TEST REPORT

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COMPLIANCE EMISSION TEST RESIN PLANT REGENERATIVE THERMAL OXIDIZER

BASF CORPORATION WYANDOTTE, MICHIGAN

B4359

PREPARED FOR:

BASF CORPORATION

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Montrose Project No. PROJ106279 ARI Test Report No. 916-04 ARI Proposal No. 29216 Revision 1 BASF Corporation P.O. No. 4932897180 Test Date: December 6, 2016



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STATEMENT OF CONFORMANCE AND TEST REPORT CERTIFICATION

I certify, to the best of my knowledge, that this test program was conducted in a manner conforming to the criteria set forth in ASTM D7036-12: <u>Standard Practice for Competence of Air Emission Testing Bodies</u>, and that project management and supervision of all project related activities were performed by qualified individuals as defined by this practice.

I further certify that this test report and all attachments were prepared under my direction or supervision in accordance with the ARI Environmental, Inc. quality management system designed to ensure that qualified personnel gathered and evaluated the test information submitted. Based on my inquiry of the person or persons who performed the sampling and analysis relating to this performance test, the information submitted in this test report is, to the best of my knowledge and belief, true, accurate, and complete.

William Craig James, QSTI Regional Vice President, Great Lakes Region ARI Environmental, Inc.

Henry M. Taylor, QSTQ Quality Assurance Manager, Source Testing Division ARI Environmental, Inc.



Introduction and Summary

ARI Environmental, Inc. (ARI), an affiliate of Montrose Environmental Group, Inc., was retained by BASF Corporation (BASF) to conduct a compliance emission test on the Resin Plant Regenerative Thermal Oxidizer (RTO) at their facility in Wyandotte, Michigan.

The purpose of the test was to determine the concentrations and emission rates of nonmethane volatile organic compounds (VOC) and ethyl acrylate and the VOC destruction efficiency (DE).

Three 60-minute test runs were conducted simultaneously on the RTO inlet and stack on December 6, 2016.

At the RTO inlet and stack, the non-methane VOC concentration was determined in accordance with USEPA Method 25A using total hydrocarbon analyzers that are equipped with a heated flame ionization detector (FID).

At the RTO stack, direct interface Fourier transform infrared (FTIR) instrumentation was used to determine the ethyl acrylate and methane concentrations in accordance with USEPA Method 320.

Where applicable, testing was conducted pursuant to the following procedures and/or regulations:

- <u>Code of Federal Regulations</u>, Title 40, Part 60 (40 CFR 60), Appendix A, USEPA Methods 1-4 and 25A
- 40 CFR 51, Appendix M, USEPA Method 205
- 40 CFR 63, Appendix A, USEPA Method 320
- Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods
- ASTM Method D6348-03 Determination of Gaseous Compounds by Extractive Direct Interface FTIR Spectroscopy

Mr. Jordan Thompson of BASF coordinated the test and monitored process operations. The testing was performed by Messrs. Steve Flaherty, Craig James, Matt McDivitt and Chris Trevillian of ARI. Mr. Tom Maza from the Michigan Department of Environmental Quality witnessed the test.

The average test results are summarized in Table 1-1.

This report summarizes the test procedures and results of the test. Included, as appendices, is complete documentation of all calculation summaries, field data, FTIR data, ARI reference method monitoring data, process data, test equipment calibration data and test program qualifications.



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Introduction and Summary

TABLE 1-1. SUMMARY OF AVERAGE TEST RESULTS

	RTO Inlet	RTO Stack	
<u>Non-Methane VOC as Carbon</u> Concentration, ppmv wb Emission rate, lb/hr Destruction efficiency, %	769 8.11	196.3 2.12 73.99	95°2
Ethyl Acrylate Concentration, ppmv wb Emission rate, lb/hr		1.03 0.09	rr ()



2.1 OVERVIEW

ARI was retained by BASF to conduct a compliance emission test on the Resin Plant RTO at their facility in Wyandotte, Michigan.

Testing was conducted on December 6, 2016 and consisted of three 60-minute test runs performed simultaneously on the RTO inlet and stack.

2.2 METHODOLOGY

Where applicable, test procedures and sampling methodology followed 40 CFR 60, Appendix A, USEPA Methods 1-4 and 25A; 40 CFR 51, Appendix M, USEPA Method 205; 40 CFR 63, Appendix A, USEPA Method 320; ASTM Method D6348-03 (FTIR); and the <u>Quality Assurance</u> <u>Handbook for Air Pollution Measurement Systems</u>, Volume III, Stationary Source Specific Methods.

