

MI-ROP-A4043-2019b Permit and MON MACT,
§63.2505(a)(1)(i)(A) & §63.2505(a)(1)(i)(C),
CEMS QA Performance Specification Test

Dow Silicones Corporation
Determination of Operating Limits to Comply
with Renewable Operating Permit
Requirements

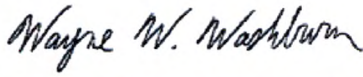
Thermal Heat-Recovery Oxidation (THROX)
Unit, Building 2512

Dow Silicones Corporation
Midland, Michigan

Test Date(s): October 23. 2024

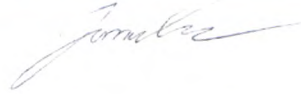
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1. Introduction

1.1 Background

Dow Silicones Corporation, a subsidiary of the Dow Chemical Company (Dow), operates a chemical manufacturing facility within the Dow Silicones Corporation complex in Midland, MI. The facility uses a thermal oxidizer with a caustic scrubber and two ionizing wet scrubbers (IWS) in Building 2512, which is referred to as the 2512 thermal heat recovery oxidation (THROX) unit, to control emissions from processes at multiple chemical production facilities at the site. The typical heat input rate to the THROX is approximately 28 million British thermal units per hour (MMBtu/hr). The permitted maximum operating rate for the THROX is 95 MMBtu/hr. The production operating rate for this test was >30 MMBtu/hr, which was the maximum achievable rate under normal process operations.

The exhaust duct for the gas stream emanating from the 2512 THROX treatment system has historically included a continuous emission monitoring system (CEMS) that continuously measures stack gas concentrations of nitrogen oxides (NO_x), carbon dioxide (CO₂), oxygen (O₂), and total hydrocarbons (THC) as well as a continuous emission rate monitoring system (CERMS) that continuously measures stack gas pollutant mass emission rates. In the third quarter of 2023, two sets (System A and System B) of Hydrogen Chloride (HCl) and Chlorine (Cl₂) CEMS were installed along with a set of additional new redundant monitors for the existing NO_x, O₂, CO₂, and THC CEMS as well as the existing emission rate CERMS.

The CEMS are extractive-type systems that each consist of three subsystems: 1) an extractive sample acquisition/conditioning system, 2) analyzers (NO_x, CO₂, O₂, HCl, Cl₂, and THC), and 3) a programmable logic controller (PLC). The CEMS/CERMS are required to meet the parameter specific performance specifications annually.

Dow uses CEMS and CERMS to demonstrate compliance with the requirements outlined in the Renewable Operating Permit (MI-ROP-A4043-2019b) as well as the MON MACT standards detailed in 40 CFR Part 63, namely §63.2505(a)(1)(i)(A) & §63.2505(a)(1)(i)(C). Each exhaust stack CEMS employs an exhaust gas volumetric flow rate monitor as part of the associated CERMS, which allows the measured concentrations of the CEMS to be equated to mass emission rates expressed in units of pounds per hour (lb/hr) and tons per year (ton/yr).

1.2 Overview of the Test Program

AECOM was retained to conduct a periodic (i.e., annual) quality assurance (QA) relative accuracy test audit (RATA) on the redundant System A and System B CEMS/CERMS that serve the Building 2512 THROX unit.

The RATA was conducted on October 23, 2024. All CEMS/CERMS RATAs were performed according to the procedures detailed in 40 CFR Part 60, Appendix B, Performance Specifications (PS) 2, 3, 6, 8, and 18 for NO_x/Cl₂, O₂/CO₂, emission rate, THC, and HCl, respectively. As of February 4, 2021 the Environmental Protection agency (EPA) has granted Dow approval to utilize PS 2 for Cl₂ measurement, this approval letter is include as Appendix F to this report. Emission concentrations of O₂/CO₂, NO_x, THC, Cl₂, and HCl were measured in accordance with US EPA reference methods (RMs) 3A, 7E, 25A, 26A, and 320, respectively. For the CEMS RATA, HCl was measured in accordance with RM 320. Exhaust gas volumetric flow rate measurements were determined in accordance with RMs 1 through 4 for subsequent calculation of mass emission rates from measured exhaust gas concentrations.

The following table summarizes the pertinent source information for this emissions compliance performance test:

Responsible Groups	• The Dow Chemical Company • Michigan Department of Environment, Great Lakes, and Energy (EGLE) • United States Environmental Protection Agency (US EPA)
Applicable Regulations	• Permit: MI-ROP-A4043-2019b • MON MACT (40 CFR 63, Subpart FFFF) • 40CFR60, App. B, Performance Specifications (PS) 2, 3, 6, 8, and 18.
Industry / Plant	• Dow Silicones – Thermal Heat Recovery Oxidation (THROX) Unit
Plant Location	• The Dow Chemical Company Dow Silicones Corporation Midland, Michigan 48667
Unit Initial Start-up	• 2003
Date of Last Performance Test	• October 2023
Air Pollution Control Equipment	• THROX • Caustic Scrubber • Two Ionizing Wet Scrubbers (IWS)
Emission Points	• Building 2512 THROX
Pollutants/Diluents Monitored/Tested	• Oxygen (O₂) • Carbon Dioxide (CO₂) • Nitrogen Oxides (NO_x) • Carbon Monoxide (CO) • Total Hydrocarbons (THC) • Chlorine (Cl₂) • Hydrogen Chloride (HCl)
Test Date(s) (CEMS RATA)	• October 23, 2024

1.3 Key Personnel

The contact for the source and test report is:

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Names and affiliations of personnel, including their roles in the test program, are summarized in the following table.

Role	Role Description	Name	Affiliation
Process Focal Point	- Coordinate plant operation during test - Ensure the unit is operating at the agreed upon conditions in the test plan - Collect any process data and provide all technical support related to process operation	Brandon Krieger	Dow
Environmental Focal Point	Ensure all regulatory requirements and citations are reviewed and considered for the testing	Sarah Maki	Dow
Test Plan Coordinator Back-up	- Leadership of the sampling program - Develop the overall testing plan - Determine the correct sample methods - Completes technical review of test data	Chuck Glenn Air Sample SME	Dow
Process Analyzer	Conducts all other QA testing and provides records for 7-day drift tests, response time tests, CGAs, etc.	Stephanie Moreno	Dow
Technical Reviewer	Completes technical review of test data	Wayne Washburn	AECOM
Field Team Leader	Ensures field sampling meets quality assurance objectives of plan	Peter Becker	AECOM
Test Project Manager	Ensures data generated meets the quality assurance objectives of the plan	James Edmister	AECOM

1.4 Executive Summary

Results summaries for redundant System A CEMS RATA and System B CEMS RATA are presented in **Table 1-1** and **Table 1-2**, respectively.

The accuracy results indicate that the O₂/CO₂, NO_x, THC, and HCl/Cl₂ CEMS and the flow rate CERMS for both System A and System B were operating within the required accuracy criteria, as applicable. In addition, flow rate measured by the original CEMS monitor (manufactured by Sick) and System A NO_x mass emission rates (lb/hr) calculated using Sick flow rates were evaluated for relative accuracy and are operating within the required accuracy criteria.

Relative accuracy results were calculated for O₂ and CO₂ in units of percent by volume on a dry basis (%vd), for NO_x and HCl in mass emission rate units of pounds per hour (lb/hr), for THC, Cl₂, and HCl in units of parts per million by volume on a wet basis (ppmvw, as measured), and for exhaust gas volumetric flow rate in units of standard cubic feet per minute (scfm, wet basis) for the Systems A and B CERMS and in units of dry standard cubic feet per minute (dscfm) for the Sick flow monitor. The results of the RATA indicate that each 2512 THROX new 2023 CEMS/CERMS and the original Sick flow monitor have passed under the performance specification QA requirements for annual periodic certification.

The remainder of this document is organized as follows. **Section 2** of this document provides a summary and discussion of results for the RATA; **Section 3** provides a description of the flue gas monitoring sample port locations and the facility CEMS system; **Section 4** describes the test procedures that were followed and a description of AECOM's portable instrumental analyzer laboratory; **Section 5** describes the Quality Assurance/Quality control measures for the test program; and **Section 6** describes how the data reduction was performed.

Test program participants included: Peter Becker, Quincy Crawford, James Edmister, Erik Drake, and Ignacio Gallardo from AECOM; as well as Brandon Krieger and Sarah Maki from Dow.

Additional information is contained in the Appendices as follows: **Appendix A** provides Reference Method (RM) Emissions Data from AECOM's test activities during the test program, **Appendix B** contains Facility CEMS Data for the RATA and supporting process operating documentation, **Appendix C** contains RM Quality Assurance Data, including Manual Equipment Calibrations and instrumental analyzer Calibration Error Tests, System Bias and Drift Checks, System Response Times, Gas Cylinder Certification Sheets, and QSTI Certificates (as applicable), and **Appendix D** contains the Test Protocol.

