

# CEMS RATA Test Report ROP-MI-A4043-2019b 40 CFR Part 60, Appendix B, Performance Specifications 2 and 3

# Gas Fired Boilers #12, #13, #14 (Building 432 Boilers)

Project number: 60724067

May 31, 2024

Dow Silicones Corporation Midland, Michigan

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DSC MiOps\_432 Building\_Boilers 12 13 14 RATAs 2024

#### Project Number: 60724067

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# 1. Introduction

### 1.1 Background

Under contract with DSC Midland Operations, AECOM, Inc., conducted Relative Accuracy Test Audit (RATA) testing on the Continuous Emission Monitoring Systems (CEMS) associated with Boiler 12 (Vent SV432-001), Boiler 13 (Vent SV432-002), and Boiler 14 (Vent SV432-003). Boilers 12, 13, and 14 are physically located in Building 432 at DSC's Infrastructure facility in Midland, Michigan. The test was conducted on May 13<sup>th</sup> and 14<sup>th</sup>, 2024.

DSC operates a chemical manufacturing facility in Midland, Michigan. This facility consists of numerous different chemical manufacturing processes including 432 Building, which produces steam from its three boilers (Units 12, 13, and 14).

432 Building is used to provide steam to chemical manufacturing plants located in the Dow Silicones Corporation Midland Operations (MiOps) site, which includes three natural gas boilers, and all required ancillary equipment. Boiler feed water is imported from existing site infrastructure. Natural gas (High Pressure Fuel Gas, HPFG) provide fuel for these three boilers. Steam produced in the auxiliary boilers is sent throughout the Dow Silicones Corporation Midland site at 150 psig.

# 1.2 Overview of the Test Program

This RATA test report describes the test procedures performed on 432 Building Boiler 12 (Vent SV432-001), Boiler 13 (Vent SV432-002), and Boiler 14 (Vent SV432-003), at the infrastructure facility, owned and operated by DSC, Michigan Operations, Midland, Michigan.

The test described in this document was designed to demonstrate compliance with the requirements of the Michigan Department of Environment, Great Lakes, and Energy (EGLE) Renewable Operating Permit (ROP-MI-A4043-2019b) as well as the regulations in US EPA 40 CFR Part 60, Appendix B, Performance Specifications 2 and 3.

The following table (Table 1-1) summarizes the pertinent data for this performance test:

Responsible Groups	<ul> <li>Dow Silicones Corporation</li> <li>AECOM</li> <li>Department of Environment, Great Lakes, and Energy (EGLE)</li> <li>U. S. Environmental Protection Agency (US EPA)</li> </ul>
Applicable Regulations	• MI-ROP-A4043-2019b
Industry / Plant	432 Building
Plant Location	Dow Silicones Corporation     Midland, Michigan 48667
Unit Initial Start-up	<ul> <li>December 2006 Boiler 12</li> <li>December 2006 Boiler 13</li> <li>December 2006 Boiler 14</li> </ul>
Date of Last RATA	<ul> <li>April 17<sup>th</sup> and 18<sup>th</sup>, 2023</li> </ul>
Air Pollution Control Equipment	<ul> <li>Low NOx Burners</li> <li>Exclusive use of Natural Gas</li> </ul>
Emission Points	<ul> <li>Boiler 12 – Vent SV432-001</li> <li>Boiler 13 – Vent SV432-002</li> <li>Boiler 14 – Vent SV432-003</li> </ul>
Pollutants/Diluent Measured	<ul> <li>Nitrogen Oxides (NOx)</li> <li>Oxygen (O<sub>2</sub>)</li> </ul>
Test Dates	<ul> <li>Boiler 12 – May 13, 2024</li> <li>Boiler 13 – May 14, 2024</li> <li>Boiler 14 – May 14, 2024</li> </ul>

#### Table 1-1. Responsible Groups

DSC MiOps\_432 Building\_Boilers 12 13 14 RATAs 2024

# 1.3 Key Personnel

The contact for the source and test report is:

Ms. Sarah Maki, Air Specialist The Dow Chemical Company 2007 Building Midland, Michigan 48674 (989) 301-6856 smaki@dow.com