2.2.1 Sampling Point Locations (USEPA Method 1)

The sampling point locations used for the determination of gas velocity and volumetric flow rate were determined following the procedural requirements detailed in USEPA Method 1. The sampling locations and number of velocity sampling points were as follows:

Sampling	Duct Diameter/ Dimensions (inches)	No. of Ports	Port Location Downstream from Flow Disturbance (inches)	Port Location Upstream from Flow Disturbance (inches)	Sampling Points per Port	Total Points
RTO Inlet	23.75	2	102	21	8	16
RTO Stack	17.13 x 38.5	4	63	45.5	4	16

Cyclonic flow checks were performed to demonstrate that cyclonic flow conditions did not exist at the sampling locations.

2.2.2 Velocity and Volume Flow Rate Determination (USEPA Method 2)

Gas velocity and volumetric flow rate were determined following USEPA Method 2 procedures. Velocity traverses were performed using a Type-S pitot tube with the velocity head pressure measured on a Dwyer oil gauge inclined manometer to the nearest 0.01 in. H_2O . Temperature measurements were performed with a chromel-alumel thermocouple connected to a digital direct read-out potentiometer.

2.2.3 Molecular Weight (USEPA Method 3A)

At the RTO stack, the carbon dioxide (CO_2) and oxygen (O_2) concentrations were determined in accordance with USEPA Method 3A using ARI's Servomex Model 1440 paramagnetic O_2 and non-dispersive infrared CO_2 analyzer. The CO_2 and O_2 concentrations determined at the RTO stack were used for the RTO inlet gas density and flow calculations.



Testing and Analytical Procedures

As shown in Figure 2-1, ARI's sampling system consisted of a heated probe followed by a calibration tee. The probe system was connected to a heated Teflon sampling line that transported the gas sample to an electronic chiller to remove moisture. The dry sample gas was then transported to a manifold system by a Teflon-lined sample pump and Teflon sample line. The manifold was connected with sample gas intake lines for ARI's analyzers.

The sampling system was calibrated with applicable zero, mid and high-range gases as specified in USEPA Method 3A. The calibration gases were generated from Protocol 1 calibration gases using an Environics Model 4040 Gas Dilution System. The dilution system was verified on site in accordance with USEPA Method 205.

Calibration error and measurement system bias tests were performed prior to testing, and a pre/post calibration drift test was performed on the analyzers. The average zero and calibration drift values obtained during each test run were used to correct each analyzer's raw data for instrument zero and drift for each respective test run.

The data were collected at 15-second intervals, and one-minute averages were calculated by ARI's data acquisition system that consisted of a datalogger connected to a computer for digital data storage and reduction.

2.2.4 Moisture Content (USEPA Method 4)

The RTO inlet flue gas moisture content was determined in accordance with USEPA Method 4 procedures. As shown in Figure 2-2, gas was extracted at a constant rate through a series of chilled impingers. The first two impingers contained deionized/distilled water, the third impinger was initially empty and the fourth impinger contained silica gel for final water vapor removal. The volume gain in the water impingers and weight gain in the silica gel impinger were used to calculate the moisture content using the psychrometric calculations listed in the method.

The RTO stack gas moisture content was determined using FTIR measurements in accordance with USEPA Method 4, Section 16.3.

2.2.5 Total VOC Determination (USEPA Method 25A)

Total VOC sampling was conducted in accordance with USEPA Method 25A using VIG Industries hydrocarbon analyzers equipped with a heated FID. As shown in Figure 2-3, the sample delivery system consisted of a stainless steel probe, filter and calibration tee (on the end of the probe) connected to a heated 250°F Teflon sampling line. The sampling lines connected directly into the analyzers located in ARI's monitoring trailer. The VOC analyzer is internally heated to keep the sample gas stream above its dew point.

The hydrocarbon analyzers were calibrated with applicable zero, low, mid and high-range gases as specified in USEPA Method 25A. The calibration gases were generated from Protocol 1 calibration standards using an Environics Model 4040 Gas Dilution System. The dilution system was verified on site in accordance with USEPA Method 205.



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FIGURE 2-2. USEPA METHOD 4 SAMPLING TRAIN (MOISTURE)

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2-4



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Testing and Analytical Procedures





Testing and Analytical Procedures

Calibration gases were introduced at the calibration tee located at the exit end of the sample probe. A pre-test calibration error test was performed prior to testing, and a post-test calibration drift test was performed after each test repetition on each analyzer. The results of the initial system calibration error test were within $\pm 5\%$ of the injected concentration. The zero and upscale calibration gas values obtained after each run were within the allowable drift of $\pm 3\%$ of span.