Table 1-1 Relative Accuracy Summary of Results – 2512 THROX System A

Monitoring System	Parameter (Reporting Tag)	RA Result	Relative Accuracy Criteria – Part 60	Pass / Fail ¹
System A CEMS	O ₂ percent, dry (O ₂ %)	0.4% of RM 0.04% O ₂	≤20.0% of RM (PS 3) ² ≤1.0% O ₂ (PS 3) ²	Pass
	CO ₂ percent, dry (CO ₂ %)	2.8% of RM 0.12% CO ₂	≤20.0% of RM (PS 3) ² ≤1.0% CO ₂ (PS 3) ²	Pass
	NO _x lb/hr (NO _x lb/hr)	11.2% of RM 4.6% of ES	≤20% of RM (PS 2) ³ ≤10% of ES (PS 2) ³	Pass
	NO _x lb/hr (NO _x lb/hr – Sick Flow)	21.3% of RM 8.5% of ES	≤20% of RM (PS 2) ³ ≤10% of ES (PS 2) ³	Pass
	THC ppmv, wet (THC ppm)	90.0% of RM 1.3% of ES	≤20% of RM (PS 8) ³ ≤10% of ES (PS 8) ³	Pass
	THC lb/hr (THC lb/hr)	102.1% of RM 0.3% of ES	≤20% of RM (PS 8) ³ ≤10% of ES (PS 8) ³	Pass
	Cl ₂ ppmv, wet (Cl ₂ ppm)	136.2% of RM 1.3% of ES	≤20% of RM (PS 2) ³ ≤10% of ES (PS 2) ³	Pass
	HCl ppmv, wet (HCl ppm)	30.8% of RM 0.2% of ES	≤20% of RM (PS 18) ⁴ ≤10% of ES (PS 18) ⁴	Pass
System A CERMS	Gas Flow Rate, scfm (wet) (Exhaust Flow, SCFM)	1.4% of RM	≤20% of RM (PS 6) ⁵	Pass
	Gas Flow Rate, dscfm (Sick Flow, DSCFM)	10.9% of RM	≤20% of RM (PS 6) ⁵	Pass

1. To meet Performance Specification (PS) requirements for relative accuracy (RA), a CEMS or CERMS monitor need only pass the least restrictive of the performance criteria as specified in the regulations under Part 60, Appendix B.
2. Part 60 RA results for O₂ or CO₂ under PS 3 must be either no greater than 20.0% of the average reference method (RM) value or no greater than 1.0% O₂ or CO₂ by difference.
3. Part 60 RA results for NO_x under PS 2 and for THC under PS 8 must be either no greater than 20% of RM value or 10% of the emission standard (ES), otherwise known as the permit limit, if applicable. Note: there is no applicable permit limit for NO_x concentrations measured in units of ppm. The MON MACT emission standard for TOC is 20 ppmv. The CEMS Cl₂ monitor is not regulated under US EPA Part 60; however, PS 2 criteria are used to evaluate Cl₂ RA in accord with Michigan EGLE guidelines.
4. Part 60 RA results for HCl under PS 18 must be either no greater than 20% of the average reference method (RM) value or 15% of 75 percent of the emission standard (ES), otherwise known as the permit limit.
5. Part 60 RA results for CERMS under PS 6 must be no greater than 20% of RM for monitored pollutant mass emission rates. RA for exhaust gas volumetric flow rate monitors is not required to be evaluated by US EPA but is evaluated as required by Michigan EGLE. There is no specification for relative accuracy of a flow rate monitor by itself within the US EPA Performance Specifications. PS 6 speaks of CERMS and provides specifications for emission rate monitors. Flow rate is a component of a CERMS, and the individual value is not addressed by PS 6. However, in this case, flow monitor RA is used as a surrogate to evaluate CERMS performance.

Table 1-2 Relative Accuracy Summary of Results – 2512 THROX System B

Monitoring System	Parameter (Reporting Tag)	RA Result	Relative Accuracy Criteria – Part 60	Pass / Fail ¹
System B CEMS	O ₂ percent, dry (O ₂ %)	0.9% of RM 0.09% O ₂	≤20.0% of RM (PS 3) ² ≤1.0% O ₂ (PS 3) ²	Pass
	CO ₂ percent, dry (CO ₂ %)	7.0% of RM 0.30% CO ₂	≤20.0% of RM (PS 3) ² ≤1.0% CO ₂ (PS 3) ²	Pass
	NO _x lb/hr (NO _x lb/hr)	12.9% of RM 5.3% of ES	≤20% of RM (PS 2) ³ ≤10% of ES (PS 2) ³	Pass
	THC ppmv, wet (THC ppm)	55.2% of RM 0.8% of ES	≤20% of RM (PS 8) ³ ≤10% of ES (PS 8) ³	Pass
	THC lb/hr (THC lb/hr)	102.1% of RM 0.3% of ES	≤20% of RM (PS 8) ³ ≤10% of ES (PS 8) ³	Pass
	Cl ₂ ppmv, wet (Cl ₂ ppm)	103.1% of RM 0.9% of ES	≤20% of RM (PS 2) ³ ≤10% of ES (PS 2) ³	Pass
	HCl ppmv, wet (HCl ppm)	55.1% of RM 0.3% of ES	≤20% of RM (PS 18) ⁴ ≤10% of ES (PS 18) ⁴	Pass
System B CERMS	Gas Flow Rate, scfm (wet) (Exhaust Flow, SCFM)	4.0% of RM	≤20% of RM (PS 6) ⁵	Pass

1. To meet Performance Specification (PS) requirements for relative accuracy (RA), a CEMS or CERMS monitor need only pass the least restrictive of the performance criteria as specified in the regulations under Part 60, Appendix B.

2. Part 60 RA results for O₂ or CO₂ under PS 3 must be either no greater than 20.0% of the average reference method (RM) value or no greater than 1.0% O₂ or CO₂ by difference.

3. Part 60 RA results for NO_x under PS 2 and for THC under PS 8 must be either no greater than 20% of RM value or 10% of the emission standard (ES), otherwise known as the permit limit, if applicable. Note: there is no applicable permit limit for NO_x concentrations measured in units of ppm. The MON MACT emission standard for TOC is 20 ppmv. The CEMS Cl₂ monitor is not regulated under US EPA Part 60; however, PS 2 criteria are used to evaluate Cl₂ RA in accord with Michigan EGLE guidelines.

4. Part 60 RA results for HCl under PS 18 must be either no greater than 20% of the average reference method (RM) value or 15% of 75 percent of the emission standard (ES), otherwise known as the permit limit.

5. Part 60 RA results for CERMS under PS 6 must be no greater than 20% of RM for monitored pollutant mass emission rates. RA for exhaust gas volumetric flow rate monitors is not required to be evaluated by US EPA but is evaluated as required by Michigan EGLE. There is no specification for relative accuracy of a flow rate monitor by itself within the US EPA Performance Specifications. PS 6 speaks of CERMS and provides specifications for emission rate monitors. Flow rate is a component of a CERMS, and the individual value is not addressed by PS 6. However, in this case, flow monitor RA is used as a surrogate to evaluate CERMS performance.

2. Summary and Discussion of Results

The purpose of this CEMS Performance Specification Test (PST) was to demonstrate compliance with US EPA's Regulations for the 2512 THROX CEMS O₂, CO₂, NO_x, THC, Cl₂, and HCl monitors and CERMS exhaust gas volumetric flow rate monitors performance at the Dow Michigan Operations (MiOps) Incineration Complex in Midland, Michigan. The specific objectives were:

- Determine the relative accuracy of the redundant System A and System B 2512 THROX O₂, CO₂, NO_x, THC, Cl₂, and HCl CEMS and exhaust gas flow rate CERMS on the stack outlet for the annual periodic PST certification.
- Determine the relative accuracy of the original 2512 THROX CERMS Sick flow rate monitor and the System A NO_x CEMS mass emission rates (lb/hr) calculated using the Sick monitor exhaust gas flow rate CERMS.

During these performance tests, the process was operated at a minimum THROX heat input rate of 30 MMBtu/hr as representative of maximum normal operating rates in accordance with the air permit and performance test plan guidelines. Summaries of the results for the Performance Specification Test of the 2512 THROX CEMS and CERMS monitors are presented below. This section summarizes and discusses the results of the PST QA test RATA along with the associated process operating data.

2.1 Relative Accuracy Test Results – 2512 THROX CEMS/CERMS

Relative accuracy testing was conducted by AECOM using the instrumental analyzer procedures detailed in 40 CFR 60, Appendix A, Reference Methods (RM) 3A, 7E, 25A, 26A, and 320 for O₂/CO₂, NO_x, THC, Cl₂, and HCl, respectively. In addition, relative accuracy testing was conducted by AECOM using the source emissions testing procedures detailed in 40 CFR 60, Appendix A, Reference Methods (RM) 2, 3A, and 4 for exhaust gas velocity, O₂/CO₂, and moisture, respectively, that were used to calculate reference method exhaust gas volumetric rate. The instrumental analysis and source emissions test results are referred to as the Reference Method Results.

The results of the RATA program for the facility CEMS and CERMS monitors are presented in **Table 2-1** for O₂ measured as percent by volume on a dry basis (%vd), in **Table 2-2** for CO₂ measured as percent by volume on a dry basis (%vd), in **Table 2-3** for NO_x measured as pounds per hour (lb/hr), in **Table 2-4** for THC measured as parts per million by volume on a wet basis (ppmvw) and as pounds per hour (lb/hr), in **Table 2-5** for Cl₂ measured as parts per million by volume on a wet basis (ppmvw), in **Table 2-6** for HCl measured as parts per million by volume on a wet basis (ppmvw), and in **Table 2-7** for flow rate measured as standard cubic feet per minute on a wet basis (scfm). In addition, primary process operating parameters for the RATA are presented in **Table 2-8** with the full list of the recorded process parameters itemized in **Table 2-9** and included in **Appendix B**. AECOM field data and calculations are presented in **Appendix A**. Facility CEMS test data and process data corresponding to the RM test run times are presented in **Appendix B**.

