

**Source Test Report for 2022 Compliance Testing
2512 Thermal Heat Recovery Oxidation Unit
Dow Silicones Corporation
State Registration No. A4043
Midland, Michigan**

Prepared For:

**Dow Chemical Company
693 Washington St #627
Midland, MI 48640**

Prepared By:

**Montrose Air Quality Services, LLC
951 Old Rand Road, Unit 106
Wauconda, IL 60084**

For Submission To:

**Technical Programs Unit
EGLE, Air Quality Division
Constitution Hall, 2nd Floor South
525 West Allegan Street
Lansing, MI 48933**

**Adam Shaffer
EGLE, Air Quality Division
401 Ketchum Street
Bay City, MI 48708**

Document Number: MW024AS-020190-RT-1549

Test Dates: August 24 and 25, 2022

Submittal Date: October 3, 2022



Review and Certification

All work, calculations, and other activities and tasks performed and presented in this document were carried out by me or under my direction and supervision. I hereby certify that, to the best of my knowledge, Montrose operated in conformance with the requirements of the Montrose Quality Management System and ASTM D7036-04 during this test project.

Signature:  **Date:** 09 / 29 / 2022

Name: William Craig James, QSTI **Title:** Vice President, Technical

I have reviewed, technically and editorially, details, calculations, results, conclusions, and other appropriate written materials contained herein. I hereby certify that, to the best of my knowledge, the presented material is authentic, accurate, and conforms to the requirements of the Montrose Quality Management System and ASTM D7036-04.

Signature:  **Date:** 09 / 29 / 2022

Name: Henry M. Taylor, QSTO **Title:** Senior Reporting QC Specialist

Table of Contents

<u>Section</u>	<u>Page</u>
1.0 Introduction	5
1.1 Summary of Test Program	5
1.2 Key Personnel	7
2.0 Plant and Sampling Location Descriptions.....	8
2.1 Process Description, Operation, and Control Equipment.....	8
2.2 Flue Gas Sampling Location	9
2.3 Operating Conditions and Process Data	9
3.0 Sampling and Analytical Procedures	10
3.1 Test Methods	10
3.1.1 EPA Method 1	10
3.1.2 EPA Method 320	10
3.2 Process Test Methods.....	11
4.0 Test Discussion and Results.....	12
4.1 Field Test Deviations and Exceptions.....	12
4.2 Presentation of Results.....	12
5.0 Internal QA/QC Activities	15
5.1 QA/QC Audits.....	15
5.2 QA/QC Discussion.....	15
5.3 Quality Statement	15

List of Appendices

A Field Data and Calculations	16
A.1 Sampling Location	17
A.2 FTIR Data	19
B Facility Process Data.....	57
C Quality Assurance/Quality Control	64
C.1 Units and Abbreviations	65
C.2 QA/QC Data.....	73
C.3 Accreditation Information/Certifications.....	88

RECEIVED
OCT 24 2022
AIR QUALITY DIVISION

List of Tables

1-1 Summary of Test Program 5
 1-2 Summary of Average Compliance Results – 2512 THROX Stack (High Flow) 6
 1-3 Summary of Average Compliance Results – 2512 THROX Stack (Low Temp) 6
 1-4 Test Personnel and Observers 7
 2-1 Sampling Location 9
 4-1 Ethylene Oxide (High Flow) Test Results - 2512 THROX Stack 13
 4-2 Ethylene Oxide (Low Temp) Test Results - 2512 THROX Stack 14

List of Figures

2-1 THROX Process Diagram 8
 3-1 EPA Method 320 Sampling Train 11

1.0 Introduction

1.1 Summary of Test Program

Dow Chemical Company (Dow) contracted Montrose Air Quality Services, LLC (Montrose) to perform a compliance emissions test program on the 2512 Thermal Heat Recovery Oxidation Unit (THROX) at the Dow Silicones Corporation (DSC) facility located in Midland, Michigan.