Each analyzer's data were collected at 15-second intervals by ARI's data acquisition system which consisted of an Omega OMB-DAQ-56 datalogger connected to a computer for digital data storage and reduction. DaqViewXL and Excel spreadsheet computer software were used for calculation of emission rates.

2.2.6 Gas Dilution System Verification (USEPA Method 205)

All applicable calibration gases were certified by USEPA Protocol 1 procedures. All diluted calibration standards were prepared using an Environics Model 4040 Gas Dilution System that was verified by a field evaluation following the requirements of USEPA Method 205.

ARI's Servomex Model 1440 paramagnetic O₂ analyzer was used for this procedure. It was initially calibrated following USEPA Method 3A procedures. After the calibration procedure was complete, two diluted standards and a USEPA Protocol 1 standard were alternately introduced in triplicate, and an average instrument response was calculated for each standard. No single response differed by more than $\pm 2\%$ from the average response for each standard. The difference between the instrument average and the predicted concentration was less than $\pm 2\%$ for each diluted standard. The difference between the certified gas concentration and the average instrument response for the USEPA Protocol 1 standard was less than $\pm 2\%$.

2.2.7 FTIR Single Instrument Spiking Validation (USEPA Method 301)

ARI has performed USEPA Method 301 spiking studies to validate the use of FTIR techniques to accurately measure the concentrations of methane and ethyl acrylate from RTO stacks.

The results of the validation studies were used to determine if the FTIR procedures are valid for this type of stationary source. USEPA Method 320 allows the validation of FTIR-based measurements by a pair-wise comparison between the results of a single FTIR system.

The results of the validation studies indicated an accuracy of $<\pm 2\%$ for the specific compounds; therefore, a bias correction factor is not needed. All of the statistical criteria in the method were met. The validation studies are on file at ARI.

2.2.8 Ethyl Acrylate and Methane Determination using FTIR Spectroscopy (USEPA Method 320)

Ethyl acrylate and methane sampling was conducted using FTIR instrumentation following the principles of USEPA Method 320 and ASTM Method D6348-03.



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Testing and Analytical Procedures

ARI used an MKS Model MultiGas 2030 FTIR to measure the concentrations of ethyl acrylate and methane. The MultiGas 2030 analyzer is composed of a 2102 process FTIR spectrometer, a high optical throughput sampling cell, analysis software and a quantitative spectral library. The analyzer collects high resolution spectra in the mid infrared spectral region (400 to 4,000 cm⁻¹), which are analyzed using the quantitative spectral library. This provides an accurate, highly sensitive measurement of gases and vapors.

As shown in Figure 2-4, the sample delivery system consisted of a stainless steel sampling probe, calibration tee, Teflon sampling line, fast loop bypass pump, dilution system and sample manifold. The gas sample was continuously extracted from the source at approximately 8 liters per minute.

It should be noted that the main principles and calibration procedures of USEPA Method 320 were followed. USEPA Method 320 specifies a number of analytical uncertainty parameters that the analyst calculated to characterize the FTIR system performance. However, this did not provide analytical detection limits. To calculate the method detection limit (MDL) for the target compounds, the guidelines in Appendix B of 40 CFR 136 were followed. With this, the Student t-test is used to calculate the MDL for each analyte at a 99% confidence level. This follows USEPA guidelines for reporting of zeroes or non-detects and also meets the NELAC requirements for determination of MDL values.

The MKS software calculates the analytical error of the FTIR measurement which includes the root mean standard deviation (RMSD). The concentration uncertainty reported by MKS is called the standard error of estimated concentration (SEC) and is also known as the marginal standard deviation. The uncertainties in the concentration are proportional to the square root of the sums of the squares of the residual. After the residual spectrum is obtained, which is called R, the error variance for the case of a single reference spectrum is calculated by the software.

Independent calculations of optical path length were not performed because the instrument has a fixed path of 5.11 meters. A signal to noise ratio test (S/N) was performed using MKS software to verify instrument performance.

Performance parameters measured included signal to noise tests, noise equivalent absorbance (NEA), detector linearity, background spectra, potential interferents 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 evaluate dilution ratios and verify the sample delivery system integrity. A dynamic matrix spike was performed using SF₆ as a tracer gas.