The 2512 THROX redundant System A and System B CEMS/CERMS NO_x/Cl₂, O₂/CO₂, flow rate, THC, and HCl monitors and the Sick CERMS, as applicable, passed the RA criteria in PS 2, PS 3, PS 6, PS 8, and PS 18, respectively.

Table 2-1 Relative Accuracy – 2512 THROX CEMS O₂ (percent by volume, dry), 10/23/2024

Oxygen Relative Accuracy Results									
10/23/2024 Run Time		REFERENCE METHOD	STACK ANALYZERS				ARITHMETIC DIFFERENCE and RATA Calculations		
			THROX-A O2		THROX-B O2		THROX-A O2		THROX-B O2
		Oxygen (% dry)	Oxygen (% dry)	Use of Run ¹	Oxygen (% dry)	Use of Run ¹	Oxygen (% dry)	Use of Run ¹	Oxygen (% dry) Use of Run ¹
RATA Run 1	08:06-08:36	10.98	10.91	x	11.05		-0.07	X	0.07
RATA Run 2	08:48-09:18	10.99	10.92	x	11.06		-0.08	X	0.06
RATA Run 3	09:50-10:20	10.95	10.91		11.03		-0.05		0.08
RATA Run 4	10:30-11:00	10.97	10.89	x	11.05		-0.08	X	0.08
RATA Run 5	11:16-11:46	10.97	10.92		11.06		-0.04		0.10
RATA Run 6	11:55-12:25	11.01	10.96		11.11		-0.05		0.09
RATA Run 7	12:41-13:11	10.97	10.94		11.07		-0.04		0.10
RATA Run 8	13:20-13:50	10.95	10.91		11.04		-0.04		0.09
RATA Run 9	14:10-14:40	10.95	10.91		11.05	x	-0.04		0.10 X
RATA Run 10	14:48-15:18	10.96	10.92		11.06	x	-0.05		0.10 X
RATA Run 11	15:37-16:07	10.89	10.85		11.00	x	-0.04		0.11 X
RATA Run 12	16:14-16:44	10.90	10.85		10.99		-0.05		0.09
Number of Runs Used in Calculation (n)							9		9
Average Difference (d _{AVG})							-0.043		0.086
Standard Deviation (S _d)							0.004		0.013
t-Value (t _{0.975})							2.306		2.306
Confidence Coefficient (CC)							0.003		0.010
Average of Reference Method (RM _{AVG})							10.950		10.966
Relative Accuracy (O ₂) (d _{AVG})							0.04		0.09
Relative Accuracy (% of Reference Method) (RA)							0.4		0.9

¹ An X in this column denotes a run which is not used in calculation of relative accuracy.

ACCEPTANCE CRITERIA

Performance Specification 3 (and 4B)		
Absolute value of difference between mean RM and mean CEMS (% O ₂)	1.0	1.0
Relative Accuracy (% of Reference Method) (RA)	20	20

Table 2-2 Relative Accuracy – 2512 THROX CEMS CO₂ (percent by volume, dry), 10/23/2024

Carbon Dioxide Relative Accuracy Results										
10/23/2024 Run Time		REFERENCE METHOD	STACK ANALYZERS				ARITHMETIC DIFFERENCE and RATA Calculations			
			THROX-A CO2		THROX-B CO2		THROX-A CO2		THROX-B CO2	
		Carbon Dioxide (% dry)	Carbon Dioxide (% dry)	Use of Run ¹	Carbon Dioxide (% dry)	Use of Run ¹	Carbon Dioxide (% dry)	Use of Run ¹	Carbon Dioxide (% dry)	Use of Run ¹
RATA Run 1	08:06-08:36	4.45	4.58		4.77		0.12		0.32	
RATA Run 2	08:48-09:18	4.45	4.56		4.77	x	0.12		0.33	X
RATA Run 3	09:50-10:20	4.43	4.55		4.75	x	0.12		0.32	X
RATA Run 4	10:30-11:00	4.42	4.52		4.71		0.10		0.30	
RATA Run 5	11:16-11:46	4.42	4.53		4.73		0.11		0.31	
RATA Run 6	11:55-12:25	4.42	4.53		4.72		0.11		0.30	
RATA Run 7	12:41-13:11	4.41	4.54	x	4.73	x	0.13	X	0.32	X
RATA Run 8	13:20-13:50	4.42	4.56	x	4.73		0.14	X	0.31	
RATA Run 9	14:10-14:40	4.43	4.56	x	4.72		0.13	X	0.30	
RATA Run 10	14:48-15:18	4.43	4.55		4.71		0.12		0.28	
RATA Run 11	15:37-16:07	4.44	4.57		4.73		0.13		0.29	
RATA Run 12	16:14-16:44	4.44	4.55		4.72		0.11		0.28	
Number of Runs Used in Calculation (n)							9		9	
Average Difference (d _{AVG})							0.118		0.299	
Standard Deviation (S _d)							0.009		0.012	
t-Value (t _{0.975})							2.306		2.306	
Confidence Coefficient (CC)							0.007		0.009	
Average of Reference Method (RM _{AVG})							4.432		4.429	
Relative Accuracy (CO ₂) (d _{AVG})							0.12		0.30	
Relative Accuracy (% of Reference Method) (RA)							2.8		7.0	
¹ An X in this column denotes a run which is not used in calculation of relative accuracy.										

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Absolute value of difference between mean RM and mean CEMS (% CO ₂)	1.0	1.0
Relative Accuracy (% of Reference Method) (RA)	20	20

Table 2-3 Relative Accuracy – 2512 THROX CEMS NOx (lb/hr), 10/23/2024

Nitrogen Oxides Relative Accuracy Results																	
10/23/2024Run Time		REFERENCE METHOD				STACK ANALYZERS						ARITHMETIC DIFFERENCE and RATA					
						THROX-A NOx (lb/hr)		THROX-B NOx (lb/hr)		THROX-A NOx Sick Flow (lb/hr)		THROX-A NOx (lb/hr)		THROX-B NOx (lb/hr)		THROX-A NOx Sick Flow (lb/hr)	
		Flow (dscfm)	Oxygen (%, dry)	Nitrogen Oxides (ppmv dry)	Nitrogen Oxides (lb/hr)	Nitrogen Oxides (lb/hr)	Use of Run ¹	Nitrogen Oxides (lb/hr)	Use of Run ¹	Nitrogen Oxides (lb/hr)	Use of Run ¹	Nitrogen Oxides (lb/hr)	Use of Run ¹	Nitrogen Oxides (lb/hr)	Use of Run ¹	Nitrogen Oxides (lb/hr)	Use of Run ¹
RATA Run 1	08:06-08:36	7,900	10.98	57.7	3.3	2.93		2.88		2.66		-0.34		-0.39		-0.61	
RATA Run 2	08:48-09:18	7,805	10.99	51.0	2.8	2.82		2.81		2.57		-0.03		-0.04		-0.28	
RATA Run 3	09:50-10:20	8,009	10.95	55.9	3.2	2.76	x	2.76	x	2.50		-0.44	X	-0.45	X	-0.71	
RATA Run 4	10:30-11:00	7,971	10.97	56.8	3.2	2.86		2.82		2.57		-0.38		-0.42		-0.67	
RATA Run 5	11:16-11:46	7,860	10.97	57.9	3.3	2.96		2.92		2.67		-0.29		-0.34		-0.59	
RATA Run 6	11:55-12:25	7,917	11.01	58.0	3.3	2.96		2.93		2.67		-0.33		-0.36		-0.62	
RATA Run 7	12:41-13:11	7,867	10.97	60.3	3.4	3.09		3.04		2.76		-0.31		-0.36		-0.64	
RATA Run 8	13:20-13:50	7,906	10.95	59.1	3.3	3.04		2.98		2.72		-0.30		-0.37		-0.62	
RATA Run 9	14:10-14:40	8,228	10.95	60.4	3.6	3.12	x	3.09	x	2.80	x	-0.45	X	-0.48	X	-0.76	X
RATA Run 10	14:48-15:18	8,026	10.96	60.6	3.5	3.17		3.12		2.83		-0.32		-0.36		-0.65	
RATA Run 11	15:37-16:07	8,185	10.89	80.9	4.7	3.91	x	3.98	x	3.66	x	-0.83	X	-0.76	X	-1.09	X
RATA Run 12	16:14-16:44	8,073	10.90	74.4	4.3	3.93		3.85		3.51	x	-0.38		-0.45		-0.79	X
Number of Runs Used in Calculation (n)												9		9		9	
Average Difference (d _{AVG})												-0.297		-0.343		-0.598	
Standard Deviation (S _d)												0.106		0.119		0.126	
t-Value (t _{0.975})												2.306		2.306		2.306	
Confidence Coefficient (CC)												0.081		0.092		0.096	
Applicable Standard (or Permit Limit)												8.219		8.219		8.219	
Average of Reference Method (RM _{AVG})												3.382		3.382		3.260	
Relative Accuracy (CO, NO _x , SO ₂ , O ₂ , CO ₂) (d _{AVG} + CC)												0.38		0.43		0.69	
Relative Accuracy (% of Reference Method) (RA)												11.5		12.8		21.2	
Relative Accuracy (% of Permit Limit) (RA)												4.6		5.3		8.5	
^ An X in this column denotes a run which is not used in calculation of relative accuracy.																	
Performance Specification 2																	
Relative Accuracy (% of Reference Method) (RA)												20		20		20	
Relative Accuracy (% of Permit Limit) (RA)												10		10		10	