Testing was conducted pursuant to the requirements of Permit Nos. MI-ROP-A4043-2019a and MI-PTI-A4043-2019a issued by the Michigan Department of Environment, Great Lakes, and Energy (EGLE) and 40 CFR, Part 63, Subpart FFFF (MON Rule).

The specific objectives were to:

- Measure the concentration of ethylene oxide (EO) from the THROX stack during each of two test conditions (maximum stack gas flow [high flow] and low combustion temperature [low temp])
- Conduct the test program with a focus on safety

Montrose performed the tests to measure the emission parameters listed in Table 1-1.

Table 1-1
Summary of Test Program

Test Date	Unit ID/Source Name	Parameters	Test Methods	No. of Runs	Duration (Minutes)
8/24/2022	2512 THROX Stack (High Flow)	H ₂ O, EO	EPA 320	3	60
8/25/2022	2512 THROX Stack (Low Temp)	H ₂ O, EO	EPA 320	3	60

To simplify this report, a list of Units and Abbreviations is included in Appendix C.1. Throughout this report, chemical nomenclature, acronyms, and reporting units are not defined. Please refer to the list for specific details.

This report presents the test results and supporting data, descriptions of the testing procedures, descriptions of the facility and sampling location, and a summary of the quality assurance procedures used by Montrose. The average emission test results are summarized and compared to their respective permit limits in Tables 1-2 and 1-3. Detailed results for individual test runs can be found in Section 4.0. All supporting data can be found in the appendices.

The tests were conducted according to Proposal No. MW024AS-026749-PQ-1236 dated August 9, 2022.

**Table 1-2
Summary of Average Compliance Results – 2512 THROX Stack (High Flow)**

August 24, 2022

Parameter/Units	Average Results	Emission Limits
Ethylene Oxide (EO)		
ppmvw	0.288	--
ppmvd	0.324	--
ppmvd @ 3% O ₂ ¹	0.510	1.0

**Table 1-3
Summary of Average Compliance Results – 2512 THROX Stack (Low Temp)**

August 25, 2022

Parameter/Units	Average Results	Emission Limits
Ethylene Oxide (EO)		
ppmvw	0.169	--
ppmvd	0.181	--
ppmvd @ 3% O ₂ ¹	0.307	1.0

¹The stack gas O₂ concentration measured by Dow’s continuous emissions monitoring system was used to correct the EO ppmvd concentrations to 3% O₂.

1.2 Key Personnel

A list of project participants is included below:

Facility Information

Source Location: Dow Silicones Corporation
 1790 Building, Washington Street
 Midland, MI 48674

Project Contact: Rebekah Meyerholt
 Role: Sr. Environmental Specialist
 Company: Dow Chemical Company
 Telephone: 989-638-7824
 Email: RMeyerholt@dow.com

Agency Information

Regulatory Agency: Michigan EGLE, Air Quality Division
 Agency Contact: Lindsey Wells Adam Shaffer
 Telephone: 517-282-2345 989-225-4789
 Email: WellsL8@Michigan.gov ShafferA1@Michigan.gov

Testing Company Information

Testing Firm: Montrose Air Quality Services, LLC
 Contact: William Craig James
 Title: Vice President, Technical
 Telephone: 847-487-1580 Ext. 12419
 Email: wjames@montrose-env.com

Test personnel and observers are summarized in Table 1-4.

Table 1-4

Test Personnel and Observers

Name	Affiliation	Role/Responsibility
William Craig James	Montrose	Vice President, Technical/QSTI/Field Team Leader/FTIR Operator
Scott Dater	Montrose	Field Technician/QI/Sample Platform Duties/Field Support
Debbie Olsen	Montrose	Report Preparation
Rebekah Meyerholt	Dow	Client Liaison/Test Coordinator
Lindsey Wells	Michigan EGLE	Observer

