

PTI Emissions Compliance Test Report for 1200 Building (EU1200) RTO-1870 and RTO-1875

Corteva Agriscience, LLC
Midland, Michigan

Project Number: 60702819

May 13, 2023

Quality information

Prepared by

Ignacio Gallardo

Checked by

Wayne Washburn

Approved by

James Edmister

Revision History

Revision	Revision date	Details	Authorized	Name	Position

Distribution List

# Hard Copies	PDF Required	Association / Company Name

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

Prepared for:

Corteva Agriscience LLC

Prepared by:

Ignacio Gallardo

Senior Scientist

T: 512-419-5380

E: ignacio.gallardo@aecom.com

AECOM

9400 Amberglen Boulevard,

Austin, TX 78729-1100 aecom.com

Table of Contents

1.	Introduction	1-1
2.	Results Summary	2-1
3.	Sampling and Analytical Procedures	3-1
4.	QAQC	4-1
	Appendix A Process Operating Data	A
	Appendix B Instrumental Analyzer Test Data	B
	Appendix C FTIR Test Data	C
	Appendix D Equipment Calibration Data and Gas Certificates	D
	Appendix E PM and Flow Rate Test Data	E
	Appendix F Laboratory Analytical Data	F
	Appendix G Protocol	G

Figures

Figure 3-1 FTIR Instrumental Sampling System	3-2
Figure 3-2 FTIR Sample System	3-4

Tables

Table 1-1 Summary of TOC Emission Concentrations	1-3
Table 1-2 Summary of Sample Collection Times	1-4
Table 2-1 RTO 1870 TOC Emissions Results Summary	2-1
Table 2-2 RTO 1875 TOC Emissions Results Summary	2-2
Table 3-1 FTIR Test Methods	3-1
Table 4-1 Instrumental Method Performance Checks	4-1

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 Emissions Compliance Testing on two new regenerative thermal oxidizers (RTOs), RTO-1870 and RTO-1875, which control emissions from the 1200 Building fermentation process to comply with the requirements of Permit to Install (PTI) Number 37-20A (dated May 5, 2022). Representatives from the Michigan Department of Environment, Great Lakes & Energy (EGLE) were present during the test program.

TTU-1875 was tested first on April 6th of 2023, and TTU-1870 was tested next on April 7th of 2023. In each case, the RTO combustion chamber temperature control setpoint was set to 1550 F early in the morning and allowed to stabilize prior to Runs 1-3 being completed on the tested unit. Process operating data for each RTO is summarized in Section 2.4 and presented in **Appendix A**.

This report presents the results for the tested list of air pollutants required in the Michigan Department of Environment, Great Lakes, and Energy (EGLE) Air Quality Division, Permit to Install (PTI No. 37-20A) to demonstrate final overall emissions compliance with the requirements cited in the permit. The testing was completed within “365 days after transfer of an inoculated broth to the first fermenter”. Testing was performed to quantify PTI parameter emissions of total organic HAP (i.e., Total Organic Compounds (TOC)), particulate matter (PM/PM₁₀/PM_{2.5}), methanol (CH₃OH), ammonia (NH₃), formic acid (HCOOH), and formaldehyde (HCHO). In addition to the PTI parameters, emissions of nitrogen oxides (NO_x) and carbon monoxide (CO) were measured concurrently, and the results are presented in **Appendix B**.

This report describes how Corteva conducted the emissions compliance testing following the test methods referenced in the EU1200 air permit (PTI No. 37-20A) and the test protocol approved by EGLE. Specifics of the program are discussed in the following sections. A summary of emissions is presented in **Table 1-1**. A comparison of emission results to permitted limits is presented in **Table 1-2**. Note that PM₁₀ and PM_{2.5} emissions exceed permit limits.

Table 1-1 Summary of PTI Parameter Emission Results

Source	RTO Operating Temperature (Primary)	Average Parameter Emissions (lb/hr or as specified) ¹						
		TOC, as CH ₄ (ppmvd / tpy ¹)	Formic Acid (HCOOH) (lb/yr) ²	Ammonia (NH ₃) Lb/hr	Methanol (CH ₃ OH) Lb/hr	Formaldehyde (HCHO) Lb/hr	PM (FPM only) (lb/klb-gas)	PM ₁₀ / PM _{2.5} (FPM + CPM) (ton/yr) ¹
RTO 1870	1,551 F	4.7 / 1.66	<228	0.54	0.72	0.17	0.0017	4.9
RTO 1875	1,550 F	3.5 / 1.20	<228	0.27	0.69	0.11	0.0017	4.3

¹ Annual emission rates are based on 8,760 source operating hours per year and 2,000 pounds per ton (i.e., tpy = 4.38 * lb/hr).

² Formic acid was not observed in the FTIR spectra and is reported as below the Method Detection Limit (MDL).

Table 1-2 PTI Parameter Emission Results versus EU1200 Permit Limits

Permit Parameter	Permit Limit	TTU-1870	TTU-1875
Organic HAP / TOC / Formaldehyde	20 ppmv	5.85 ppmv	4.24 ppmv
VOC + Acetone ¹	20 ppmv 18.5 ton/year	4.7 ppmv 1.66 ton/year	3.5 ppmv 1.20 ton/year
PM (FPM only)	0.006 lb/1,000 lb exhaust gas	0.0017 lb/1,000 lb-gas	0.0017 lb/1,000 lb-gas
PM ₁₀ (FPM + CPM)	1.3 ton/year	4.9 ton/year*	4.3 ton/year*
PM _{2.5} (FPM + CPM)	1.3 ton/year	4.9 ton/year*	4.3 ton/year*
Ammonia	0.75 lb/hr	0.54 lb/hr	0.27 lb/hr
Formic acid	1,889 lb/year	< 228 lb/year	< 228 lb/year
Formaldehyde	0.4 lb/hr	0.17 lb/hr	0.11 lb/hr

¹ VOC measured as THC using US EPA Method 25A includes any acetone present in the gas stream sample.