Table 2-4 Relative Accuracy – 2512 THROX CEMS THC (ppmw and lb/hr), 10/23/2024

Total Hydrocarbon Relative Accuracy Results											
10/23/2024 Run Time		REFERENCE		STACK ANALYZERS				ARITHMETIC DIFFERENCE and RATA Calculations			
		RM 7E THC, wet (ppmw)	RM7E THC (lb/hr)	THROX-A THC (ppm)	THROX-B THC (ppm)	THROX-A THC (lb/hr)	THROX-B THC (lb/hr)	THROX-A THC (ppm)	THROX-B THC (ppm)	THROX-A THC (lb/hr)	THROX-B THC (lb/hr)
				THC Use (ppmw) of Run ¹	THC Use (ppmw) of Run ¹	THC Use (lb/hr) of Run ¹	THC Use (lb/hr) of Run ¹	THC Use (ppmw) of Run ¹	THC Use (ppmw) of Run ¹	THC Use (lb/hr) of Run ¹	THC Use (lb/hr) of Run ¹
RATA Run 1	08:06-08:36	0.27	0.016	0.43	0.23	0.000	0.000	0.16	-0.04	-0.016	-0.016
RATA Run 2	08:48-09:18	0.27	0.016	0.49	0.22	0.000	0.000	0.22	-0.05	-0.016	-0.016
RATA Run 3	09:50-10:20	0.28	0.017	0.50	0.30	0.000	0.000	0.22	0.02	-0.017	-0.017
RATA Run 4	10:30-11:00	0.27	0.016	0.50	0.34	0.000	0.000	0.23	0.07	-0.016	-0.016
RATA Run 5	11:16-11:46	0.27	0.016	0.51	0.41	0.000	0.000	0.24	0.14	-0.016	-0.016
RATA Run 6	11:55-12:25	0.27	0.016	0.51	0.41	0.000	0.000	0.24	0.14	-0.016	-0.016
RATA Run 7	12:41-13:11	0.25	0.015	0.50	0.42	0.000	0.000	0.25	0.17	-0.015	-0.015
RATA Run 8	13:20-13:50	0.27	0.016	0.50	0.47	0.000	0.000	0.23	0.21	-0.016	-0.016
RATA Run 9	14:10-14:40	0.27	0.017	0.59	0.48	x	0.000	0.32	0.21	x	-0.017
RATA Run 10	14:48-15:18	0.27	0.016	0.60	x	0.43	0.000	0.33	x	0.16	-0.016
RATA Run 11	15:37-16:07	0.27	0.017	0.66	x	0.48	0.000	0.39	x	0.21	-0.017
RATA Run 12	16:14-16:44	0.27	0.016	0.69	x	0.49	0.000	0.42	x	0.22	-0.016
Number of Runs Used in Calculation (n)								9	9	12	12
Average Difference (d _{AVG})								0.234	0.090	-0.0162	-0.0162
Standard Deviation (S _d)								0.042	0.095	0.0005	0.0005
t-Value (t _{0.975})								2.306	2.306	2.201	2.201
Confidence Coefficient (CC)								0.032	0.073	0.0003	0.0003
Applicable Standard (or Permit Limit)								20	20	7	7
Average of Reference Method (RM _{AVG})								0.296	0.296	0.0162	0.0162
Relative Accuracy (CO, NO _x , SO ₂ , O ₂ , CO ₂) (d _{AVG} + CC)								0.27	0.16	0.017	0.017
Relative Accuracy (% of Reference Method) (RA)								90.9	95.3	100.1	100.1
Relative Accuracy (% of Permit Limit) (RA)								1.3	0.8	0.3	0.3
¹ An X in this column denotes a run which is not used in calculation of relative accuracy.											
Performance Specification 8											
Relative Accuracy (% of Reference Method) (RA)								20	20	20	20
Relative Accuracy (% of Permit Limit) (RA)								10	10	10	10

Table 2-5 Relative Accuracy – 2512 THROX CERMS Flow Rate (dscfm/scfm), 10/23/2024

		REFERENCE METHOD		STACK ANALYZERS				ARITHMETIC DIFFERENCE							
				THROX Sick Flow (dscfm)		THROX-A Flow (scfm)		THROX-B Flow (scfm)		THROX Sick Flow (dscfm)		THROX-A Flow (scfm)		THROX-B Flow (scfm)	
Run Number	Run Time	Flow (dscfm)	Flow (scfm)	Flow Rate (dscfm)	Use of Run ¹	Flow Rate (scfm)	Use of Run ¹	Flow Rate (scfm)	Use of Run ¹	Flow Rate (dscfm)	Use of Run ¹	Flow Rate (scfm)	Use of Run ¹	Flow Rate (scfm)	Use of Run ¹
Flow Run 1	08:06-08:36	7,900	8,657	7,230		8,794		8,480		-670		137		-178	
Flow Run 2	08:48-09:18	7,805	8,594	7,203		8,739		8,441		-601		145		-153	
Flow Run 3	09:50-10:20	8,009	8,789	7,100		8,642		8,362	x	-909		-147		-427	X
Flow Run 4	10:30-11:00	7,971	8,788	7,137		8,720		8,360	x	-834		-68		-428	X
Flow Run 5	11:16-11:46	7,860	8,613	7,193		8,795	x	8,435		-666		182	X	-179	
Flow Run 6	11:55-12:25	7,917	8,732	7,180		8,789		8,433		-737		57		-299	
Flow Run 7	12:41-13:11	7,867	8,617	7,127		8,751		8,369		-740		134		-247	
Flow Run 8	13:20-13:50	7,906	8,682	7,127		8,761		8,356		-779		80		-325	
Flow Run 9	14:10-14:40	8,228	9,002	7,223		8,809	x	8,479	x	-1,005		-192	X	-523	X
Flow Run 10	14:48-15:18	8,026	8,818	7,223		8,858		8,509		-802		40		-308	
Flow Run 11	15:37-16:07	8,185	8,941	7,243		8,572	x	8,537		-942		-369	X	-404	
Flow Run 12	16:14-16:44	8,073	8,878	7,213		8,863		8,493		-860		-15		-385	
Number of Runs Used in Calculation (n)										12		9		9	
Average Difference (d _{AVG})										-795.4		40.3		-275.4	
Standard Deviation (S _c)										120.9		100.4		91.7	
t-Value (t _{0.975})										2.201		2.306		2.306	
Confidence Coefficient (CC)										76.8		77.2		70.5	
Average of Reference Method (RM _{AVG})										7,978.7		8,728.2		8,725.6	
Relative Accuracy (in dscfm) (d _{AVG} + CC)										872.2		117.4		345.8	
Relative Accuracy (% of Reference Method) (RA)										10.9		1.3		4.0	

¹ An X in this column denotes a run which is not used in calculation of relative accuracy.

¹ An X in this column denotes a run which is not used in calculation of relative accuracy.

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Relative Accuracy (% of Reference Method) (RA)	20
Note: There is no specification for Relative Accuracy of a Flow Monitor by itself within the EPA Performance Specifications. PS6 speaks of CERMS, and provides specifications for emission rate monitors. Flow rate is a component, and the individual value is not addressed.	

Table 2-6 Relative Accuracy – 2512 THROX CEMS Cl₂ (ppmv, wet), 10/23/2024

Chlorine Relative Accuracy Results															
10/23/2024Run Time		REFERENCE METHOD					STACK ANALYZERS				ARITHMETIC DIFFERENCE				
		Measured Moisture and Chlorine (ppm, wet)					THROX-A Cl2 (ppm)		THROX-B Cl2 (ppm)		THROX-A Cl2 (ppm)		THROX-B Cl2 (ppm)		
		Flow (dscfm)	Oxygen (% dry)	Chlorine (ppm, dry)	Moisture (%)	Chlorine (ppm, wet)	Chlorine (ppm, wet)	Use of Run ¹	Chlorine (ppm, wet)	Use of Run ¹	Chlorine (ppm, wet)	Use of Run ¹	Chlorine (ppm, wet)	Use of Run ¹	
RATA Run 1	08:06-08:36	7,900	10.98	0.197	8.75	0.180	0.453	x	0.000			0.274	X	-0.180	
RATA Run 2	08:48-09:18	7,805	10.99	0.209	9.18	0.190	0.437		0.000			0.247		-0.190	
RATA Run 3	09:50-10:20	8,009	10.95	0.203	8.87	0.185	0.443		0.000			0.258		-0.185	
RATA Run 4	10:30-11:00	7,971	10.97	0.213	9.30	0.193	0.440		0.000	x		0.247		-0.193	X
RATA Run 5	11:16-11:46	7,860	10.97	0.213	8.75	0.194	0.433		0.000	x		0.239		-0.194	X
RATA Run 6	11:55-12:25	7,917	11.01	0.198	9.34	0.180	0.437		0.000			0.257		-0.180	
RATA Run 7	12:41-13:11	7,867	10.97	0.240	8.70	0.219	0.420		0.000	x		0.201		-0.219	X
RATA Run 8	13:20-13:50	7,906	10.95	0.211	8.93	0.192	0.437		0.000			0.245		-0.192	
RATA Run 9	14:10-14:40	8,228	10.95	0.193	8.59	0.176	0.453	x	0.000			0.277	X	-0.176	
RATA Run 10	14:48-15:18	8,026	10.96	0.209	8.98	0.190	0.447		0.000			0.256		-0.190	
RATA Run 11	15:37-16:07	8,185	10.89	0.199	8.45	0.182	0.447	x	0.000			0.264	X	-0.182	
RATA Run 12	16:14-16:44	8,073	10.90	0.186	9.07	0.169	0.427		0.000			0.258		-0.169	
Number of Runs Used in Calculation (n)											9		9		
Average Difference (d _{AVG})											0.245		-0.183		
Standard Deviation (S _d)											0.018		0.007		
t-Value (t _{0.975})											2.306		2.306		
Confidence Coefficient (CC)											0.014		0.006		
Applicable Standard (or Permit Limit)											20		20		
Average of Reference Method (RM _{AVG})											0.190		0.183		
Relative Accuracy (CO, NO _x , SO ₂ , O ₂ ,CO ₂ , HCl, Cl ₂) (d _{AVG} + CC)											0.26		0.19		
Relative Accuracy (% of Reference Method) (RA)											136.2		103.1		
Relative Accuracy (% of Permit Limit) (RA)											1.3		0.9		
An X in this column denotes a run which is not used in calculation of relative accuracy.															
Performance Specification 2															
Relative Accuracy (% of Reference Method) (RA)											20		20		
Relative Accuracy (% of Permit Limit) (RA)											10		10		