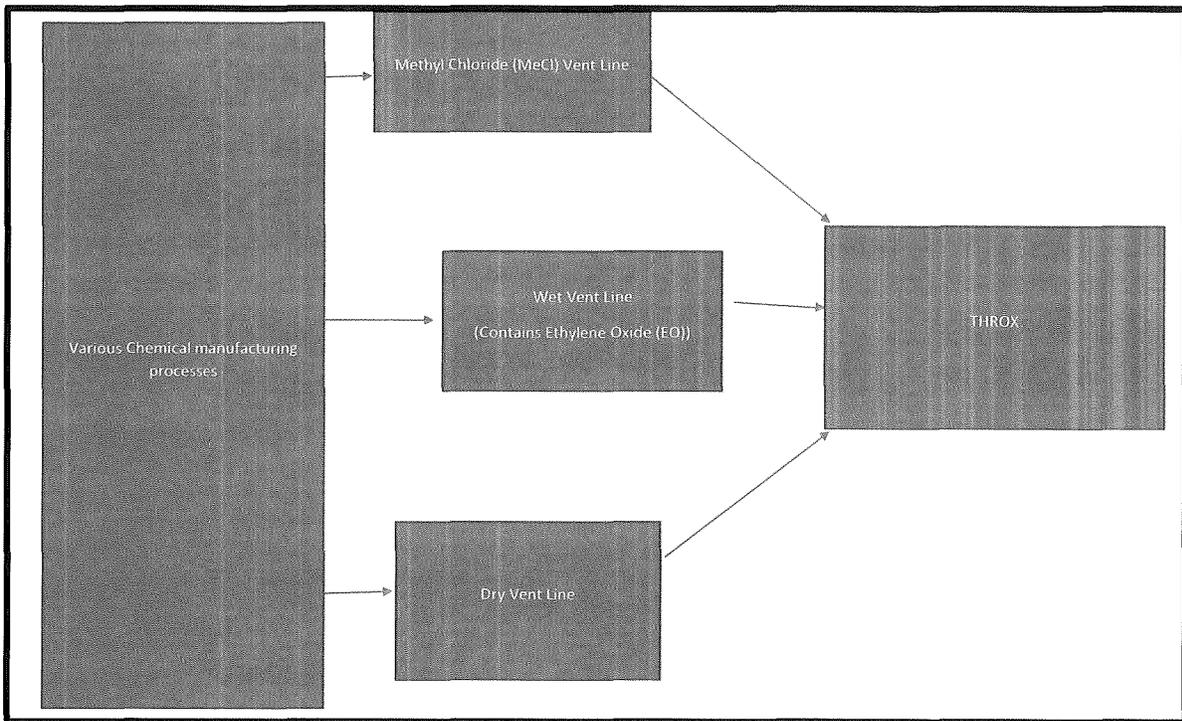
2.0 Plant and Sampling Location Descriptions

2.1 Process Description, Operation, and Control Equipment

Dow Silicones Corporation (DSC), a subsidiary of Dow, operates a chemical manufacturing facility in Midland, Michigan. The facility uses a thermal oxidizer with a caustic scrubber and two ionizing wet scrubbers, which is referred to as the 2512 thermal heat recovery oxidation unit (THROX), to control emissions from multiple chemical production facilities at the site. Emissions are routed from both batch and continuous process vents to the THROX through 3 consolidated vent header systems called the Wet Vent, Dry Vent, and the Methyl Chloride vent. Emissions controlled by the THROX include: VOCs, hazardous air pollutants (HAPs), PM₁₀, hydrogen chloride, and other toxic air contaminants.

The process diagram is presented in Figure 2-1.

Figure 2-1
THROX Process Diagram



2.2 Flue Gas Sampling Location

Information regarding the sampling location is presented in Table 2-1.

**Table 2-1
Sampling Location**

Sampling Location	Stack Inside Diameter (in.)	Distance from Nearest Disturbance		Number of Traverse Points
		Downstream EPA "B" (in./dia.)	Upstream EPA "A" (in./dia.)	
2512 THROX Stack	54	600 / 11.1	300 / 5.6	Gaseous: 1

The sample location was verified in the field to conform to EPA Method 1. Sampling was performed at a single point located at the centroid of the stack.

2.3 Operating Conditions and Process Data

Testing was performed while the batch process vents and continuous process vents were operating at maximum representative operating conditions as required by the permit and regulations.