* Note: The test results show that EU1200 is exceeding the PM10 and PM2.5 emission limits. The facility was in normal operation at the time of testing and there were no malfunctions that occurred during testing. When putting together the original EU1200 permit application, the PM emission estimate was based on the 2019 Harbor Beach (SRN B4942) EUPROCESS test result of 0.3 lb/hour which only included filterable PM. The EU1200 filterable PM results (~0.26 lb/hr) were similar to Harbor Beach's filterable PM results, but adding in the condensable PM puts the facility over the PM10 and PM2.5 limits. The facility has submitted a revised permit application to increase the PM limit.

1.1 Process Operations

RTO-1870 and RTO-1875 currently operate at a minimum firebox temperature of 1554 F and 1552 F (Primary RTD), respectively, per the October 2022 MON MACT performance test. Note that these are the actual respective operating temperatures that resulted on each RTO during the MON MACT test when the control system operating setpoint was 1,550 F. During this PTI compliance test in April 2023, RTO-1870 and RTO-1875 operated at minimum firebox temperatures of 1551F and 1549 F (Primary RTD) respectively, when the control system operating setpoint was 1,550 F. See Section 2.3 of this report for summaries of the process operating data.

Worst case test 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 ≤ 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 was in a different day of its individual batch cycle time. Therefore, the previous described operating condition results in a normal worst-case scenario of maximum methanol generation rate.

Capture and control system information: The RTOs were operated at a minimum firebox temperature setpoint of 1550 F based on the October 2022 MON MACT test. 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.

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

1.2 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 as well as reporting of results for the test program.

- 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 O₂, CO₂, CO, NO_x, and THC analyzers. Mr. Washburn also coordinated with plant operations for the success of the test and, subsequently, development of the test report.
- Jack Hoard, QSTI was the wet chemistry Senior Scientist and was responsible for the preparation, performing, and overseeing PM testing, flow rate and isokinetic data analysis, and PM sample recovery.
- Ignacio Gallardo was the FTIR Senior Scientist and was responsible for the FTIR preparation, performing and overseeing FTIR testing, FTIR data analysis and QA/QC, and report generation.
- Additional technicians with supporting roles in the field test program included Quincy Crawfish, Christopher Trevillian, Brandy Dangler, and Peter Becker.

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.

1.3 Test Chronology

Table 1-3 Summary of Sample Collection Times

Stack	Run	Operating Temperature [Primary RTD] (degrees F)	Date/Time		
			Date	Run Start	Run End
RTO 1870	1	1,551	07-April-2023	08:21	09:40
	2			10:43	11:54
	3			12:45	13:56
RTO 1875	1	1,549	06-April-2023	08:35	09:56
	2			11:20	12:33
	3			15:20	16:38

2. Results Summary

The emissions results of the PTI compliance testing are summarized in **Tables 2-1** through **2-4** in Sections 2.1 through 2.2. Corresponding process operating data is summarized in the tables in Section 2.3.

2.1 PTI Emissions Summary – Gaseous Parameters

Table 2-1 RTO 1870 PTI Emissions Results Summary – Gaseous Parameters

Run Identification	1870-R1	1870-R2	1870-R3	Average
Flow Run Number	Flow Run 1	Flow Run 2	Flow Run 3	
Run Date	4/7/23	4/7/23	4/7/23	
Run Time	08:21-09:40	10:43-11:54	12:45-13:56	
<u>Exhaust Gas Conditions</u>				
Oxygen (% dry)	18.56	18.52	18.69	18.59
Carbon Dioxide (% dry)	1.90	1.92	1.80	1.87
Flue Gas Moisture (%)	3.21	4.44	3.37	3.67
Flue Gas Flow Rate (dscfm)	31,171	31,424	33,668	32,087
<u>Total Hydrocarbons (as Methane)</u>				
Concentration (ppmvd)	4.62	4.84	4.75	4.74
Emission rate (lb/hr) (as methane)	0.360	0.381	0.399	0.380
<u>Ammonia</u>				
Concentration (ppmvw)	6.65	7.25	4.29	6.06
Concentration (ppmvd)	6.87	7.59	4.44	6.30
Emission rate (lb/hr)	0.568	0.633	0.397	0.536
<u>Formaldehyde</u>				
Concentration (ppmvw)	1.06	1.05	1.09	1.07
Concentration (ppmvd)	1.10	1.10	1.13	1.11
Emission rate (lb/hr)	0.160	0.162	0.178	0.167
<u>Formic Acid</u>				
Concentration (ppmvw)	<0.126	<0.098	<0.098	<0.107
Concentration (ppmvd)	<0.130	<0.103	<0.101	<0.111
Emission rate (lb/hr)	<0.029	<0.023	<0.024	<0.026
<u>Methanol</u>				
Concentration (ppmvw)	4.62	4.29	4.13	4.35
Concentration (ppmvd)	4.77	4.49	4.27	4.51
Emission rate (lb/hr)	0.743	0.705	0.718	0.723