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	<ul> <li>Coordinate plant operation during the test.</li> <li>Ensure the unit is operating at the agreed upon conditions in the test plan.</li> <li>Collect any process data required.</li> <li>Provide all technical support related to process operation</li> </ul>	Brandon Krieger	Dow Chemical	
Environmental Focal Point	<ul> <li>Ensure all regulatory requirements and citations are reviewed and considered for the testing</li> </ul>	Sarah Maki	Dow Chemical	
Technical Reviewer	Completes technical review of the test data	Wayne Washburn	AECOM	
Field Team Leader	<ul> <li>Ensures field sampling meets the quality assurance objectives of the plan</li> </ul>	Peter Becker	AECOM	
Sample Project Leader	<ul> <li>Ensures data generated meets the quality assurance objectives of the plan</li> </ul>	James Edmister	AECOM	

#### Table 1-2. Key Personnel

## 1.4 Executive Summary

A results summary for the 432 Building RATAs on Boilers 12,13, and 14 are presented in **Table 1-3**. The results show that the Boilers are within the allowable limits specified in 40 CFR Part 60, Appendix B, Performance Specifications 2 and 3.

Test program participants included: Peter Becker, Quincy Crawford, and James Edmister from AECOM; as well as Brandon Krieger and Sarah Maki from The Dow Chemical Company.

Additional information is contained in the Appendices as follows: **Appendix A** provides Emissions Data from AECOM's test activities. **Appendix B** contains Facility Data for the Compliance Test. **Appendix C** contains Quality Assurance Data, including Calibration Error Tests, System Bias and Drift Checks, System Response Times, and Gas Cylinder Certification Sheets.

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	Boiler 12	(Vent SV432-001)	
Test Type	NOx Monitor Results lb/MMBtu	Allowable	Pass/Fail
	8.7%		Pass
<b>Relative Accuracy</b>	5.6%	20% RA using RM or	Pass
			Pass
Test Type	O2 Monitor Results	Allowable	Pass/Fail
	6.1%	No greater than 20.0% of mean	Pass
	0.32 %O <sub>2</sub>	value of RM	Pass
Relative Accuracy		or the absolute difference between RM and CEMS <= $1.0 \ \text{\%O}_2$	Pass
	Boiler 13	(Vent SV432-002)	
Test Type	NOx Monitor Results lb/MMBtu	Allowable	Pass/Fail
	3.8%		Pass
Relative Accuracy	3.0%	20% RA using RM or	Pass
			Pass
Test Tune	02 Monitor Poculto	Allowable	Pass/Fail
rest type	02 Monitor Results	Allowable	Semi/Annual
	7.6%	No greater than 20.0 % of mean	Pass
	0.38 %O2	value of RM	Pass
Relative Accuracy	14	or the absolute difference between RM and CEMS <= $1.0 \ \%O_2$	Pass
	Boiler 14	(Vent SV432-003)	
Test Type	NOx Monitor Results lb/MMBtu	Allowable	Pass/Fail
	6.4%	200/ 24	Pass
Relative Accuracy	5.1%	20% RA using RM or	Pass
			Pass
Test Type	O2 Monitor Results	Allowable	Pass/Fail
	10.3%	No greater than 20.0 % of mean	Pass
	0.57 %O <sub>2</sub>	value of RM	Pass
Relative Accuracy		or the absolute difference between RM and CEMS $\leq 1.0 \%O_2$	Pass

#### Table 1-3. Boilers 12, 13, and 14 Summary of Results

\*Emission limit is 0.10 lb/MMBtu NOx based on instantaneous value found in NSPS Subpart Db.

# 2. Summary and Discussion of Results

# 2.1 Objectives and Test Matrix

The purpose of this test was to demonstrate compliance with MI-ROP-A4043-2019b, 40 CFR Part 60, Appendix B, Performance Specification 2 and 3 for relative accuracy (RA).

- Measure the NOx emissions from the boiler stacks and compare to facility CEMS for RA.
- Determine the O<sub>2</sub> concentrations from the boiler stacks and compare to facility CEMS for RA.

# 2.2 Facility Operations

During the CEMS tests, the plant was operated at greater than 50% of the full load rating of the boiler being tested. Although these units are currently operated as standby units, which is different than how they were operated in the past (and during past tests), it was proposed to operate the units at greater than 50% of the previous normal load during testing. Prior to becoming standby units, the previous normal load was approximately 60 MMBtu/hr heat input.

# 2.3 Comments/Exceptions

This Performance Specification Test for the boiler stacks consisted of up to 12 total 21-minute runs. A minimum of nine runs were used to determine relative accuracy with a maximum of three runs excluded for RATA calculations as allowed by 40 CFR Part 60, PS 2 and 3.

