# 1.0 INTRODUCTION

Montrose Air Quality Services, LLC (MAQS) was retained by Corteva Agriscience (Corteva) to conduct an evaluation of the Ammonia (NH3) concentrations and emissions from the TTU-865 and TTU-870 exhaust stacks. The scrubber is located at the Corteva facility in Harbor Beach, Michigan. The evaluation consisted of triplicate approximately 60-minute test runs at each sampling location. US EPA Methods 1, 2, 3, 4, CTM-027 and 320 were utilized to perform the study.

EGLE has published a guidance document entitled "Format for Submittal of Source Emission Test Plans and Reports" (March 2018). The following is a summary of the emissions test plan in the format suggested by the EGLE test plan format guide.

## 1.a IDENTIFICATION, LOCATION, AND DATES OF TEST

Sampling and analysis for the emission test program was conducted on January 27-28, 2020 at the Corteva facility in Harbor Beach, Michigan. The test program included evaluation of NH3 emissions from the TTU-865 and TU-870 exhaust stacks.

## 1.b PURPOSE OF TESTING

Permit No. ROP MI-ROP-B4942 and PTI 107-18A, issued by State of Michigan Division of Environmental Quality, governs this process.

The allowable NH3 emission rate by permit is:

31 pounds per hour of ammonia from EUPROCESS pursuant to rule 201(1)(b).

## 1.c SOURCE DESCRIPTION

EU_PROCESS process vent emissions are collected in a common header and routed to one of five thermal treatment units. Four of the units are catalytic thermal treatment units (TTUs). The fifth unit is a newly commissioned regenerative thermal oxidizer (RTO) installed under Permit 107-18A. The additional control device was installed to increase redundancy and to improve the reliability of the control system for EU_PROCESS.

Prior to venting to the atmosphere, all associated fermentation, crystallization, and packaging process vents are sent to one of the five TTUs. The 4 catalytic units currently operate at a minimum firebox temperature of 650°F. The RTO operates at a minimum firebox temperature of 1,550°F.

The TTUs primary function is to control VOC. VOC may include MeOH, organic acids, and cyclical volatiles. Ammonia may also be present in process vents routed to the TTUs.

### 1.d TEST PROGRAM CONTACT

Mr. Matthew Young
District Manager
Montrose Air Quality Services
4949 Fernlee Avenue
Royal Oak, Michigan 48073
Phone (586) 744-9133

Mr. Jim McGee
Corteva Agriscience
Harbor Beach Operations
305 North Huron Avenue
Harbor Beach, Michigan 48441
(989) 479-5283

**Table 1**
**Testing Personnel Summary**

| Name and Title | Affiliation | Telephone |
|---|---|---|
| Mr. Jim McGee<br>Envrionment, Health, Safety, an<br>Security | Corteva Agriscience<br>305 North Huron Avenue<br>Harbor Beach, Michigan<br>48441 | (989) 479-5283 |
| Mr. Matthew Young<br>District Manager | MAQS<br>4949 Fernlee Avenue<br>Royal Oak, MI 48073 | (586) 744-9133 |
| Mr. Mike Nummer<br>Field Technician | MAQS<br>4949 Fernlee Avenue<br>Royal Oak, MI 48073 | (248) 548-8072 |
| Mr. Dave Schuberg<br>Field Technician | MAQS<br>2625 Denison Drive<br>Mt Pleasant, MI 48858 | (989) 772-5088 |

## 2.0 SUMMARY OF RESULTS

Sections 2.a through 2.d summarize the results of the emissions compliance test program.

### 2.a OPERATING DATA

Operating data monitored included the firebox temperature of each TTU. TTU-865 has a minimum firebox temperature of 650°F. The RTO operates at a minimum firebox temperature of 1,550°F.

### 2.b APPLICABLE PERMIT

The applicable permit for this emissions test program is Permit No. ROP MI-ROP-B4942 and PTI 107-18A.

### 2.c RESULTS

The overall results of the emission test program are summarized by Table 2 (see Section 5.a). Detailed results for each run can be found in Tables 3-4.

### 2.d EMISSION REGULATION COMPARISON

The results summarized by Table 2 (section 5.a) shows that the NH3 emissions are below the limits summarized by section 1.b.

## 3.0 SOURCE DESCRIPTION

Sections 3.a through 3.e provide a detailed description of the process.

### 3.a PROCESS DESCRIPTION

EU_PROCESS process vent emissions are collected in a common header and routed to one of five thermal treatment units. Four of the units are catalytic thermal treatment units (TTUs). The fifth unit is a newly commissioned regenerative thermal oxidizer (RTO) installed under Permit 107-18A. The additional control device was installed to increase redundancy and to improve the reliability of the control system for EU_PROCESS.