Table 2-2 RTO 1875 PTI Emissions Results Summary – Gaseous Parameters

Run Identification	1875-R1	1875-R2	1875-R3	Average
Flow Run Number	Flow Run 1	Flow Run 2	Flow Run 3	
Run Date	4/6/23	4/6/23	4/6/23	
Run Time	08:35-09:56	11:20-12:33	15:20-16:38	
<u>Exhaust Gas Conditions</u>				
Oxygen (% dry)	18.38	18.40	18.25	18.34
Carbon Dioxide (% dry)	2.10	2.05	2.16	2.10
Flue Gas Moisture (%)	3.28	3.58	3.98	3.61
Flue Gas Flow Rate (dscfm)	30,457	32,709	32,002	31,722
<u>Total Hydrocarbons (as Methane)</u>				
Concentration (ppmvd)	3.44	3.50	3.46	3.47
Emission rate (lb/hr) (as methane)	0.262	0.286	0.276	0.275
<u>Ammonia</u>				
Concentration (ppmww)	2.84	3.23	3.30	3.12
Concentration (ppmvd)	2.94	3.35	3.44	3.24
Emission rate (lb/hr)	0.238	0.290	0.292	0.273
<u>Formaldehyde</u>				
Concentration (ppmww)	0.65	0.84	0.73	0.74
Concentration (ppmvd)	0.67	0.87	0.76	0.77
Emission rate (lb/hr)	0.095	0.133	0.114	0.114
<u>Formic Acid</u>				
Concentration (ppmww)	<0.102	<0.120	<0.112	<0.111
Concentration (ppmvd)	<0.105	<0.124	<0.117	<0.116
Emission rate (lb/hr)	<0.023	<0.029	<0.027	<0.026
<u>Methanol</u>				
Concentration (ppmww)	4.07	4.23	4.30	4.20
Concentration (ppmvd)	4.21	4.39	4.48	4.36
Emission rate (lb/hr)	0.640	0.717	0.716	0.691

RECEIVED

JUN 12 2023

2.2 Emissions Summary – Particulate Matter

Table 2-3 RTO 1870 PTI Emissions Results Summary – Particulate Matter

Run No. Date Start Time Stop Time		R1 07-Apr-23 8:20 9:40	R2 07-Apr-23 10:43 11:54	R3 07-Apr-23 12:45 13:56	AVG
Units					
<u>Sampling Parameters</u>					
Moisture	% v/v	3.2	4.5	3.4	3.7
O ₂ at Stack	% dry	1.90	1.92	1.80	1.87
CO ₂ at Stack	% dry	18.56	18.52	18.69	18.59
Stack Gas Volumetric Flowrate /min.	dscfm	29,974	30,240	32,365	30,860
Stack Gas Volumetric Flowrate /hr.	dscfh	1,798,423	1,814,402	1,941,928	1,851,584
Stack Gas Mass Flowrate	klb/hr	144.8	146.1	156.5	149.1
<u>Method 5 Front Half Particulate Emission Results</u>					
FH Grain Loading	gr/dscf	< 0.00089	< 0.00080	< 0.00121	< 0.00097
FH Emission Rate	lb/hr	< 0.229	< 0.206	< 0.335	< 0.257
	lb/klb-gas	< 0.0016	< 0.0014	< 0.0021	< 0.0017
<u>Method 202 Back Half Condensable Particulate Emission Results --</u>					
CPM Grain Loading	gr/dscf	0.00375	0.00356	0.00254	0.00328
CPM Emission Rate	lb/hr	0.964	0.923	0.705	0.864
Total FH + CPM Grain Loading	gr/dscf	< 0.00464	< 0.00436	< 0.00375	< 0.00425
Total FH + CPM Emission Rate	lb/hr	< 1.193	< 1.130	< 1.040	< 1.121

<- Value below minimum detection limit. The results are reported as less than because one or both fractions are below detection limit.

Table 2-4 RTO 1875 PTI Emissions Results Summary – Particulate Matter

Run No. Date Start Time Stop Time		R1 06-Apr-23 8:35 9:55	R2 06-Apr-23 11:20 12:32	R3 06-Apr-23 15:20 16:37	AVG
	Units				
<u>Sampling Parameters --</u>					
Moisture	% v/v	3.3	3.6	4.0	3.6
O ₂ at Stack	% dry	2.10	2.05	2.16	2.10
CO ₂ at Stack	% dry	18.38	18.40	18.25	18.34
Stack Gas Volumetric Flowrate /min.	dscfm	29,522	31,703	31,035	30,753
Stack Gas Volumetric Flowrate /hr.	dscfh	1,771,292	1,902,163	1,862,100	1,845,185
Stack Gas Mass Flowrate	klb/hr	142.5	153.1	149.8	148.5
<u>Method 5 Front Half Particulate Emission Results --</u>					
FH Grain Loading	gr/dscf	< 0.00104	< 0.00105	< 0.00085	< 0.00098
FH Emission Rate	lb/hr	< 0.263	< 0.285	< 0.226	< 0.258
	lb/klb-gas	< 0.0018	< 0.0019	< 0.0015	< 0.0017
<u>Method 202 Back Half Condensable Particulate Emission Results --</u>					
CPM Grain Loading	gr/dscf	0.00189	0.00363	0.00260	0.00271
CPM Emission Rate	lb/hr	0.478	0.986	0.692	0.718
Total FH + CPM Grain Loading	gr/dscf	< 0.00293	< 0.00468	< 0.00345	< 0.00368
Total FH + CPM Emission Rate	lb/hr	< 0.741	< 1.271	< 0.917	< 0.976

<- Value below minimum detection limit. The results are reported as less than because one or both fractions are below detection limit.

2.3 Process Operations Data

During each test run, process data was recorded by Corteva's data historian and reported as one-minute snapshots. The following tables summarize the process data. The process data collected included the tabulated, as a minimum, along with other pertinent information to demonstrate that the process was operating normally (not during a startup, shutdown, or malfunction) and at worst-case conditions during the performance test: In addition, approximate normal operating conditions are listed in the tables. More detailed process data is presented in Appendix A.