The general FTIR field sampling procedure was as follows:



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Testing and Analytical Procedures





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Testing and Analytical Procedures

PRE-TEST

- 1) Background spectrum
 - Evaluate diagnostics of the instrumentation
- 2) Baseline (cylinder UHP-N₂ for zero check)
 - Determine the level of background noise
 - Observe spectrum for baseline tilt, i.e., indicates vibrations/perturbations affecting instrument
 - Calibration transfer standard (cylinder 100 ppm ethylene for span check)
 - Determine level of response to evaluate the spectral response and stability of the instrument
 - Create a field reference spectrum
- 4) Baseline evaluation
 - Note baseline flush/clean out FTIR sample cell
 - Observe spectrum for baseline tilt
- 5) Collection of spectra stack gas
 - Determine stack gas analyte concentrations
- 6) Measurement of analyte calibration gases
- 7) Perform dynamic spiking recovery study (recovery must be $0.7 \le R \le 1.3$)

TEST (REPEAT EACH RUN)

3)

- 1) Baseline determination
- 2) Measurement of calibration transfer standard
- 3) Collect sequential spectra of stack gas
- 4) Baseline determination
- 5) Measurement of calibration transfer standard

POST-TEST

- 1) Baseline determination
- 2) Measurement of calibration transfer standard (i.e. span check)
- 3) Measurement of analyte calibration gas





The test results are presented in Tables 3-1 and 3-2.

The calculation summaries, field data, FTIR data, ARI reference method monitoring data, process data, calibration data and test program qualifications are included in the appendices.



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Test Results

TABLE 3-1. RTO INLET TEST RESULTS

TEST RUN NO. :	1	2	3	
TEST DATE :	12/6/2016	12/6/2016	12/6/2016	
TEST TIME :	<u>11:06-12:06</u>	<u>13:02-14:02</u>	<u>14:30-15:30</u>	<u>Average</u>
Inlet Gas Parameters				
Temperature, °F	109.4	114.8	117.4	113.9
Velocity, av. ft/sec	33.80	32.95	32.61	33.12
Volumetric flow, acfm	6,239	6,082	6,020	6,114
Volumetric flow, scfm	5,822	5,618	5,477	5,639
Volumetric flow, sofh	349,311	337,089	328,599	338,333
Volumetric flow, dscfm	5,775	5,506	5,425	5,569
Volumetric flow, dscfh	346,523	330,384	325,491	334,133
Moisture, av. % vol	0.80	1.99	0.95	1.24
Carbon Dioxide, av. % vol	0.2	0.3	0.3	0.3
Oxygen, av. % vol	19.9	20.0	20.2	20.0
Inlet Total VOC as Carbon				
Concentration				
ppmv wb	727	867	714	769
x10 ⁻⁶ lb/scf	22.635	27.000	22.248	23.961
Loading rate				
lb/hr	7.907	9 .101	7.311	8.106



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Test Results

TABLE 3-2. RTO STACK TEST RESULTS

TEST RUN NO.	1	2	3	
TEST DATE :	12/6/2016	12/6/2016	12/6/2016	
TEST TIME :	<u>11:06-12:06</u>	<u>13:02-14:02</u>	<u>14:30-15:30</u>	<u>Average</u>
Stack Gas Parameters				
Temperature, °F	161.5	165.6	165.8	164.3
Velocity, av. ft/sec	27.05	24.92	22.75	24.91
Volumetric flow, acfm	7,434	6,847	6,252	6,844
Volumetric flow, scfm	6,292	5,757	5,255	5,768
Volumetric flow, scfh	377,510	345,442	315,286	346,079
Volumetric flow, dscfm	6,208	5,682	5,188	5,693
Volumetric flow, dscfh	372,467	340,937	311,289	341,564
Moisture, av. % vol	1.34	1.30	1.27	1.30
Carbon Dioxide, av. % vol	0.2	0.3	0.3	0.3
Oxygen, av. % vol	19.9	20.0	20.2	20.0
Stack Non-Methane VOC as	Carbon			
Concentration				
dw vmqq	184.4	232.6	171.8	196.3
x10 ⁻⁶ ib/scf	5.745	7.246	5.353	6,115
Emission rate				
lb/hr	2.169	2,503	1.688	2.120
Destruction efficiency				
% by weight	72.57	72.50	76.92	73.99
Stack Ethyl Acrylate				
Concentration				
dw vmqq	1,364	0.144	1.573	1.027
x10 ⁻⁶ lb/scf	0.3544	0.0375	0.4088	0.2669
Emission rate				
lb/hr	0.134	0.013	0.129	0.092