Table 2-7 Relative Accuracy – 2512 THROX CEMS HCl (ppmv, wet), 10/23/2024

Hydrogen Chloride Relative Accuracy Results															
10/23/2024Run Time		REFERENCE METHOD						STACK ANALYZERS				ARITHMETIC DIFFERENCE			
						Measured Moisture and Hydrogen Chloride (ppm, wet)		THROX-A HCl (ppm)		THROX-B HCl (ppm)		THROX-A HCl (ppm)		THROX-B HCl (ppm)	
		Flow (dscfm)	Oxygen (% dry)	Hydrogen Chloride (ppm, dry)	Hydrogen Chloride (lb/hr)	Moisture (%)	Hydrogen Chloride (ppm, wet)	Hydrogen Chloride (ppm, wet)	Use of Run ¹	Hydrogen Chloride (ppm, wet)	Use of Run ¹	Hydrogen Chloride (ppm, wet)	Use of Run ¹	Hydrogen Chloride (ppm, wet)	Use of Run ¹
RATA Run 1	08:06-08:36	7,900	10.98	0.066	0.003	8.75	0.060	0.100	x	0.137	x	0.040	X	0.077	X
RATA Run 2	08:48-09:18	7,805	10.99	0.066	0.003	9.18	0.060	0.100	x	0.157	x	0.040	X	0.097	X
RATA Run 3	09:50-10:20	8,009	10.95	0.088	0.004	8.87	0.080	0.100		0.100		0.020		0.020	
RATA Run 4	10:30-11:00	7,971	10.97	0.088	0.004	9.30	0.080	0.100		0.107		0.020		0.027	
RATA Run 5	11:16-11:46	7,860	10.97	0.090	0.004	8.75	0.082	0.100		0.117		0.018		0.035	
RATA Run 6	11:55-12:25	7,917	11.01	0.090	0.004	9.34	0.082	0.100		0.107		0.018		0.025	
RATA Run 7	12:41-13:11	7,867	10.97	0.090	0.004	8.70	0.082	0.100		0.127		0.018		0.045	
RATA Run 8	13:20-13:50	7,906	10.95	0.090	0.004	8.93	0.082	0.100		0.107		0.018		0.025	
RATA Run 9	14:10-14:40	8,228	10.95	0.083	0.004	8.59	0.076	0.100		0.110		0.024		0.034	
RATA Run 10	14:48-15:18	8,026	10.96	0.083	0.004	8.98	0.076	0.100		0.153	x	0.024		0.077	X
RATA Run 11	15:37-16:07	8,185	10.89	0.076	0.004	8.45	0.070	0.100		0.130		0.030		0.060	
RATA Run 12	16:14-16:44	8,073	10.90	0.077	0.004	9.07	0.070	0.103	x	0.103		0.033	X	0.033	
Number of Runs Used in Calculation (n)												9		9	
Average Difference (d _{AVG})												0.021		0.034	
Standard Deviation (S _d)												0.004		0.012	
t-Value (t _{0.975})												2.306		2.306	
Confidence Coefficient (CC)												0.003		0.009	
Applicable Standard (or Permit Limit)												20		20	
Average of Reference Method (RM _{AVG})												0.079		0.078	
Relative Accuracy (CO, NO _x , SO ₂ , O ₂ , CO ₂ , HCl, Cl ₂) (d _{AVG} + CC)												0.024		0.043	
Relative Accuracy (% of Reference Method) (RA)												30.8		55.1	
Relative Accuracy (% of Permit Limit) (RA)												0.2		0.3	
¹ An X in this column denotes a run which is not used in calculation of relative accuracy.															
Performance Specification 18															
Relative Accuracy (% of Reference Method) (RA)														20	
Relative Accuracy (% of 75% of Permit Limit) (RA)														15	

Table 2-8 Process Data for CEMS RATA, 10/23/2024

RATA Run	CPT Run	Natural Gas Input (MMBtu/hr)	Gas Flow Dry Vent (lb/hr)	Gas Flow Wet Vent (lb/hr)	Gas Flow MeCl (lb/hr)	SiO ₂ Loading (lb/hr)	Combustion Chamber Temp (°F)	Absorber pH
1	1	22.2	635	600	115	0.17	2,023	7.7
2		22.1	660	600	65	0.16	2,023	7.7
3	2	22.2	646	590	84	0.17	2,023	7.8
4		22.5	699	618	102	0.17	2,022	7.8
5	3	22.3	722	593	81	0.16	2,022	7.8
6		22.3	706	587	77	0.16	2,022	7.8
7	N/A	22.2	680	637	79	0.17	2,021	7.8
8		22.5	739	572	92	0.16	2,021	7.8
9	N/A	22.3	672	581	83	0.16	2,023	7.8
10		22.7	806	600	78	0.16	2,022	7.8
11	N/A	22.2	780	580	56	0.16	2,021	7.8
12		22.2	750	605	69	0.16	2,021	7.8
Average:		22.31	708.0	596.9	81.9	0.16	2,022	7.8

Table 2-9 Process Data Parameters for the Performance Test RATA

Process Monitoring Parameter	Process Tag Unit
NOx (lb/hr)	lb/hr
NOx (lb/hr) – using Sick flow rate	lb/hr
THC (ppmvw)	ppm
THC (lb/hr)	lb/hr
O ₂ (% dry)	%
CO ₂ (% dry)	%
Cl ₂ (ppmvw)	ppm
HCl (ppmvw)	ppm
Exhaust Gas Flow, THROX Out Stack (scfm, wet)	SCFM
Exhaust Gas Flow, THROX Out Stack (dscfm x 1,000) – Sick flow monitor	KDSCFM
Natural Gas Heat Input (MMBtu/hr)	MMBTU
Combustion Chamber Temperature – Thermocouple 1	Degrees F
Combustion Chamber Temperature – Thermocouple 2	Degrees F
Absorber (pH units)	PH
Gas Flow, Acetylene	lb/hr
Gas Flow, Dry Vent	lb/hr
Gas Flow, Wet Vent	lb/hr
Gas Flow, MeCl	lb/hr
SiO ₂ Loading (lb/hr)	pph
IWS 1 Water Flow Rate	GPM
IWS 1 Voltage	KV
IWS 1 Current	mA
IWS 2 Water Flow Rate	GPM
IWS 2 Voltage	KV
IWS 2 Current	mA

3. Facility Process and CEMS Description

3.1 Process Description

This section briefly describes the 2512 THROX treatment system. The THROX and its associated air pollution control equipment are utilized to treat emissions from various processes at the chemical facility. Some of these processes are continuous and others are batch, the test was conducted at maximum representative normal operating conditions of the THROX. Operating parameters for the THROX and its associated air pollution control equipment are specified in table FGTHROX of renewable operating permit (ROP) No. MI-ROP-A4043-2019b and the malfunction abatement plan.

Building 2512 uses a site wide thermal heat recovery oxidation (THROX) unit that destroys/removes TOC, hazardous air pollutants (HAPs), PM₁₀, hydrogen halides, and other toxic air contaminants from the consolidated vent system prior to discharge to atmosphere. Air pollution control equipment associated with the THROX includes a quencher, absorber, and two-stage ionizing wet scrubbers (IWS) in series.

3.2 Applicable Regulations and Performance Requirements

Applicable Regulations

MI-ROP-A4043-2019b

CFR Part 63, Subpart FFFF

CFR 50.21 PSD

40 CFR Part 98 GHG Rule

40 CFR Part 60, Appendix B, Performance Specifications 2, 3, 6, 8, and 18

Pollutants/Diluent Measured - Relative Accuracy (RATA)

NO_x RA <20% of RM – PS 2

Cl₂ RA <20% of RM or 10% of ES (20 ppmv) – PS 2 (per Michigan EGLE)

Oxygen (O₂) RA <20.0% of RM or absolute difference <1.0% – PS 3

Carbon Dioxide (CO₂) RA <20.0% of RM or absolute difference <1.0% – PS 3

Flow RA <20% of RM (as surrogate for PS 6 compliance)

Total Hydrocarbon (THC) RA <20% of RM or 10% of ES (20 ppmv) – PS 8

Hydrogen Chloride (HCl) RA <20% of RM or 15% of 75% of ES (15 ppmv) – PS 18

Under the Miscellaneous Organic NESHAP (40 CFR Part 63, Subpart FFFF – MON MACT), the facility is choosing to comply with the alternative standard in §63.2505 and is subject to the following emission limitations:

- §63.2505(a)(1)(i)(A) requires the THROX to reduce HAP emissions to an outlet total organic compounds (TOC) concentration of 20 ppmv or less.
- §63.2505(a)(1)(i)(C) provides an alternative for reducing hydrogen halide and halogen HAP generated in the combustion device by ≥95 percent by weight in the scrubber.
- In accordance with the provisions for hydrogen halide and halogen HAP emissions from process vents in §63.2465 and Table 3 to Subpart FFFF, the scrubbers must reduce the hydrogen halide and halogen HAP to ≥ 99% (or to an outlet concentration of ≤ 20 ppmv or the halogen atom mass emission rate must be reduced to ≤ 0.45 kg/hr).