Prior to venting to the atmosphere, all associated fermentation, crystallization, and packaging process vents are sent to one of the five TTUs. The 4 catalytic units currently operate at a minimum firebox temperature of 650ºF. The RTO operates at a minimum firebox temperature of 1,550ºF.

The TTUs primary function is to control VOC. VOC may include MeOH, organic acids, and cyclical volatiles. Ammonia may also be present in process vents routed to the TTUs.

### 3.b RAW AND FINISHED MATERIALS

The TTUs primary function is to control VOC. VOC may include MeOH, organic acids, and cyclical volatiles. Ammonia may also be present in process vents routed to the TTUs.

### 3.c PROCESS CAPACITY

N/A

### 3.d PROCESS INSTRUMENTATION

The Start and Stop times were recorded by Corteva personnel and the firebox temperatures are included in appendix F.

## 4.0 SAMPLING AND ANALYTICAL PROCEDURES

Sections 4.a through 4.d provide a summary of the sampling and analytical procedures used.

### 4.a SAMPLING TRAIN AND FIELD PROCEDURES

Measurement of exhaust gas velocity, molecular weight, and moisture content was conducted using the following reference test methods codified at Title 40, Part 60, Appendix A of the Code of Federal Regulations (40 CFR 60, Appendix A):

- Method 1 - "Location of the Sampling Site and Sampling Points"
- Method 2 - "Determination of Stack Gas Velocity and Volumetric Flowrate"
- Method 3 - "Determination of Molecular Weight of Dry Stack Gas"
- Method 4 - "Determination of Moisture Content in Stack Gases"
- CTM-027 - "Procedure for Collection and Analysis of Ammonia in Stationary Sources"
- Method 320 - "Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy"

Stack gas velocity traverses were conducted in accordance with the procedures outlined in Methods 1 and 2. Figures 1 and 2 present the test port and traverse/sampling point locations used. A cyclonic flow evaluation was conducted at each sampling location. An S-type pitot tube and thermocouple assembly calibrated in accordance with Method 2, Section 4.1.1 was used to measure exhaust gas velocity pressures and temperatures during testing. Because the pitot tube dimensions outlined in Sections 2.6 through 2.8 were within the specified limits, the baseline pitot tube coefficient of 0.84 (dimensionless) was assigned for this testing.

Molecular weight determinations were conducted according to Method 3. The equipment used for this evaluation consisted of a one-way squeeze bulb with connecting tubing and a set of Fyrite® combustion gas analyzers. Moisture content was determined from the condensate collected in the CTM-027 sampling trains according to Method 4.

Conditional Test Method 027 (CTM-027) is a manual, isokinetic test method used to determine $NH_3$ emissions. This method is performed in conjunction with EPA Methods 1, 2, 3, and 4. The stack gas is sampled through a nozzle, an in-stack filter, probe and impinger train. A diagram of the CTM-027 train is included as figure 3. $NH_3$ is analyzed via ion chromatography and results are reported in emission concentrations and emission rate units.

A sampling train and pitot tube leak test was conducted before and after each test run. Upon completion of the final leak check for each test run, the impinger train was carefully disassembled. The liquid volume of each impinger was measured gravimetrically and any volume increase was noted on field sheets. The impinger catch solution was then transferred to a pre-cleaned sample container. Each impinger was then triple rinsed with deionized water (DI $H_2O$), and the rinses added to a specfic sample container. Each container was labeled with the test number, test location, test date and the level of liquid was marked on the outside of each container. The samples were then placed in a sealed cooler for storage. In addition, blank samples of the 0.1N H2SO4 and DI were collected. MAQS personnel shipped the samples to

Enthalpy Analytical Laboratories in Durham, North Carolina for analysis. All appropriate QA/QC measures were strictly adhered to. Results of the laboratory tests are included in Appendix D.

### 4.b RECOVERY AND ANALYTICAL PROCEDURES

Recovery and analytical procedures were described in Section 4.a.

### 4.c SAMPLING PORTS

Sampling ports are located on the stack and meet method 1 criteria.

### 4.d TRAVERSE POINTS

Sampling port and traverse point locations for TTU-865 and TTU-870 exhaust stacks are illustrated by Figures 1 and 2.

## 5.0 TEST RESULTS AND DISCUSSION

Sections 5.a through 5.k provide a summary of the test results.

### 5.a RESULTS TABULATION

The results of the emissions test program are summarized by Table 2.

**TABLE 2**
**Test Program NH3 Emission Rates Summary**

| Unit | Emission Rate | | Permit Limit | |
|---|---|---|---|---|
| | NH3 (lb/hr) | NH3 (PPMV, Dry) | NH3 (lb/hr) | NH3(PPMV, Dry) |
| TTU-865 | 0.003 | 0.1 | 31 | |
| TTU-870 | 0.138 | 1.9 | 31 | |

Detailed data for each test run can be found in Tables 3-4.