TTU-1870 (April 7, 2023)

Instrument ID #	Description	Normal Operating Range	Value during test
TTU-1870_2723TC	RTO-1870 Firebox temperature #1 (F); PRIMARY*	Minimum of 1,500 F	1,550.6
TTU-1870_2726TC	RTO-1870 Firebox temperature #2 (F); BACKUP*	Minimum of 1,500 F	1,550.3
TTU70_2921FT	RTO-1870 Natural gas feed rate (scfh)	Minimum of 360 scfh	2,231 scfh
TTU70_2501FT	RTO-1870 Combustion air feed rate (scfh)	Minimum 8,000 scfh	50,970 scfh
Fermentation production %	% of fermentors at > 50% of batch cycle (number of fermentors and batch cycle time is confidential)	33-50%	≥50%
FC_40307	Harvest tank discharge flow rate (gpm). Indicates operating rate of the back half of process	15-30 gpm	22.1 gpm

TTU-1875 (April 6, 2023)

Instrument ID #	Description	Normal Operating Range	Value during test
TTU-1875_2723TC	RTO-1875 Firebox temperature #1 (F); PRIMARY*	Minimum of 1,500 F	1,549.1
TTU-1875_2726TC	RTO-1875 Firebox temperature #2 (F); BACKUP*	Minimum of 1,500 F	1,553.5
TTU75_2921FT	RTO-1875 Natural gas feed rate (scfh)	Minimum of 360 scfh	2,383 scfh
TTU75_2501FT	RTP-1875 Combustion air feed rate (scfh)	Minimum 8,000 scfh	59,150 scfh
Fermentation production %	% of fermentors at > 50% of batch cycle (number of fermentors and batch cycle time is confidential)	33-50%	≥50%
FC_40307	Harvest tank discharge flow rate (gpm). Indicates operating rate of the back half of process	15-30 gpm	17.9 gpm

* Each TTU has two temperature instruments to measure the firebox temperature. The instruments are located about 90 degrees apart within the combustion chamber. One instrument is primary which control compliance is based on. If the primary instrument fails, the TTU will be controlled based on the backup instrument.

*The RTO temperature instruments were calibrated in September 2022 in accordance with the manufacturer's written specifications or recommendations for installation, operation, and calibration of the system.

3. Sampling and Analytical Procedures

3.1 Sample Time

The duration of each test run was approximately sixty minutes for a total minimum sampling duration of 180 minutes (three test runs) for each RTO at the tested operating temperature setpoint and maximum process loading conditions.

3.2 Filterable and Condensable Particulate Matter

Filterable particulate matter (FPM) and condensable particulate matter (CPM) emissions were measured using a combined EPA Methods 5 and 202 sampling train. The results of FPM provide a measurement of the PM emissions from each source for evaluation of compliance with air permit PM limits. The combined results of FPM and CPM provide a measurement of the maximum potential PM₁₀ and PM_{2.5} emissions from each source for comparison to air permit PM₁₀ and PM_{2.5} limits.

The basic EPA Method 5 sampling train configuration was employed, which isokinetically ($\pm 10\%$) extracted sample gas from the source and collected front-half particulate matter (nozzle/probe rinse and particulate filter) for subsequent gravimetric analysis. The basic EPA Method 5 sampling train uses a glass nozzle and glass lined probe, a Teflon union, a tared glass fiber or quartz fiber filter, a Teflon frit, a heated filter box (maintained at 248 °F ± 25 °F) and a series of leak-free impingers that contain a known amount of water and known quantity of silica gel. The sampling train was operated isokinetically ($\pm 10\%$) by extracting a gas sample from the exhaust stack and collecting the particulate matter from the gas sample for subsequent gravimetric analysis. Prior to sample recovery, the volume of liquid collected in the impingers was quantified to allow for determination of gas stream moisture content (EPA Method 4).

Routine adjustment to the sampling rate were performed to provide a gas sample velocity through the probe nozzle nominally equal to the velocity of the gas stream being sampled, based on multi-point measurements of the gas stream differential pressure and temperature. The sample gas was passed through a heated glass probe liner and Pall Gelman "Pallflex" Type TX40HI45 Teflon-coated binderless borosilicate glass fiber mat filter, maintained at a temperature of 248 \pm 25 °F. This filter media, exhibiting at least 99.95 percent filtration efficiency on 0.3 μ m particles in accordance with ASTM Method D-2986-71 as demonstrated by the manufacturer, served to collect the filterable particulate matter sample.

At the conclusion of sampling for each test run, the filterable, or "front-half", particulate sample was recovered from the sampling train by brushing and rinsing the internal surfaces of the nozzle, probe, and "front-half" connecting glassware with acetone into a storage container, and by quantitatively transferring the sample filter and filtered material into a separate container. The amount of filterable particulate matter recovered by the brushings and acetone rinsings of these "front-half" components was determined by quantitatively transferring the acetone solvent and particulate sample into an evaporating container tared to a constant weight, and by evaporating the water solvent to dryness. The evaporating container and the filter from each test run were each desiccated for a minimum of 24 hours, weighed to a constant weight, and the results reported to the nearest 0.1 milligram. A blank of the acetone solvent used was analyzed in the same manner, with the results of this blank analysis used to correct the sample results. The net weight of filterable particulate matter collected by the sampling train as determined from these weighings, after blank corrections, was related to the measured dry standard volume of sample gas pulled through the sampling train, to calculate the emission concentration of filterable particulate matter in the source gas stream.