3.3 Process Emissions Control Description

The air pollution control system downstream of the THROX consists of a quencher, absorber, and two-stage ionizing wet scrubbers (IWS) in series. The THROX is designed to thermally treat liquid and solid wastes. As necessary, fuel gas is used as a supplemental fuel. Destruction of organic compounds takes place in the combustion chambers. The THROX typically operates above 1,800°F. The permitted maximum nominal thermal output capacity of this unit is 95 million British thermal units per hour (MMBtu/hr). The typical feed rate to the THROX is 28 MMBtu/hr. The waste supplies most of the heat. Natural gas is used to maintain the temperature when the Btu content of the waste is limited and to maintain the flame during startups and shutdowns.

After the combustion gases exit the oxidizer chamber, they enter the boiler section where heat is recovered to generate steam. Next, the gases enter the quench section, then a packed bed absorber. The absorber uses caustic water to neutralize hydrogen chloride in the vapor. Finally, the gases pass through two (2) ionizing wet scrubbers in series. The ionizing wet scrubbers remove particulate by passing the stream through a charged field. The particles become charged and are attracted to the charged plates, then they are removed by a continuous flow of water down the plates and through the packed beds.

The ROP currently requires Dow Silicones Corporation to use the Verantis equation to demonstrate compliance with the lb/hr PM₁₀ emission rate (as described in the plan entitled "Parametric Monitoring Plan and Verification of IWS Particulate Removal Efficiency from EUTHROX").

The emission test point for this test was the 2512 THROX Scrubber Stack.

3.4 Flue Gas Sampling Locations

Sampling was conducted on the 2512 THROX scrubber outlet stack. The reference method sampling ports in the stack are at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration occurs, and at least one-half equivalent diameters upstream from the effluent exhaust or control device. The stack has sampling ports installed as shown in **Figure 3.1**.

For the RATA performed on October 23, the instrumental analyzer and Method 26A train samples were drawn from the stack for a sampling run duration of thirty (30) minutes each. A stratification test was conducted at the three traverse points of 16.7, 50.0, and 83.3 percent of the measurement line that passes through the centroidal area of the stack cross section. For RATA velocity measurements, pitot tube and temperature readings were taken from the stack for each 21 to 30-minute run at twelve (12) US EPA Method 1 sampling points in accordance with the following table.

Isokinetic 12 Point Circular Traverse Layout for Outlet

Division: MIOP

Facility/Block: DSC 2514 THROX

Stack ID: 54 inches

Port Ext: 6 inches

Duct Downstream Length: 50 Feet

Duct Downstream Diameters: 11 Diameters

Duct Upstream Length: 25 Feet

Duct Upstream Diameters: 5.5 Diameters

Traverse Point	Stack ID	Port Ext	Traverse Pt Distance	Traverse Pt Distance ↓	Final Probe Mark
1	54	6	2 6/16	2 6/16	8 6/16
2	54	6	7 14/16	7 14/16	13 14/16
3	54	6	16	16	22
4	54	6	38	38	44
5	54	6	46 2/16	46 2/16	52 2/16
6	54	6	51 10/16	51 10/16	57 10/16

3.5 Facility CEMS Description

The facility employs redundant CEMS (known as System A and System B) to monitor NO_x, O₂, CO₂, HCl, Cl₂, and THC, along with two exhaust gas flow rate CERMS in order to comply with MON MACT monitoring requirements and to demonstrate continuous compliance with the emission limits specified in their air permit (Michigan EGLE Permit MI-ROP-A4043-2019b).

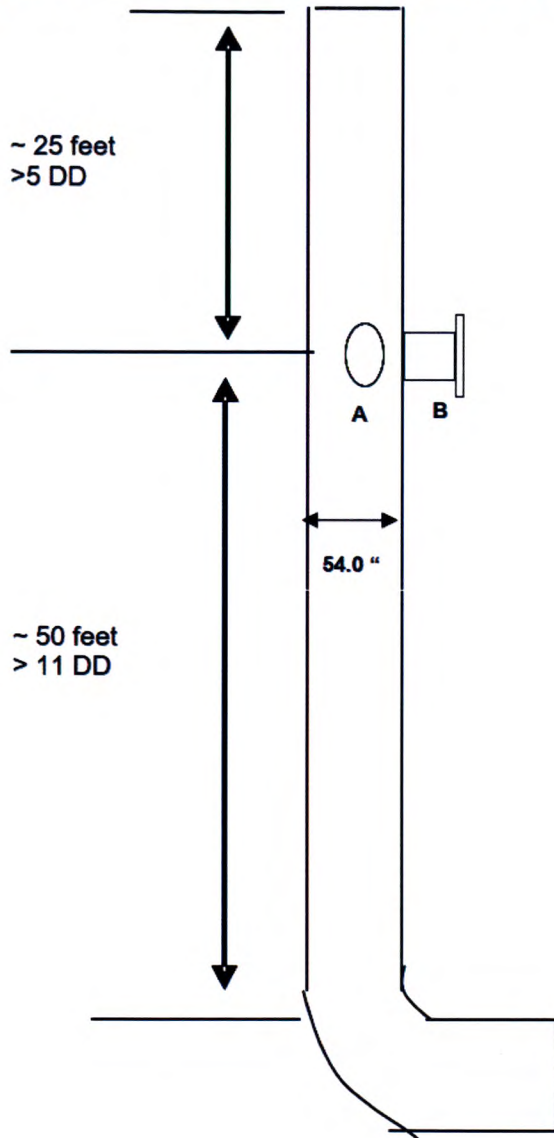
The CEMS are extractive type systems that were designed and installed to meet emissions monitoring requirements outlined in 40 CFR Part 60, Appendix B, Performance Specifications (PS) 2, 3, 6, 8, and 18 for emissions of NO_x/Cl₂, O₂/CO₂, emission rate, THC and HCl, respectively.

Each CEMS consists of an extractive sample probe, with a sintered metal element filter at the probe inlet tip. A heated sample line runs between the probe and CEMS cabinet to a sample conditioning system. The CEMS analyzers are housed in a climate-controlled shelter, which is located at the base of the stack. The CEMS analyzers are wired into the DAHS, which in turn calculates emissions from analyzer outputs and provides the required regulatory reports. Specifications for each CEMS/CERMS monitor are presented in **Table 3-1**. A schematic of the facility emissions stack layout showing the sample test port locations is provided in **Figure 3-1**.

Table 3-1 Facility CEMS/CERMS Equipment Specifications

Monitor System	Measurement Units	Equipment	ID/Serial number (S/N)
Oxygen FGTHROX	%v, dry	Teledyne API T200H	S/N: 950 (System B) and 951 (System A)
Carbon Dioxide FGTHROX	%v, dry	California Analytical Instruments Model 701LX	S/N: 2208009 (System B) and 2208008 (System A)
Total Hydrocarbon FGTHROX	ppmv, wet	California Analytical Instruments Model 700 HFID and California Analytical Instruments Model 700 LXHFID	S/N: 2208007 (System A) and 2205019 (System B)
Nitrogen Oxides FGTHROX	%v, dry	Teledyne API T200H	S/N: 950 (System B) and 951 (System A)
Air Flow FGTHROX	scfm, wet	EMRC GFM	S/N: 1488 (System B) and 1489 (System A)
Air Flow FGTHROX	kdscfm	Sick Model FLSE100-PRK17835HSHS	S/N: 21488420
Chlorine	ppmv, wet	ABB Limas 21	S/N: 3.454828.3 (System A) and 3.454829.3 (System B)
Hydrogen Chloride	ppmv, wet	Unisearch Associates Inc. Model LAS-RB101-CBS-HCIH20H20 LAUNCHER/RECEIVER RETROREFLECTOR	S/N: LAS22-046 (System B) and LAS22-047 (System A)

Figure 3-1 Schematic of Stack Sample Port Locations



4. Performance Test Procedures

The following is a description of the testing that was completed on the 2512 THROX scrubber stack to fulfill the annual CEMS/CERMS RATA and emissions compliance requirements of 40 CFR Part 60 as specified in the Michigan EGLE air permit (MI-ROP-A4043-2019b).

4.1 Manual Test Methods

4.1.1 Flow Rate, Gas Composition, and Moisture

Concurrent with the performance of RATA test runs, emissions compliance test runs, and isokinetic sampling trains, measurements were made to determine stack gas volumetric flow rate from measurements of gas velocity and temperature (EPA Method 2), gas molecular weight composition (EPA Method 3A), and gas moisture (EPA Method 4).