Plant personnel were responsible for establishing the test conditions and collecting all applicable unit-operating data. The process data that was provided is presented in Appendix B. Data collected includes the following parameters:

- Flow Rates (2504, Dry Vent, Wet Vent, Methylene Chloride), lb/hr
- Exhaust Flow Rate, scfm
- Heat Input, MMBtu
- Temperatures (Zones 1 and 2), °F
- CEMS O₂, %

3.0 Sampling and Analytical Procedures

3.1 Test Methods

The test methods for this test program have been presented in Table 1-1. Additional information regarding specific applications or modifications to standard procedures is presented below.

3.1.1 EPA Method 1, Sample and Velocity Traverses for Stationary Sources

EPA Method 1 is used to assure that representative measurements of volumetric flow rate are obtained by dividing the cross-section of the stack or duct into equal areas, and then locating a traverse point within each of the equal areas. Acceptable sample locations must be located at least two stack or duct equivalent diameters downstream from a flow disturbance and one-half equivalent diameter upstream from a flow disturbance.

3.1.2 EPA Method 320, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive FTIR Spectroscopy

EPA Method 320 is an instrumental test method used to measure specific analyte concentrations for which EPA reference spectra have been developed or prepared. Extractive measurements of moisture and EO are performed using FTIR spectroscopy.

A MAX Analytical FTIR system enhanced with StarBoost™ technology was used for the EO analysis. StarBoost™ is a MAX Analytical add-on to an existing MKS Model 2030 FTIR analyzer. It combines infrared filtering, signal amplification, and advanced software algorithms to greatly increase the signal intensity, resulting in much lower detection limits.

The sample gas is withdrawn from the test location at a constant rate through a stainless-steel probe, a glass fiber filter and a Teflon sample line. The probe, filter and sample line are operated at a temperature of approximately 370°F to prevent the condensation of moisture and EO, and the clean, wet gas is directed to the FTIR spectrometer gas cell. Results from the analyzer are determined on a "wet" volume basis.

A calibration transfer standard (CTS) is introduced into the system and two spectra are recorded at least two minutes apart. As long as the second spectrum is no greater than the first and within the uncertainty of the gas standard, it is used as the CTS spectrum.

After the required pre-test procedures have been performed, stack gas is sampled continuously. Sample interferograms, processed absorbance spectra, background interferograms, CTS sample interferograms, and CTS absorbance spectra are recorded. Sample conditions, instrument settings, and test records are also recorded throughout the test. A new CTS spectrum is obtained after each sampling run. The post-test CTS spectrum is compared to the pre-test spectrum. The peak absorbance from each spectrum must be within 5% of the mean value.