For collection of condensable (i.e., non-filterable) particulate matter (CPM) and the water vapor (moisture) in the sample gas stream, the filtered gas sample was then passed through a condenser (circulating water at approximately 85 °F), then a water dropout impinger followed by a series of Greenburg-Smith impingers (modified by removal of the standard orifice tip), charged in the following manner:

Impinger No. 1: dry (water drop out impinger)

Impinger No. 2: dry (modified Greenburg-Smith impinger)

Impinger No. 3: 100 mL water (modified Greenburg-Smith impinger)

Impinger No. 4: at least 250 g silica gel desiccant

The first and second impingers were placed in a water bath, maintained at approximately 85°F by an electric heater. Between the second and third impinger was a nonreactive, non-disintegrating polymer filter with inorganic binder, having 99.95 percent (less than 0.05 percent penetration) on 0.3 micrometer dioctyl phthalate particles. A thermocouple was placed in the gas stream of this filter, and the water bath temperature was varied to ensure this temperature remained as close as feasible to 85°F for the duration of sampling.

During sampling, the third and fourth impingers were immersed in an ice bath, providing an impinger outlet temperature of 68° or less, in order to effect efficient condensation and collection of water vapor in the sample gas as well as condensable particulate matter. At the conclusion of sampling, the volume or mass gain of the impinger contents was measured to determine the amount of condensate collected. The water vapor content of the source gas stream was calculated from the measurement of condensate collected and from data for the volume of dry gas sample that passes through the dry gas meter in the sampling system over the test run period, corrected to standard conditions.

At the conclusion of sampling, a nitrogen purge was performed as described in Method 202, to remove any purgeable SO₃ from the impinger train. The aqueous contents of the first two dry impingers was quantitatively recovered, along with water rinsings of these impingers and connecting glassware and the front half of the CPM filter performed at least twice. The water rinses of the impingers and connecting glassware were followed by at least two rinses with hexane, with these rinses stored in a separate sample container. The final volume of the rinses for each test run was made nominally consistent between test runs, and a blank of the hexane at the same consistent volume was prepared. The CPM filter was transferred into a petri dish for transportation and storage prior to analysis. These sample components were used to determine the amount of CPM collected.

The CPM collected by the filter was recovered by extraction with water (extract is added to the water rinses from the impingers and glassware) and hexane (extract is added to the hexane rinses from the impingers and glassware) in a sonicating bath. This procedure is repeated for a total of three water and three hexane extractions. The organic condensable fraction was separated from the aqueous sample recovered from the impingers and rinsings, by three hexane extractions using a 1000-mL separatory funnel. The first extraction was performed by adding the hexane sample component (from sample recovery impinger rinses) to the aqueous sample component in the separatory funnel. After mixing and allowing the aqueous and organic phases to fully separate, most of the hexane organic phase was drained off and retained. This extraction procedure was repeated twice more with fresh hexane, each time leaving a small amount of hexane organic phase in the separatory funnel to ensure that none of the water is drained off. The total of the hexane organic extracts was placed into an evaporating container tared to a constant weight, evaporated to dryness at room temperature and pressure in a laboratory hood, and then desiccated for a minimum of 24 hours and weighed to a constant weight, with the results reported to the nearest 0.1 mg. The hexane blank was analyzed in the same manner. The net weight of this material represents the non-filterable, organic condensable particulate matter collected, and, after blank correction, was related to the measured dry standard volume of sample gas pulled through the sampling train, to calculate the emission concentration of condensable particulate matter in the source gas stream.

To determine the mass of the condensable inorganic fraction collected, the aqueous sample after completion of the extraction was placed into a separate evaporating container tared to a constant weight. This aqueous solution was evaporated under heat, up to 105°C in an oven, to near dryness, air dried at ambient temperature, and then desiccated for a minimum of 24 hours and weighed to a constant weight, with the results reported to the nearest 0.1 mg. The water blank was analyzed in the same manner. This weight of inorganic condensable particulate matter sample was related to the measured dry standard volume of sample gas pulled through the sampling train, to calculate the emission concentration of inorganic condensable particulate matter in the source gas stream.

Finally, the volume of liquid collected in the impingers located downstream of the dry impinger was measured to allow for determination of gas stream moisture content (EPA Method 4).

3.2.1 Gas Stream Velocity and Moisture

Gas stream flow rate and moisture were determined during each test run. In conjunction with each test run, gas stream velocity and temperature measurements were recorded in order to set the isokinetic sampling rate or velocity measurement and for determination of exhaust gas flowrate. Velocity is measured at each traverse point using an

"S"-Type pitot tube connected to an inclined water manometer as specified in Method 2. The temperature profile of the gas stream was obtained by taking readings using a calibrated thermocouple concurrent with the velocity head measurements.

Stack gas moisture was measured in accordance with the EPA Method 4, "Determination of Moisture Content in Stack Gases", 40 CFR 60, Appendix A. In this procedure a known volume of stack gas is extracted at a fixed flow rate through a series of impinger condensers and silica gel and the resultant condensate is measured to determine the percent moisture in the gas stream prior to sample recovery, the volume of liquid collected in the impingers is quantified to allow for determination of gas stream moisture content (EPA Method 4).

3.3 Instrumental (non-FTIR) Methods

Emission gas was withdrawn from each RTO exhaust and transported to the AECOM GEMS 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 O₂ and CO₂ as well as NO_x and CO 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 CO₂ 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, 7E, 10, and 25A. Only EPA Traceability Protocol gases or certified pure zero nitrogen and air gases were used for calibration.

For the O₂ and CO₂ as well as NO_x and CO measurements, 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 (i.e., instrument 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 measurements, 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 ±5% of the calibration gas standard 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.