4.1.2 Filterable and Condensable Particulate Matter Sampling and Analysis

EPA Method 5 was utilized in conjunction with EPA Method 202 to determine both filterable particulate matter (FPM) and condensable particulate matter (CPM) concentrations during each PM₁₀ emissions compliance test run.

Using EPA Method 5 procedures, total particulate matter (i.e., FPM) is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The FPM mass is determined gravimetrically after the removal of uncombined water.

EPA Method 202 procedures were used to collect CPM in dry impingers after FPM had been collected on a filter maintained as specified in Method 5 of Appendix A-6 to 40 CFR Part 60. The organic and aqueous fractions of the impingers and an out-of-stack CPM filter were then taken to dryness and weighed at an off-site analytical laboratory. The total of the impinger fractions and the CPM filter represents the CPM test result. Analyses for FPM and CPM were completed by Enthalpy Analytical.

4.1.3 Hydrogen Chloride and Chlorine Sampling and Analysis

The stack gas was sampled isokinetically for determination of HCl and Cl₂ using a sampling train meeting the requirements of EPA Method 26A. Gas is withdrawn from the duct isokinetically, utilizing a gooseneck nozzle of proper size to allow isokinetic sample collection. S-type pitot differential pressure was monitored to determine the isokinetic sampling rate.

From the heated filter, sample gas enters the series of impingers which are charged with absorbing solutions in accordance with EPA Method 26A. The first two impingers contained a solution of 1N H₂SO₄. The third and fourth impingers contained a solution of 1N NaOH. The fifth and final impinger contained a desiccant to dry the sample gas before metering. A pump and dry gas meter are used to control and monitor the sample gas flow rate. The impingers are recovered and rinsed into separate containers and analyzed in accordance with the requirements of Method 26A.

The modifications listed in the approved test plan under "Proposed Test Method Modifications" apply to the EPA Method 26A sampling train.

4.2 Instrumental Analyzer Test Methods

AECOM followed the instrumental analyzer procedures specified in EPA Methods 3A, 7E, 10, 25A, (40 CFR Part 60, Appendix A), and Method 320 (40 CFR Part 63, Appendix A) for the determination of O₂/CO₂, NO_x, CO, THC, and HCl concentrations, respectively. Exhaust gas volumetric flow rates were

calculated using measurements made following the source testing procedures specified in EPA Methods 2 and 4 (40 CFR Part 60, Appendix A) for the determination of gas velocity and moisture, respectively. The following subsections describe the sample procedures in more detail.

AECOM conducted a minimum of nine 21 to 30-minute test periods for the RATA using the AECOM transportable instrumental analyzer laboratory, which is described later in this section. For emissions compliance testing, each set of two (2) consecutive 30-minute RATA test runs were combined to comprise one 60-minute compliance test run. Average undiluted dry concentrations by volume of O₂, CO₂, NO_x, and CO as well as undiluted hot-wet concentrations by volume of THC and HCl were determined for each test run. During each test run, the sample probe extracted a continuous sample along a traverse line through the center of the stack cross section as is specified in Performance Specification 2 (PS 2) of 40 CFR Part 60, Appendix B. Prior to sampling, a stratification test was completed where the sample probe was traversed across the stack at three points (16.7%, 50.0%, and 83.3%) of a measurement line passing through the stack centroid. The results of the Stratification Test are presented in **Appendix A**.

Relative accuracy (RA) determinations followed calculations delineated in PS 2, PS 3, PS 6, PS 8, and PS 18 (40 CFR 60, Appendix B) for NO_x/Cl₂, O₂/CO₂, flow rate, THC, and HCl, respectively. RA results are evaluated in accordance with the criteria specified in 40 CFR Part 60, Appendix B (PS 2, 3, 6, 8, and 18). Each monitor of the CEMS/CERMS passes the RATA if it meets the least restrictive RA criterion in the applicable performance specification. The least restrictive Part 60 RA criterion for each O₂/CO₂ monitor was 1.0% O₂/CO₂ by difference, for each NO_x and flow rate monitor was ≤20 percent of the average RM value, for each THC monitor was ≤10 percent of the emission standard (20 ppmv MON MACT emission standard), and for each Cl₂ and HCl monitor was ≤15 percent of 75% of the emission standard (20 ppmv MON MACT emission standard).

The O₂, CO₂, NO_x, CO, THC, Cl₂, HCl, and flow rate RM test run data and calculation results are presented in **Appendix A**.

4.3 Transportable Instrumental Analyzer Laboratory

A transportable instrumental analyzer laboratory (i.e., Mobile Lab) was used to provide an environmentally controlled shelter to house RM analyzers and the sample delivery and conditioning system to measure O₂, CO₂, NO_x, and CO by volume on a dry basis as well as THC by volume on a hot-wet basis. The AECOM RM monitoring system is contained in a temperature controlled portable shelter that was delivered to the site and set up prior to the start of the test program. The sample delivery and conditioning system consists of a stainless-steel sample probe, a heated particulate filter assembly, a heat-traced Teflon sample line, a refrigerated gas conditioning system (for moisture and condensable particulate removal), a sample gas manifold, and a sample pump. The clean dry sample was then delivered to the gas analyzers for the determination of undiluted O₂, CO₂, NO_x, and CO concentrations. For measurement of THC, a portion of the hot-wet sample is diverted directly to the THC analyzer via a heated jumper line prior to the sample being introduced to the moisture condenser.

The analog output signals from each analyzer were connected to a data acquisition system (DAS) using a software package to perform the test calculations. The DAS then stored the data in engineering units and provided 1-minute and 10-second averages based upon a minimum of 60 readings per minute. The O₂ and CO₂ were measured using a Servomex 1440 Series analyzer with paramagnetic and non-dispersive infrared (NDIR) detectors on approximate span gas ranges of 0-25% and 0-20%, the NO_x was measured using a Thermo Model 42 chemiluminescent analyzer on an approximate span gas range of 0-100 ppm, the CO was measured using a Thermo Model 48 gas filter correlation (GFC) / NDIR analyzer on an approximate span gas range of 0-100 ppm, and the THC was measured using a VIG Model 20 flame ionization analyzer (FIA) on an approximate span range of 0-100 ppm.

4.4 RM Instrumental Analyzer Calibration Procedures

The initial phase of the instrumental analyzer methods (e.g., Methods 3A, 6C, 7E, 10, and 25A) requires initial measurement system performance tests to be performed, including calibration error tests, system bias checks, response-time tests, an NO₂ converter test (for NO_x analyzers), and interference checks, as applicable.

Prior to performing test runs with the dry-measurement analyzers (i.e., Methods 3A, 6C, 7E, and 10 instruments), AECOM conducted direct instrument calibration error tests using zero and two upscale gases each for the O₂/CO₂, NO_x, and CO analyzers prior to initiation of testing. Following these direct calibrations, an initial system bias check was performed by sending zero and one upscale gas, from one gas cylinder at a time, up to the sample probe and back down through the components of the sampling system. Following the initial system bias checks, response-time data was obtained for each analyzer. Subsequently, system bias and drift checks were performed both prior to and following each test run set of up to three consecutive runs using zero and one upscale calibration gas. These system checks allowed for the determination of initial and final system bias, as well as system drift for each test run set.

Prior to performing test runs with the hot-wet measurement analyzers (i.e., Method 25A instruments), AECOM conducted whole-system calibration error tests using zero and three upscale gases for the THC analyzer prior to initiation of testing. The initial system calibration error test was performed by sending zero and each of three upscale gases, from one gas cylinder at a time, up to the sample probe and back down through the components of the sampling system. Following these system calibrations, response-time data was obtained. Subsequently, system drift checks were performed both prior to and following each test run set of up to three consecutive runs using zero and one upscale calibration gas. These system checks allowed for the determination of system drift for each test run set.

Test run sets of three 21-minute RATA test runs were performed during a continuous and uninterrupted period of 63 minutes followed by a system bias and drift check. The calibration gases used during this program were prepared in accordance with EPA Protocol G1 procedures as specified by the National Institute of Standards and Technology (NIST). The O₂/CO₂/CO combination, NO_x, and THC (propane) calibration compressed gas standards were contained in individual cylinders having a purified nitrogen gas balance.

Interference check data provided by each instrument's manufacturer is maintained on file to meet the requirements of Method 7E (Subsection 8.2.7) as referenced in Methods 3A, 6C, and 10, as applicable.

The RM calibration data, including initial calibration error tests, pre-run and post-run system bias and drift checks, system response time tests, NO₂ converter efficiency test data, and certificates of analysis for the RM test calibration gases, are provided in **Appendix A**.

4.5 RM FTIR Analyzer Measurement Procedures

HCI was measured in accordance with EPA Method 320 using the procedures outlined in ASTM Method D6348-12. 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 FTIR measured parameter are presented in the following subsections.

The FTIR extractive system comprises a stainless-steel probe (~1 foot), a stainless-steel spiking "T", a 50-ft heated (185°C) PFA-grade Teflon line, a MKS 2030 FTIR spectrometer 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. Given the presence of stack gas 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 12 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.

4.5.1 Analyte Spiking System

Per Annex 5 (A5) of the ASTM FTIR 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.