# 3. Facility Description

# 3.1 Process Description

432 Building is used to provide steam to chemical manufacturing plants located in the Dow Silicones Corporation Midland Site, which includes three natural gas boilers and all required ancillary equipment. Boiler feed water is imported from existing site infrastructure. Natural gas (High Pressure Fuel Gas, HPFG) provide fuel for these three boilers. Steam produced in the auxiliary boilers is sent throughout the Dow Silicones Corporation Midland site at 150 psig.

#### **Table 3-1. Operating Parameter Summary**

Parameter	Maximum	Normal Highest	Test Condition
Heat Input (MMBtu/hr)	~ 103 MMBtu/hr	~ 60 MMBtu/hr	≥ 30 MMBtu/hr

# 3.2 Control Equipment Description

The boilers utilize a low NOx burner design with O2 trim to reduce the stack NOx concentration.

# 3.3 Flue Gas Sampling Locations

Emission sampling was conducted from each boiler stack for the RATA testing. Each stack has sampling ports installed at a height which complies with the requirements of 40 CFR 60, Appendix A, Reference Method 1. The sample locations are a minimum of two diameters downstream and 0.5 diameters upstream of gas flow disturbances.

# Figure 3-1. Facility Process Diagram



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# 4. Sampling and Analytical Procedures

The following is a description of the testing that was completed at 432 Building (Boilers 12, 13, and 14) as specified in the air permit (ROP-MI-A4043-2019b).

### 4.1 Test Performance Specifications and Methods

- PS 2 Method 7E for NOx; and
- PS 3 Method 3A for O<sub>2</sub>.

#### 4.2 Procedures

The above methods were performed using a mobile laboratory with instrumental analyzers and the associated sample acquisition equipment. Gases were withdrawn from the stack and transported to monitors located at ground level. A stainless-steel probe was inserted into the stack and used to collect sample gas. A Teflon sample line heated to 250°F transported sample gas from the probe to the analyzers. The analyzers were kept at a constant temperature inside the mobile laboratory.

Sample gas was collected continuously from the stack for a period of 21 minutes per run at the three traverse points of 16.7%, 50.0% and 83.3% of the measurement line that passes through the centroidal area of the stack or duct cross section. A Stratification test outlined in EPA Method 7E was performed for all three boilers and determined the three points listed above were adequate for testing. At the mobile laboratory, the stack gas was routed to a condenser and then transported to the analyzers for analysis.

The RATAs were conducted by comparison of the facility CEMS response to a value measured by the reference method (RM) instrumental analyzer, which made measurements in accordance with RM 7E for nitrogen oxides and RM 3A for O<sub>2</sub>.

## 4.3 Determination of Oxygen Concentrations – EPA Method 3A

EPA Method 3A (Instrumental Analyzer Method) was utilized to determine the exhaust gas O<sub>2</sub> concentration during each run on the tested boiler.

An analyzer measured  $O_2$  content based on the strong paramagnetic properties of  $O_2$  relative to other compounds present in combustion gases. In the presence of a magnetic field,  $O_2$  molecules become temporary magnets. The analyzer determines the sample gas  $O_2$  concentration by detecting the displacement torque of the sample test body in the presence of a magnetic field.

# 4.4 Determination of Nitrogen Oxides – EPA Method 7E

EPA Method 7E (Instrumental Analyzer Method) was utilized to determine the exhaust gas nitrogen oxide concentration during each run on the tested boiler.

An analyzer measured NOx using chemiluminescence technology. Ozone is combined with nitric oxide to form nitrogen dioxide in an activated state. The activated NO<sub>2</sub> luminesces broadband visible to infrared light as it reverts to a lower energy state. A photomultiplier tube and associated electronics counts the photons that are proportional to the amount of NO present. Since the stream contains both NO and NO<sub>2</sub>, the amount of nitrogen oxide (NO<sub>2</sub>) must first be converted to nitric oxide (NO) by passing the sample through a converter before the above ozone activation reaction is applied. The above reaction yields the amount of NO and NO<sub>2</sub> combined in the air sample.

Please note Dow Silicones Corporation has elected to complete a post-run bias and drift assessment after each set of three 21-minute runs for all analytes as allowed in EPA Method 7E 8.5 for all gas phase analyzer methods. EPA Method 7E section 8.5 reads as follows:

Post-Run System Bias Check and Drift Assessment. How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

# 4.5 Sampling Equipment

CEMS RATA sampling was conducted on the outlet stack of each of the three boilers for NOx using EPA Method 7E, and for Oxygen using EPA Method 3A. The NOx and O<sub>2</sub> sampling were conducted by continuously extracting sample from three points on the centroidal plane of the stack and analyzing a portion of the sample by chemiluminescence for NOx and Paramagnetic technology for O<sub>2</sub> concentrations. Calibrations were performed using EPA Protocol 1 standards of NOx and O<sub>2</sub>. Nine to twelve test runs of twenty-one-minute durations were conducted on each stack. A diagram of the sampling system is shown in **Figure 4-1**, and in **Table 4-1** a list of Facility CEMS and AECOM RM Sampling equipment.