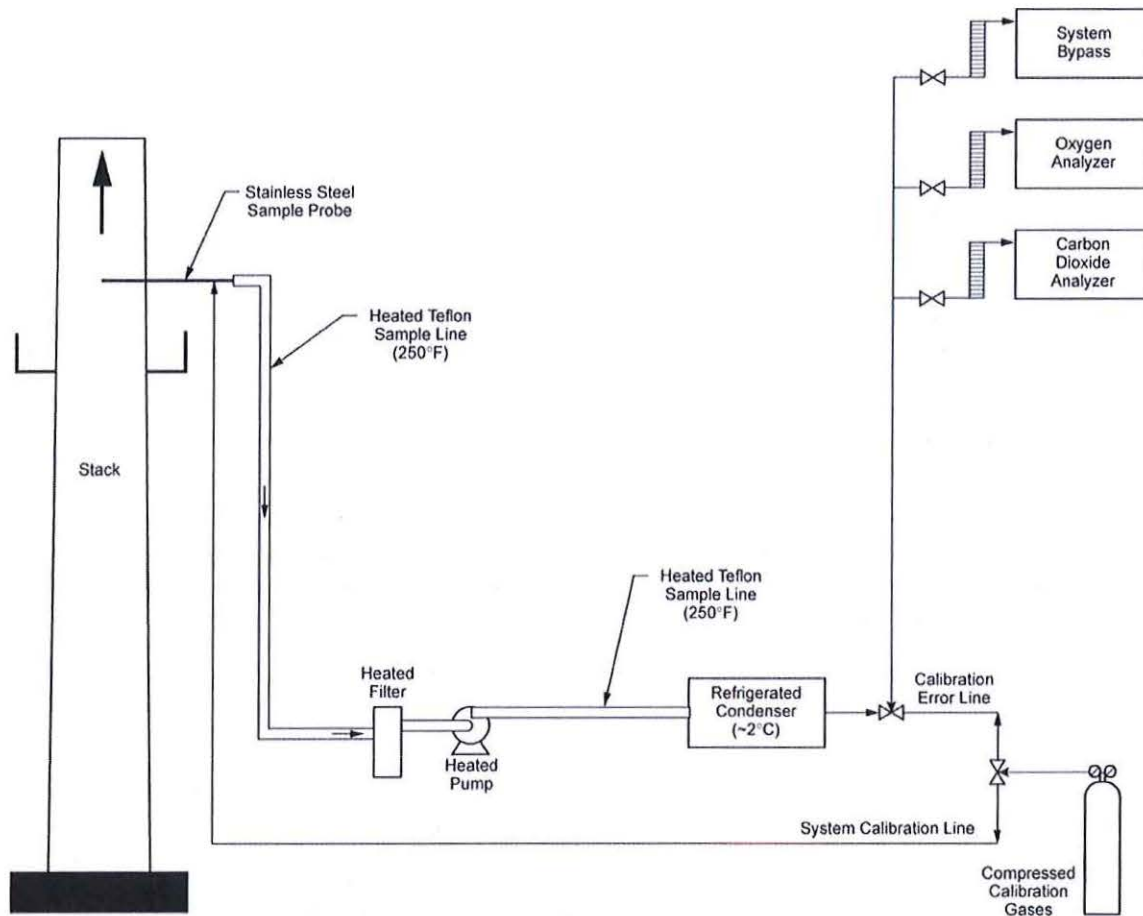
A system response time test for each parameter was performed and documented.

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

3.3.1 EPA Method 3A (O₂/CO₂)

AECOM used a Servomex Model 1440 analyzer to measure O₂ and CO₂ 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:\WA85A\YGRAPHICS\Figures\CEMS System_G_Youngeman_CEMS System_Schematic Full System

3.4 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.

3.4.1 Analyte Spiking System

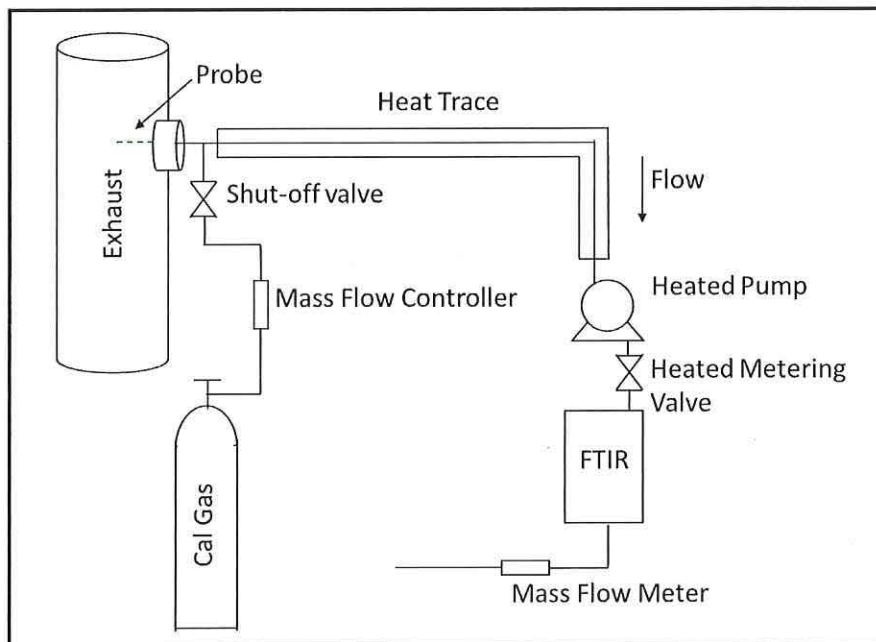
Precise volumes of the analyte gas standards were delivered into the extracted stack gas (system recovery checks). Since the injected standard flow was low compared to the extracted sample flow (maximum of 10% of total extracted flow), the sample gas matrix (including interferences) was not significantly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

Figure 3-2 FTIR Sample System



Note: This figure shows a typical configuration for the test. The heated pump was placed between the sample line and the FTIR analyzer, inducing positive pressure inside the instrument.

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.

3.4.2 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

Compound Monitored	Test Methodology
Formic Acid	EPA Method 320/ASTM
Ammonia	EPA Method 320/ASTM
Formaldehyde	EPA Method 320/ASTM
Methanol	EPA Method 320/ASTM
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 4.7.4.