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Calculation Summaries

SUMMARY OF TEST RESULTS

TABLE

RTO Inlet Total Non-Methane VOC Results Summary

BASF Wyandotte, MI Resin Plant RTO Inlet				
12/6/2016 1106-1206 1	12/6/2016 1302-1402 2	12/6/2016 1430-1530 3	Average	
109.4	114.8	117.4	113.9	
33.80	32.95	32.61	33.12	
6,239	6,082	6,020	6,114	
5,822	5,618	5,477	5,639	
349,311	337,089	328,599	338,333	
5,775	5,506	5,425	5,569	
346,523	330,384	325,491	334,133	
0.80	1.99	0.95	1.24	
/OC (as C1) Emis	sions:			
727	867	714	769	
22.635	27.000	22.248	23.961	
7,907	9.101	7,311	8.106	
	BASF Wyandotte, MI Resin Plant RTO 12/6/2016 1106-1206 1 109.4 33.80 6,239 5,822 349,311 5,775 346,523 0.80 /OC (as C1) Emis 727 22.635 7.907	BASF Wyandotte, MI Resin Plant RTO Inlet 12/6/2016 12/6/2016 1106-1206 1302-1402 1 2 . 109.4 114.8 33.80 32.95 6,239 6,082 5,822 5,618 349,311 337,089 5,775 5,506 346,523 330,384 0.80 1.99 /OC (as C1) Emissions: 727 867 22.635 27.000 7.907 9.101	BASF Wyandotte, MI Resin Plant RTO Inlet 12/6/2016 $12/6/2016$ $12/6/20161106-1206$ $1302-1402$ $1430-15301$ 2 3 1 2 3 109.4 114.8 117.4 33.80 32.95 $32.616,239$ $6,082$ $6,0205,822$ $5,618$ $5,477349,311$ $337,089$ $328,5995,775$ $5,506$ $5,425346,523$ $330,384$ $325,4910.80$ 1.99 $0.95/OC (as C1) Emissions:727$ 867 714 22.635 27.000 $22.2487.907$ 9.101 7.311	

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USEPA Method 4 Moisture Determination Sample Calculations

Client:BASFLocation:Wyandotte, MISource:Resin Plant RTO Inlet FlowsDate:12/6/2016Run #:1Time:1106-1206

Data Input:

Volume metered (V _m):	39.761 ft°
Meter calibration coefficient (Y _d):	0.997 dimensionless
Barometric pressure (P _{bar}):	29.80 inches Hg
Meter sample rate (∆H):	1.50 inches H ₂ O
Meter inlet/outlet temperature (T _m):	50.9 °F
Volume of moisture collected (V _{to}):	7.0 milliliters
Stack Temperature (T _s):	109.4
Static Pressure (St):	4.20 inches H ₂ O

Sample calculations @ standard conditions (29.92 inches Hg, 68.0 °F):

Volume of sample, dry basis:

$Vm_{std} = V_m \times Y_d \times \left(\frac{528.0^{\circ} R}{29.92'' Hg}\right) \times \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m + 460}\right)$	=	40.955 dscf
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Volume of water vapor in sample:

$$Vw_{std} = \frac{0.04707ft^3}{ml} \times V_{tc}$$
 = 0.329 scf

Fractional moisture content of stack gas:

$$B_{wo} = \frac{Vw_{sd}}{(Vm_{sd} + Vw_{sd})} = 0.0080 B_{wo}$$

Percent Moisture:

%moisture =
$$B_{wo} \times 100$$
 = 0.80 %

Fractional moisture content of stack gas at saturated conditions:

$T_{s(PK)} = ((T_s - 32) * 0.5556) + 273 = 316.0$	°Kelvin
---	---------

$$P_{s(mmHg)} = \left(P_{bar} + \frac{S_{t}}{13.6}\right) \times 25.401 = 756.95 \text{ mm Hg}$$

$$B_{wos} = \frac{\left(\frac{10^{\left(A_{v}\left(\frac{B}{(T_{u(v_{0})},C)}\right)}\right) - 0.5}{P_{s(mmH_{0})}} \frac{where:}{A = 0.361}{B = 1.693.5} = 0.0816 B_{wos}$$

Percent moisture at saturated conditions:

%moisture _{saturated}	$= B_{wos} \times 100$	=	8.16 %
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Percent moisture used for emissions calculations:

0.80 %

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