AECOM Analyzers (RM)							
Constituent	Unit	Manuf.	Model	Serial #	Span		
Nitrogen Oxides	ppmv	Thermo	42C	NOX-MI902	0-100		
Oxygen	vol %	Servomex	1440 Series	OXC-MI901	0-25		
		Boiler 12 Cl	EMS				
Constituent	Unit	Manuf.	Model	Serial #	Span		
Nitrogen Oxides	ppmv	Thermo	42Q-LS	1192884871	0-100		
Oxygen	vol %	Brand Gaus	4705	10478	0-25		
		Boiler 13 Cl	EMS				
Constituent	Unit	Manuf.	Model	Serial #	Span		
Nitrogen Oxides	ppmv	Thermo	42Q-LS	1192884872	0-100		
Oxygen	vol %	Brand Gaus	4705	10556	0-25		
	Boiler 14 CEMS						
Constituent	Constituent Unit Manuf. Model Serial # Span						
Nitrogen Oxides	ppmv	Thermo	42Q-LS	1192884873	0-100		
Oxygen	vol %	Brand Gaus	4705	10555	0-25		

#### Table 4-1. Reference Method and Facility CEMS Analyzers



# Figure 4-1. Sampling Train used for NOx & O2 (RM 7E & RM 3A)

# 4.6 Transportable Instrumental Analyzer Laboratory

Gas stream samples were withdrawn from each individual exhaust stack and transported to the AECOM mobile instrumental measurements laboratory located at ground level. A stainless-steel sampling probe will be inserted into the stack and used to collect sample gas. Traverse points across each stack will be selected according to the procedure outlined in EPA Method 7E, Section 8.1, and marked clearly on the sampling probe. A heated Teflon sample line transported the sample gas from the sampling probe to the mobile laboratory. The instrumental analyzers were kept at a stable temperature inside the AECOM mobile laboratory. At the mobile laboratory, stack exhaust gas was routed to a moisture condenser and then transported to each individual analyzer for analysis on a dry basis (i.e., for O<sub>2</sub>/CO<sub>2</sub>, and NOx).

The analog electronic output signals from each analyzer are converted to a digital format and stored by AECOM's computerized data acquisition system. The system translates this digital signal into the proper units of measurement (e.g., ppmv NOx, dry basis) and stores them on a hard drive. The system stores the data as ten second averages.

# 4.7 Calibration Procedures

The analyzers were calibrated prior to initiating testing using appropriately certified standards as specified by EPA Methods 3A, 7E, and 10, as applicable. Only EPA Protocol calibration gases or certified pure zero nitrogen and air gases were used for calibration.

A three-point analyzer calibration error test was performed on each instrumental analyzer prior to testing. Zero and span gases were introduced directly to the instruments to establish calibration set points. Then, the mid-range gas was introduced as a QC check of instrument linearity. The calibration error of the response to each of these gases was no more than  $\pm 2\%$  of span from the calibration gas value, or the analyzer was re-calibrated, and the calibration error test was repeated.

The AECOM instrumental sampling system bias was then checked. The total system, which includes the probe, heated filter, sample line, sample pump, and moisture condenser, is incorporated into the system bias check.

A system response time test for each parameter was performed and documented during the initial system bias check. A stratification test was performed including the required traverse points determined according to EPA Method 7E, Section 8.1.2.

# 5. Quality Assurance/Quality Control

# 5.1 Overview

During the monitoring phase of the program, a strict quality assurance/quality control (QA/QC) program was followed. The QA/QC aspects of the program are discussed below.

# 5.2 Leak Check Procedures

During equipment setup, prior to conducting the RATA program, AECOM's instrumental measurements systems were leak-checked and verified to be leak free. Following the initial leak check, the bias and drift criteria specified in EPA Method 7E (40 CFR 60, Appendix A) served as a continuous system integrity check. The leak checks are not a method requirement but helped ensure that bias and drift criteria were met during the test program.