4. QAQC

A very important aspect of pre-sampling preparations and post sampling checks is the inspection and calibration of all mechanical and electronic equipment planned to be used for the field effort. Equipment is inspected for proper operation and durability prior to calibration. Calibration of equipment is conducted in accordance with the procedures outlined in the EPA document entitled "Quality Assurance Handbook for Air Pollution Measurement Systems; Volume III—Stationary Source Specific Methods" (EPA/600/R-94/038c, September 1994). Equipment calibration is performed in accordance with EPA guidelines and/or manufacturer's recommendations. Documentation of all calibration records were kept in the project file during the field program and available for inspection by test observers. Recommended practices from the QA Handbook for field equipment that were used during this program, as needed, and specific calibration procedures performed by AECOM are listed below.

4.1 Pitot Tubes

[QA Handbook Section 3.1.2, pp. 1-13 - measured for appropriate spacing and dimensions or calibrate in a wind tunnel. Rejection criteria are given on the calibration sheet. Post-test check - inspect for damage.] Each S-type stainless steel Pitot tube used is designed to meet geometric configurations as defined in EPA Method 2.

4.2 Thermocouples

[QA Handbook Section 3.4.2, pp. 15-18 - verify against a mercury-in-glass thermometer at two or more points including the anticipated measurement range. Acceptance limits - impinger $\pm 2^\circ\text{F}$; DGM $\pm 5.4^\circ\text{F}$; stack ± 1.5 percent of stack temperature.] The Type K thermocouples in each meter control box, heated sample box, impinger umbilical connector, XAD resin trap and sample probe are calibrated against ASTM mercury-in-glass thermometers at two or more points: an ice bath, ambient temperature, and a boiling water bath.

4.3 Dry Gas Meters

[QA Handbook Section 3.4.2, pp. 1-12 - calibrate against a wet test meter or calibrated orifice. Acceptance criteria - pretest $Y_i = Y \pm 0.02$; post-test $Y = \pm 0.05 Y_i$.] Dry gas meters for all sampling trains are calibrated using critical orifices. The procedure entails four runs using four separate critical orifices running at an actual vacuum 1-2 in. greater than the theoretical critical vacuum. The minimum sample volume required per orifice is 5 ft³. Meter boxes are calibrated annually and then verified by use of the alternative EPA Method 5 post-test calibration procedure. This procedure is based on the principles of the optional pretest orifice meter coefficient check outlined in Section 4.4.1 of EPA Method 5. The average Y-value obtained by this method must be within 5% of the initial Y-value.

4.4 Field Balance

The analytical balance used in the field to determine initial and final silica gel weights is calibrated against Class M weights provided by the Mettler Corporation.

4.5 Field Barometer

[QA Handbook Section 3.4.2, pp. 18-19 - compare against a mercury-in-glass barometer or use Airport Station BP and correct for elevation. Acceptance criteria - ± 0.02 in. Hg; post-test check - same.] In the absence of pressure readings from an onsite laboratory or other weather station, BP readings were obtained from the closest airport and corrected for elevation (-0.10 in. Hg per 100-ft of elevation increase as per Section 6.1.2 of EPA Method 5).

4.6 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 O₂/CO₂ 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 ₂ or CO ₂)
		Mid-range gas within $\pm 2.0\%$ of calibration span (or $\pm 0.5\%$ for O ₂ or CO ₂)
		Zero gas within $\pm 2.0\%$ of calibration span (or $\pm 0.5\%$ for O ₂ or CO ₂)
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 ₂ or CO ₂)
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 ₂ or CO ₂)
		Zero gas within $\pm 3.0\%$ of calibration span of pre-test reading (or $\pm 0.5\%$ for O ₂ or CO ₂)
	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

4.7 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.

4.7.1 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.

4.7.2 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.

4.7.3 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⁻¹ 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 H₂O absorption peak which was injected by leaking air and N₂ 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.

Table 4-2 Line Position and Resolution Checks

Source	Description	Pre-Test Line Position (cm ⁻¹)	Difference (cm ⁻¹)	Set Resolution (cm ⁻¹)	Actual Resolution (cm ⁻¹)
RTO1875	Pre-Test	3920.0910	0.0013	0.5	0.4979
	Post-Test	3920.0923		0.5	0.4988
RTO1875	Pre-Test	3920.0923	0.0010	0.5	0.4988
	Post-Test	3920.0913		0.5	0.4699

Note: Passing criterion is line position stability within 15% of the resolution (.075cm⁻¹). For resolution, criteria are not defined but stability and reference match are demonstrated here.

4.7.4 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 (SF₆) was the tracer used in the system recovery checks. After the cell was sufficiently

purged with the Formaldehyde/SF₆ standard, the analysis method returned values for SF₆ and Formaldehyde that were then compared to the certified cylinder values (SF₆_{cylinder} & Formaldehyde_{cylinder}). Upon direct injection of the certified Formaldehyde/ SF₆ standard into the FTIR sample cell, the SF₆ and the Formaldehyde concentrations read from the FTIR compared within acceptable criterion for reactive gases to the cylinder certified values as listed in **Table 4-5** below.

