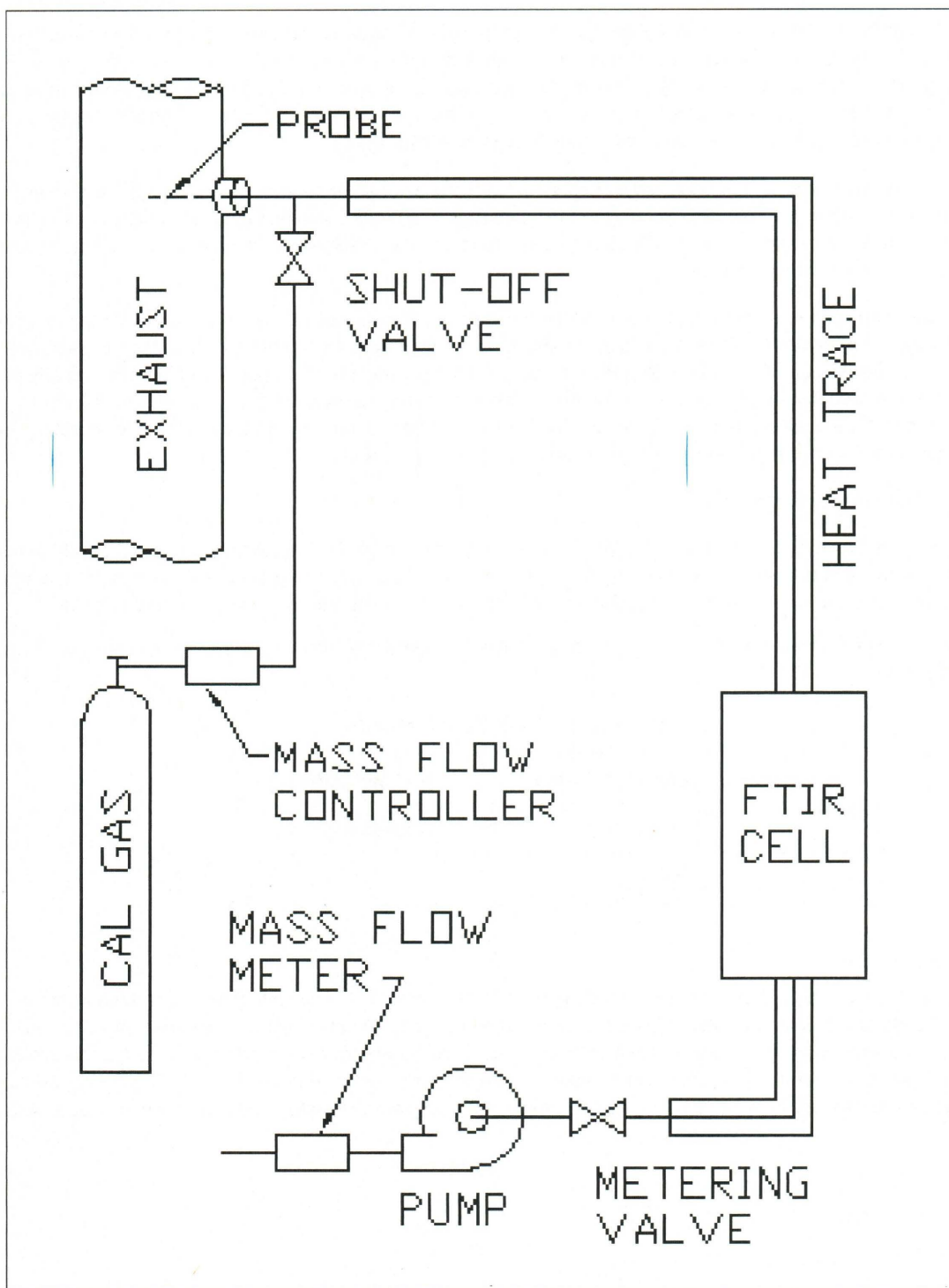
The ASTM FTIR Method stipulates an analyte spike equal to the native concentration at no more than 10% of the total flow be delivered through the entire sampling system. Spikes at, above, and below the 1-5 ppm expected limit will be performed. Controlled by a needle valve, precise volumes of the analyte gas standard will be delivered into the extracted stack gas (system recovery checks). Furthermore, since the injected standard flow is negligible compared to the extracted sample flow (maximum of 10% of total flow), the sample gas matrix (including interferences) will not be significantly changed.

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:

- 16.03 ppm formaldehyde
- 7.98 ppm SF<sub>6</sub> as a tracer gas.

Figure 3-2 FTIR Sample System



Note: This figure shows the configuration for the system leak check. For the 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.



### 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, formaldehyde on a hot wet basis. Table 3-1 correlates the component and its corresponding analysis method.

**Table 3-1 FTIR Test Methods**

<b>Compound Monitored</b>	<b>Test Methodology</b>
Formaldehyde	EPA Method 320
Moisture	FTIR

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 Appendix C. and the QA spiking results are presented and discussed in Section 4.2.4

## 4. QA/QC

### 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 C.

#### 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, as shown in Appendix C.

#### 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 in the absence 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 each 3-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 Appendix C and 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 (or 2 spikes as allowed by EGLE) of the target analyte must be performed prior and after testing, for each source. As a matter of good practice, AECOM performed at least 2 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 formaldehyde below.

A test, in which the formaldehyde gas standard, was introduced directly into the heated sample cell (bypassing the extractive assembly), was performed. In addition to Formaldehyde, 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 Formaldehyde/SF<sub>6</sub> standard, the analysis method returned values for SF<sub>6</sub> and Formaldehyde that were then compared to the certified cylinder values (SF<sub>6</sub><sub>cylinder</sub> & Formaldehyde<sub>cylinder</sub>). Upon direct injection of the certified Formaldehyde/ SF<sub>6</sub> standard into the FTIR sample cell, the SF<sub>6</sub> and the Formaldehyde concentrations read from the FTIR compared within acceptable criterion for reactive gases to the cylinder certified values (7.99 to 7.982 ppm for SF<sub>6</sub>, 15.27 to 16.03 to ppm for Formaldehyde).

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 Formaldehyde/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</sub><sub>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</sub><sub>sample</sub> by the SF<sub>6</sub><sub>cylinder</sub>.

The expected concentration of Formaldehyde (HCHO<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:

$$\text{HCHO}_{\text{Theoretical}} = \left( \frac{\text{SF}_6\text{sample}}{\text{SF}_6\text{cylinder}} \right) (\text{HCHO}_{\text{cylinder}}) + \left[ 1 - \left( \frac{\text{SF}_6\text{sample}}{\text{SF}_6\text{cylinder}} \right) \right] (\text{HCHO}_{\text{stack}})$$

Where:

- HCHO<sub>Theoretical</sub> = Theoretical HCHO concentration (ppm);
- SF<sub>6</sub><sub>sample</sub> = SF<sub>6</sub> concentration (ppm) as seen by the FTIR during QA spiking;
- SF<sub>6</sub><sub>cylinder</sub> = SF<sub>6</sub> concentration observed during the direct inject;
- HCHO<sub>cylinder</sub> = HCHO concentration observed during the direct inject; and
- HCHO<sub>stack</sub> = The native HCHO 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 70 – 129%.

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 C.

#### 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 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.



#### **4.2.7 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.