# 5.3 Initial Calibration and QA Tests

The O<sub>2</sub>, CO<sub>2</sub>, CO, and NO<sub>x</sub> continuous emissions analyzers, as applicable, used in the AECOM instruments laboratory were first calibrated directly with nitrogen based zero gases followed by two upscale gases to adjust the calibration set points prior to method prescribed calibration QA tests. Results of QA tests including instrument calibration error, system bias, and system drift determinations are presented in **Appendix C**. Calibration gases used by AECOM were prepared in accordance with EPA Protocol 1 procedures. Copies of the calibration gas certification sheets are presented in **Appendix C**.

## 5.3.1 Calibration Error Tests

The O<sub>2</sub>, CO<sub>2</sub>, CO, and NO<sub>x</sub> continuous emissions analyzers, as applicable, were tested directly for responses to nitrogen based zero gases followed by two upscale gases in order to determine calibration error. During the calibration error tests, no adjustments were made to the analyzer calibration set points. Next, the analyzer responses through the entire sampling system were checked with zero and one upscale EPA Protocol 1 gas prior to and following each set of test runs.

Calibration Error limit =  $\pm 2\%$  of calibration span

## 5.3.2 Sampling System Bias Checks

A sample acquisition and conditioning system bias check was performed by first challenging each analyzer directly to determine calibration error and then conducting a system check using zero gas and one representative upscale gas. During the system bias check, each gas was introduced at the base of the probe through the three-way valve and passed through the entire sample delivery and conditioning system from that point. The results were then compared to evaluate the absence or presence of any sample delivery or conditioning system bias. The criteria for system bias were met during the test program.

System Bias Limit = ±5% of calibration span

## 5.3.3 System Calibration Drift

Calibration drift was assessed for each analyzer during each test period as specified in EPA Method 7E, 40 CFR 60, Appendix A. Calibration drift for each analyzer was determined utilizing the following equation:

Percent Drift = <u>(initial system response - final system response) x 100</u> calibration span

Drift Limit =  $\pm 3\%$  of calibration span

# 5.4 Response Time Tests

During the system bias checks following the initial direct calibration error tests of each analyzer, system response time for both upscale and downscale tests were recorded. The upscale response test is the time required for 95% of the step change from a stable zero to a stable upscale reading. Similarly, the downscale response test is the time required for 95% of the step change from a stable zero to a stable upscale to a stable upscale to a stable zero reading. Results of system response time tests are presented in **Appendix C**.

# 5.5 NO<sub>2</sub> Converter Efficiency Test

Prior to, during, or following the test program, AECOM performed a nitrogen dioxide (NO<sub>2</sub>) converter efficiency test of each chemiluminescent analyzer in accordance with Section 16.2.25 of EPA Method 7E in 40 CFR 60, Appendix A. Copies of the instrument specific test results for this field program are presented in **Appendix C** of this document.

# 6. Reference Method Data Reduction

# 6.1 Overview

The objective of this program was to determine the emissions of NO<sub>X</sub> as well as exhaust gas  $O_2$  concentrations for the purposes of comparing the reference method (RM) determined values to the facility CEMS recorded values. A discussion of the data reduction process used to arrive at the RM emission values is presented below.

## 6.2 NO<sub>X</sub> Emission Rates – Pounds per Million Btu

Emission rates were calculated in units of pollutant mass per quantity of heat input (i.e., lb/MMBtu). The lb/MMBtu emission rates were calculated using the average measured pollutant and diluent concentrations (corrected for measurement bias and drift) along with the US EPA published "F Factor (Fd)" (Fd= 8,710 for natural gas). The measured average concentrations, expressed in units of parts per million by volume on a dry basis (ppmvd), were first converted to mass per unit dry volume (lb/dscf) for these calculations. The conversion factor for ppmvd to lb/dscf, as stated in Method 19 is:

$$\frac{lb}{dscf} = (ppmvd) * (Conversion Factors)$$

Note: Conversion factors used were NO<sub>X</sub> = 1.1947E-07, CO = 7.274E-08, NH<sub>3</sub> = 4.423E-08.

Next, the lb/dscf result was converted to the emission rate expressed in units of pounds per million British thermal units (lb/MMBtu) as follows:

$$\frac{lb}{MMBtu} = \left(\frac{lb}{dscf}\right) * (F_d) * (\frac{20.9}{20.9 - \% O_2})$$

Where:

F<sub>d</sub> = Ratio of the dry gas volume of the products of combustion to the heat content of the fuel expressed in units of dry standard cubic feet per million British thermal units (dscf/MMBtu). The oxygen-based dry F Factor (F<sub>d</sub>) of 8,710 dscf/MMBtu is taken from EPA Method 19 in 40 CFR 60, Appendix A.