RECEIVED

OCT 24 2022

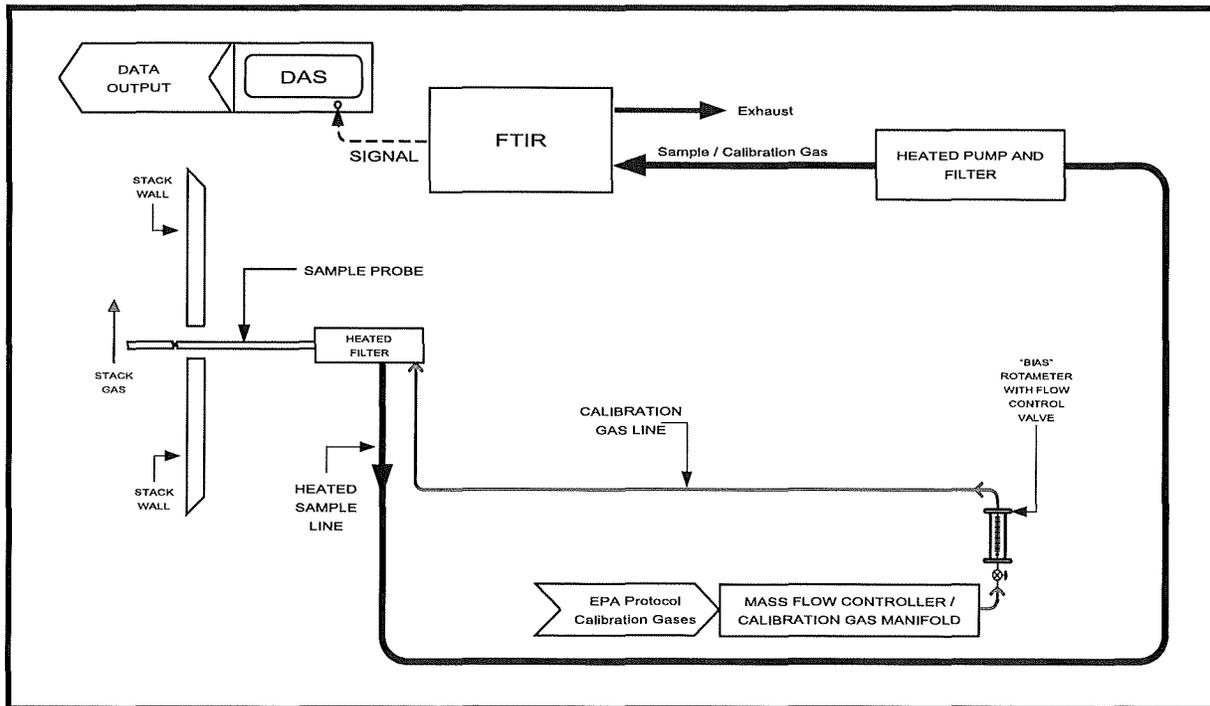
AIR QUALITY DIVISION

A system recovery check using the analyte spiking technique is performed prior to testing. First, some of the effluent gas is sampled in order to determine native concentration of target analytes. The analyte spike calibration gas is introduced to the FTIR gas cell and the results are determined using the analytical algorithm. Results from the calibration gas are recorded and compared to the certified value of the calibration gas. For reactive condensable gases the results must be within 10% or 5 ppm.

The analyte spike calibration gas is then directed through the entire sampling system and allowed to mix with effluent gas sample at a known flow rate. The flow ratio of calibration gas to source effluent must be no greater than a ratio of 1:10 for the determination of sample recovery. The dilution factor of the analyte spike concentration gas is calculated, and the bias between the observed spike value and the expected response is determined. The percent recovery of the spiked analytes is calculated. Spike recovery results must meet the data quality objectives of the test program. The average spiked concentration must be within 70% - 130% of the expected concentration.

The typical sampling system is detailed in Figure 3-1.

Figure 3-1
EPA Method 320 Sampling Train



3.2 Process Test Methods

The regulations did not require that process samples be collected during this test program; therefore, no process sample data are presented in this test report.

4.0 Test Discussion and Results

4.1 Field Test Deviations and Exceptions

No field deviations or exceptions from the test plan or test methods occurred during this test program.

4.2 Presentation of Results

The average results are compared to the permit limits in Table 1-2. The results of individual compliance test runs performed are presented in Tables 4-1 and 4-2. Emissions are reported in units consistent with those in the applicable regulations or requirements. Additional information is included in the appendices as presented in the Table of Contents.

**Table 4-1
Ethylene Oxide (High Flow) Test Results -
2512 THROX Stack**

Parameter/Units	1-High Flow	2-High Flow	3-High Flow	Average
Date	8/24/2022	8/24/2022	8/24/2022	--
Time	09:34-10:34	11:05-12:05	12:33-13:33	--
THROX Operational Parameters				
2504 flow, lb/hr	137.1	134.8	159.8	143.9
temperature, zone 1, °F	1,999.5	1,998.4	1,997.9	1,998.6
temperature, zone 2, °F	1,999.3	1,998.6	1,998.2	1,998.7
dry vent flow, lb/hr	2,838	2,805	2,770	2,804
wet vent flow, lb/hr	647	691	744	694
MeCl flow, lb/hr	48.6	46.9	113.9	69.8
THROX exhaust flow, scfm	8,476.2	8,256.9	7,890.9	8,208.0
heat input, MMBtu	25.7	25.6	26.0	25.8
CEMS oxygen, %	9.56	9.55	9.47	9.53
Ethylene Oxide (EO)				
ppmvw	0.301	0.253	0.311	0.288
moisture, % vol.	10.77	11.43	10.87	11.02
ppmvd	0.337	0.286	0.349	0.324
ppmvd @ 3% O ₂	0.533	0.450	0.547	0.510