Table 4-3 FTIR QA Analytical Direct Injections

Analyte	DI Measurement Result (ppm)	Certified Concentration (ppm)	Relative % Difference	Pass/Fail	Cylinder
Ethylene	10.18	10.21	0.3	Pass	CTS
R22	10.06	10.32	2.5	Pass	
Formic Acid	17.11	18.81	9.0	Pass	Analyte 1
SF ₆	10.44	10.16	2.8	Pass	
Ammonia	27.85	29.34	5.1	Pass	Analyte 2
R23	28.92	30.5	5.2	Pass	
Formaldehyde	14.00	15.82	1.82ppm	Pass	Analyte 3
SF ₆	8.42	7.99	5.3	Pass	
Methanol	30.88	30.11	2.6	Pass	Analyte 4
SF ₆	9.76	10.21	4.4	Pass	

Note: R23 is the tracer gas in all cylinders except for R22 in CTS, all present at different concentrations

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/SF₆ 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 (SF₆_{sample}) which represents the concentration of SF₆ diluted by the stack effluent. From the SF₆ concentrations the dilution factor (DF) can be determined by dividing the SF₆_{sample} by the SF₆_{cylinder}.

The expected concentration of Formaldehyde (HCHO_{Theoretical}) is the sum of diluted cylinder concentration (spiked) and the native stack concentration (also diluted by the injected spike) and was calculated as follows:

$$HCHO_{Theoretical} = \left(\frac{SF6_{sample}}{SF6_{cylinder}}\right)(HCHO_{cylinder}) + \left[1 - \left(\frac{SF6_{sample}}{SF6_{cylinder}}\right)\right](HCHO_{stack})$$

Where:

- HCHO_{Theoretical} = Theoretical HCHO concentration (ppm);
- SF₆_{sample} = SF₆ concentration (ppm) as seen by the FTIR during QA spiking;
- SF₆_{cylinder} = SF₆ concentration observed during the direct inject;
- HCHO_{cylinder} = HCHO concentration observed during the direct inject; and
- HCHO_{stack} = 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 71 – 115%.

Table 4-4 FTIR QA Analytical Spiking Recoveries

Source	Analyte	Spike #	Native Analyte	Tracer Spike (ppmv)	Analyte Spike (ppmv)	Expected Spike (ppmv)	Percent Recovery (%)	Comment
RTO1875	Formic Acid	Pretest #1	BDL (0.0)	0.638	1.124	1.045	107	Pass
		Pretest #2	BDL (0.0)	0.796	0.930	1.305	71	Pass
		Posttest #1	BDL (0.0)	0.992	1.218	1.626	75	Pass
		Posttest #2	BDL (0.0)	0.934	1.191	1.530	78	Pass
	Ammonia	Pretest #1	2.844	2.631	3.415	3.746	92	Pass
		Pretest #2	2.844	0.126	2.800	3.747	74	Pass
		Posttest #1	2.844	1.710	3.883	4.334	90	Pass
		Posttest #2	2.844	2.197	4.016	4.771	84	Pass
	Formaldehyde	Pretest #1	0.440	0.674	1.603	1.526	105	Pass
		Pretest #2	0.440	0.284	0.801	0.898	89	Pass
		Posttest #1	0.77	0.275	1.149	1.202	96	Pass
		Posttest #2	0.77	0.746	1.955	1.942	101	Pass
	Methanol	Pretest #1	2.73	0.776	4.423	4.967	89	Pass
		Pretest #2	2.73	0.678	4.551	4.686	97	Pass
		Posttest #1	4.141	0.337	4.834	5.066	96	Pass
		Posttest #2	4.141	0.691	5.649	6.036	94	Pass
RTO1870	Formic Acid	Pretest #1	BDL (0.0)	0.800	1.080	1.403	77	Pass
		Pretest #2	BDL (0.0)	0.763	1.246	1.343	93	Pass
		Posttest #1	BDL (0.0)	0.878	1.119	1.439	78	Pass
		Posttest #2	BDL (0.0)	0.680	1.010	1.115	91	Pass
	Ammonia	Pretest #1	4.61	2.388	5.398	6.561	82	Pass
		Pretest #2	4.61	2.062	5.534	6.289	88	Pass
		Posttest #1	3.9	1.265	4.071	4.945	82	Pass
		Posttest #2	3.9	1.317	4.198	4.989	84	Pass
	Formaldehyde	Pretest #1	0.54	0.336	0.839	1.078	78	Pass
		Pretest #2	0.54	0.556	1.229	1.429	86	Pass
		Posttest #1	0.81	0.569	1.985	1.702	117	Pass
		Posttest #2	0.81	0.710	2.158	1.923	112	Pass
	Methanol	Pretest #1	3.97	0.357	4.948	4.954	100	Pass
		Pretest #2	3.97	0.430	5.275	5.156	102	Pass
		Posttest #1	3.97	0.784	6.897	6.131	112	Pass
		Posttest #2	3.97	0.655	6.627	5.775	115	Pass

Note: Results are on a wet basis, uncorrected for O2 concentration.

4.7.5 QC System Stability and System Zero

Method 320 requires a system stability check before testing, between each run and at the end of the day or the end of the test per each source. This was accomplished by direct injection of the calibration transfer standard (CTS) into the FTIR cell. The quantified concentrations of the CTS component, (C2H4) for this test, were directly compared. If the quantified concentration varies by more than ±5% from the certified value, it is indicative of an unstable system. All the CTS stability checks were within ±5% of the certified concentration and are presented in **Table 4-7**.

Table 4-5 Calibration Transfer Standard Stability Results

Source	Description	Ethylene Result (ppm)	Direct Inject Ethylene Concentration (ppm)	Relative % Difference	Comments
RTO1875	Pre-Test	10.36	10.18	1.8	Pass
	Post-Run1	10.36		1.8	Pass
	Post-Run2	10.17		0.1	Pass
	Post-Run3	10.66		4.7	Pass
RTO1870	Pre-Test	10.6		4.1	Pass
	Post-Run1	10.18		0.0	Pass
	Post-Run2	10.13		0.5	Pass
	Post-Run3	10.04		1.4	Pass

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.

4.7.6 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.

4.7.7 Deviations from the US EPA Method 320 Procedures

There were no deviations.

4.7.8 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.

4.7.9 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.