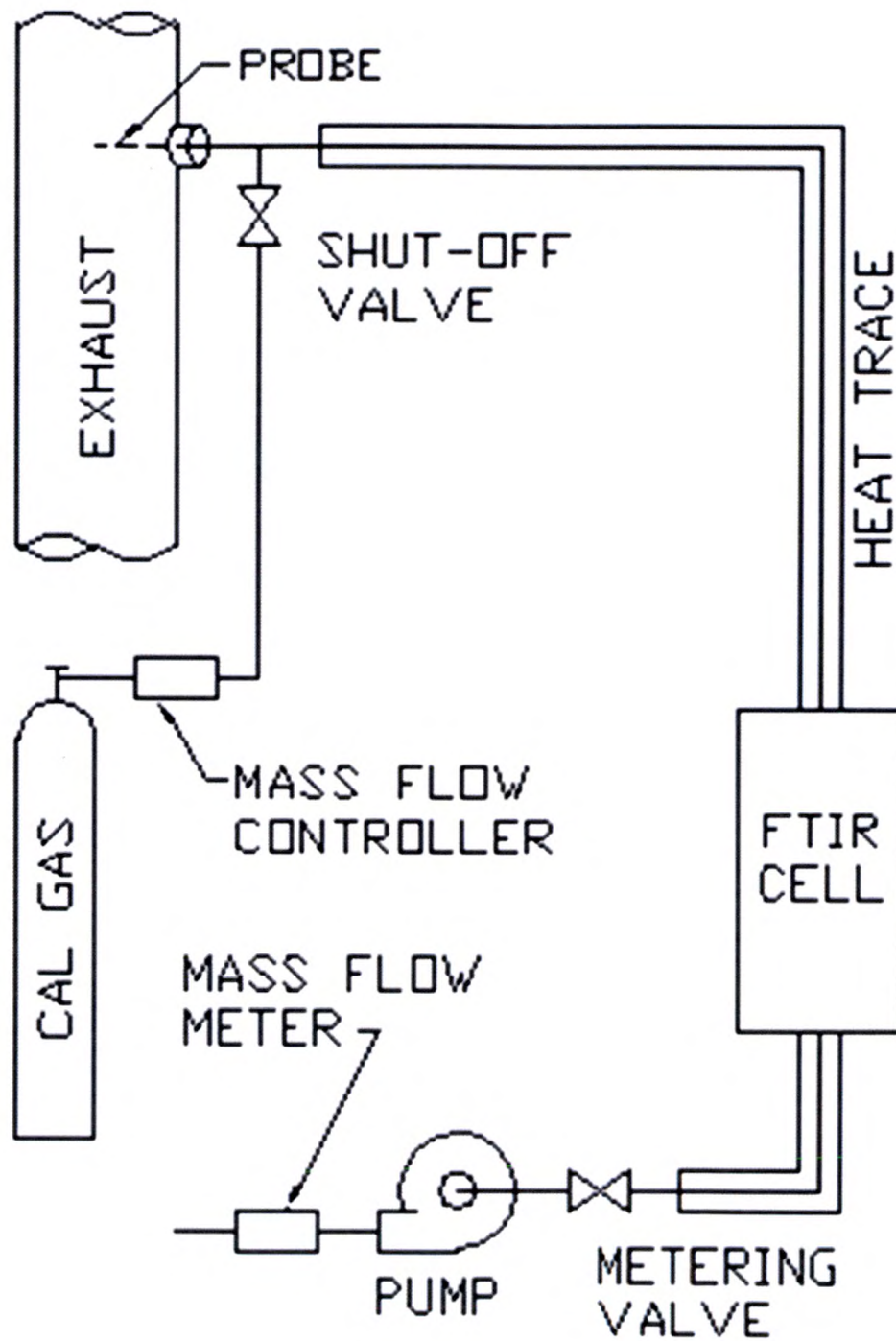
4.5.2 Analyte Spectrum Analyses Method

An infrared spectrum will 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 will be signal averaged for two minutes (~130 individual spectra) and all QA spiking data will be averaged for 1/2 minute (~32 individual spectra). Shorter scan durations are used for the equilibrium and mechanical response tests to better characterize system retention/response time.

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 (e.g., water vapor for this data set) are included in the analyte analysis region. The analysis method for this sampling is optimized for HCl analysis during sampling and later refined to best fit the interferences within the analysis region.

Figure 4-1 Instrumental Wet Extractive Sampling System – FTIR (HCI)



5. Quality Assurance/ Quality Control Measures

5.1 Overview

During the sampling and measurements phase of the program, a strict quality assurance/quality control (QA/QC) program was adhered to. The QA/QC aspects of the program are discussed below.

5.2 Leak Check Procedure

Prior to conducting the instrumental analyzer testing, AECOM's Instrumental Measurements System was leak checked and verified to be leak free. Following the initial leak check, the system bias and drift criteria (as referenced in EPA Method 7E, 40 CFR Part 60, Appendix A) served as a continuous sample integrity check.

5.3 Instrumental Measurements System Calibrations

During the test program, AECOM used EPA instrumental analyzer methods (i.e., 3A, 6C, 7E, and 10, as applicable, in 40 CFR Part 60, Appendix A) for the measurement of O₂/CO₂, NO_x, and CO. The initial phase of instrumental analysis requires calibration of the involved monitors. Prior to performing test runs, AECOM conducted direct instrument calibration error tests using zero and two upscale gases each for the O₂/CO₂ and CO instruments prior to initiation of testing. Following these direct calibrations, an initial system bias check was performed by sending zero and one upscale gas, from one gas cylinder at a time, up to the sample probe and back down through the relevant components of the sampling system. During the initial system bias checks, response-time data was obtained for each analyzer. Subsequently, system bias checks were performed both prior to and following each test run using zero and one upscale calibration gas. These system checks allowed for the determination of initial and final system bias, as well as system drift for each test run. The calibration gases used during this program were prepared to EPA Protocol G1/G2 standards. Certificates of analysis for the calibration gases are presented in Appendix B. The measurement system performance criteria in 40 CFR Part 60, Appendix A, Methods 3A and 10 are listed below and were the performance criteria for the reference method instruments during this program.

<u>Procedure</u>	<u>Performance Criterion</u>
Calibration error	<±2% of the calibration span
System bias	<±5% of the calibration span
System drift	<±3% of the calibration span

The instrumental analysis methods also require correction of data for calibration drift and/or bias. The values used for the determination of relative accuracy were corrected for system drift and bias observed during each test run. System bias and drift as well as response-time data are presented in **Appendix A** of this report.

5.4 Interference Checks

Interference checks are required for each make and model of instrumental analyzer used for reference method measurements and signed documentation of the results must be included in each test report (as referenced in 40 CFR 60, Appendix A, Method 7E, Subsection 8.2.7). Copies of the instrument specific test results are presented in **Appendix A** of this document.

6. Data Reduction

6.1 Overview

The objective of the monitoring program was to determine the relative accuracy (RA) of the MACT CO/O₂ CEMS/CERMS. RA results have been reported on an individual analyzer basis (concentrations) and for exhaust gas volumetric flow rate. Photocopies of the raw field data sheets and data printouts are also presented in the appendices. Equations and example calculations from the data reduction process are presented in **Appendix A**. Equations for the calculation of relative accuracy (RA) are presented in this section.

6.2 Calculation of Relative Accuracy

Standard Deviation

The standard deviation (SD) between the minimum of nine test runs chosen must be calculated. The following equation was used to calculate standard deviation:

$$S_D = \sqrt{\left[\frac{(\text{Sum of } d^2) - \frac{(\text{Sum of } d)^2}{n}}{n - 1} \right]}$$

Where:

SD = Standard deviation of a minimum of nine selected runs

d = Arithmetic difference between the facility CEMS and RM test run averages

n = Number of sample test runs used for standard deviation calculation

Confidence Coefficient

The 95% confidence coefficient (CC) of the minimum of nine test runs chosen must be calculated. The student T Value of 2.306 (for nine runs) in the equation comes from Table 2-1 (t-Values) of PS 2 in 40 CFR Part 60, Appendix B. The T Value needs to be adjusted for the chosen number of test runs according to Table 2-1 in PS 2. The following equation was used to calculate the confidence coefficient:

$$CC = 2.306 \times \left(\frac{S_D}{\sqrt{n}} \right)$$

Where:

CC = Confidence coefficient

Sd = Standard deviation of the minimum of nine selected test runs

n = Number of sample test runs used for standard deviation calculation

Relative Accuracy

The relative accuracy of the CEMS/CERMS were calculated as required by PS 3, PS 4B, and PS 6 for O₂ (%vd), CO (ppmvd), and flow rate (scfm and dscfm), respectively. The relative accuracies are calculated to verify:

- RA for O₂ (%vd) is no greater than 20.0% of RM or 1.0% O₂ absolute difference (not including CC) as specified in PS 3 of 40CFR60, Appendix B
- RA for CO (ppmvd) is no greater than 10% of RM, 5% of ES (applicable emission standard), or 5 ppm CO absolute difference plus CC as specified in PS 4B of 40CFR60, Appendix B
- RA for flow rate (scfm and dscfm) is no greater than 20% as specified in PS 6 of 40CFR60, Appendix B

Relative Accuracy (% of RM or % of ES)

$$RA = \left[\frac{(|avg\ d| + |CC|)}{avg\ RM} \right] \times 100\%$$

Relative Accuracy (by Absolute Difference)

For Pollutant Parameters (e.g., SO₂, NO_x, CO): RA = |avg d| + |CC|

For Diluent Gas Parameters (e.g., O₂ and CO₂): RA = |avg d|

Where:

RA = Relative accuracy

CC = Confidence coefficient

d = Arithmetic difference between RM and CEMS values for each test run

avg d = Average arithmetic difference between RM and CEMS values for all test runs

RM = Reference Method value

ES = Emission Standard substituted for RM