EO Calculations:

$$EO_{\text{ppmvd}} = (EO_{\text{ppmvw}}) \left(\frac{1}{1 - \text{fractional moisture}} \right)$$

$$EO_{\text{ppmvd@3\%O}_2} = (EO_{\text{ppmvd}}) \left(\frac{20.9\% - 3\%}{20.9\% - \text{Stack O}_2} \right)$$

**Table 4-2
Ethylene Oxide (Low Temp) Test Results -
2512 THROX Stack**

Parameter/Units	1-Low Temp	2-Low Temp	3-Low Temp	Average
Date	8/25/2022	8/25/2022	8/25/2022	--
Time	09:26-10:26	10:47-11:47	12:14-13:14	--
THROX Operational Parameters				
2504 flow, lb/hr	212.5	199.3	195.1	202.3
temperature, zone 1, °F	1,812.5	1,803.2	1,803.3	1,806.3
temperature, zone 2, °F	1,814.6	1,806.2	1,806.4	1,809.1
dry vent flow, lb/hr	2,226	2,265	2,318	2,270
wet vent flow, lb/hr	685	684	666	678
MeCl flow, lb/hr	72.4	66.0	26.2	54.9
THROX exhaust flow, scfm	5,475.8	5,207.9	5,114.7	5,266.1
heat input, MMBtu	14.2	13.9	13.8	14.0
CEMS oxygen, %	10.54	10.22	10.31	10.36
Ethylene Oxide (EO)				
ppmvw	0.102	0.078	0.327	0.169
moisture, % vol.	7.27	6.43	6.46	6.72
ppmvd	0.110	0.083	0.350	0.181
ppmvd @ 3% O ₂	0.190	0.139	0.591	0.307

EO Calculations:

$$EO_{ppmvd} = (EO_{ppmvw}) \left(\frac{1}{1 - \text{fractional moisture}} \right)$$

$$EO_{ppmvd@3\%O_2} = (EO_{ppmvd}) \left(\frac{20.9\% - 3\%}{20.9\% - \text{Stack } O_2} \right)$$

5.0 Internal QA/QC Activities

5.1 QA/QC Audits

The EPA Method 320 performance parameters measured included signal to noise tests, noise equivalent absorbance (NEA), detector linearity, background spectra, potential interferences, and cell and system leakage. Quality assurance procedures included baseline measurement with ultra-high purity nitrogen, measurement of a calibration transfer standard (~100 ppm ethylene), direct analyte calibration measurements, and measurements to determine baseline shift. SF₆ was also used as a tracer gas in the calibration gases to verify the sample delivery system integrity. A dynamic matrix spike was performed using EO with ethane as a tracer gas. The method QA/QC criteria were met.

5.2 QA/QC Discussion

All QA/QC criteria were met during this test program.

5.3 Quality Statement

Montrose is qualified to conduct this test program and has established a quality management system that led to accreditation with ASTM Standard D7036-04 (Standard Practice for Competence of Air Emission Testing Bodies). Montrose participates in annual functional assessments for conformance with D7036-04 which are conducted by the American Association for Laboratory Accreditation (A2LA). All testing performed by Montrose is supervised on site by at least one Qualified Individual (QI) as defined in D7036-04 Section 8.3.2. Data quality objectives for estimating measurement uncertainty within the documented limits in the test methods are met by using approved test protocols for each project as defined in D7036-04 Sections 7.2.1 and 12.10. Additional quality assurance information is included in the report appendices. The content of this report is modeled after the EPA Emission Measurement Center Guideline Document (GD-043).