### 5.b DISCUSSION OF RESULTS

Emission limitations for Permit No. MI-ROP-B4942 and PTI 107-18A are summarized by section 1b. The results of the emissions test program are summarized by Table 2 (see section 5.a). Detailed results for each run are summarized by Tables 3-4.

USEPA Method 320 was performed onsite during testing of TTU-870 for comparison purposes with the CTM-027 sampling train. The FTIR was run from approximately 11:00-17:20, and yielded an average of 1.9 ppmv wet. The CTM-027 sampling train was run from approximately 13:00-17:20, and yielded an average of 1.9 ppmv dry. The FTIR average moisture for the

duration of the sample was 3.19 percent. The FTIR average was then corrected to ppmv dry using the following equation:

$$\frac{1.9\ ppmv\ wet}{1 - 0.0319} = 1.96\ ppmv\ dry$$

The results of the FTIR are within 3% of the CTM-027. The FTIR was again used on January 28th, 2020 as an investigation of the higher than anticipated ammonia results for both TTU-865 and TTU-870 from the testing performed on October 22-23, 2019 during the PAI MACT test program. After completion of testing on TTU-865, the FTIR was used to sample on TTU-870 while simulating process scenarios that were anticipated to have caused the higher than normal readings from the October test program.

Test results from the October testing showed an average NH3 result of 0.48 pounds per hour per CTM-027. The Results from the testing performed on January 27th, 2020 showed an average NH3 result of 0.14 pounds per hour per CTM-027. FTIR Data was calculated during the investigation testing and showed an average NH3 result of 0.19 pounds per hour. A detailed FTIR report is included in this report as Appendix E.

### 5.c SAMPLING PROCEDURE VARIATIONS

There were no sampling procedure variations during the test program.

### 5.d PROCESS OR CONTROL DEVICE UPSETS

No upset conditions occurred during testing.

### 5.e CONTROL DEVICE MAINTENANCE

No maintenance was performed during the test program.

### 5.f AUDIT SAMPLE ANALYSIS

There was no audit sample during the test program.

### 5.g CALIBRATION SHEETS

Relevant equipment calibration documents are provided as Appendix B.

### 5.h SAMPLE CALCULATIONS

Sample Calculations are provided in Appendix C.

### 5.i FIELD DATA SHEETS

Field documents relevant to the emissions test program are presented in Appendix A.

## 5.j LABORATORY DATA

Laboratory results are presented in Appendix D.

# Tables

**Table 3**
**NH3 Emission Rates**

| **Company** | **Corteva** | | | |
|---|---|---|---|---|
| **Source Designation** | **TTU 865** | | | |
| **Test Date** | **1/28/2020** | **1/28/2020** | **1/28/2020** | |
| | | | | |
| **Meter/Nozzle Information** | P-1 | P-2 | P-3 | Average |
| Meter Temperature Tm (F) | 64.6 | 66.5 | 68.6 | 66.6 |
| Meter Pressure - Pm (in. Hg) | 29.5 | 29.5 | 29.5 | 29.5 |
| Measured Sample Volume (Vm) | 54.3 | 52.5 | 53.9 | 53.6 |
| Sample Volume (Vm-Std ft3) | 54.6 | 52.5 | 53.7 | 53.6 |
| Sample Volume (Vm-Std m3) | 1.55 | 1.49 | 1.52 | 1.52 |
| Condensate Volume (Vw-std) | 2.452 | 2.310 | 2.923 | 2.562 |
| Gas Density (Ps(std) lbs/ft3) (wet) | 0.0740 | 0.0740 | 0.0738 | 0.0739 |
| Gas Density (Ps(std) lbs/ft3) (dry) | 0.0752 | 0.0752 | 0.0752 | 0.0752 |
| Total weight of sampled gas (m g lbs) (wet) | 4.22 | 4.06 | 4.18 | 4.15 |
| Total weight of sampled gas (m g lbs) (dry) | 4.11 | 3.95 | 4.04 | 4.03 |
| Nozzle Size - An (sq. ft.) | 0.000504 | 0.000491 | 0.000504 | 0.000500 |
| Isokinetic Variation - I | 98.0 | 99.1 | 99.9 | 99.0 |
| **Stack Data** | | | | |
| Average Stack Temperature - Ts (F) | 289.1 | 305.3 | 309.0 | 301.1 |
| Molecular Weight Stack Gas- dry (Md) | 29.1 | 29.1 | 29.1 | 29.1 |
| Molecular Weight Stack Gas-wet (Ms) | 28.6 | 28.6 | 28.5 | 28.6 |
| Stack Gas Specific Gravity (Gs) | 0.989 | 0.989 | 0.985 | 0.988 |
| Percent Moisture (Bws) | 4.30 | 4.21 | 5.16 | 4.56 |
| Water Vapor Volume (fraction) | 0.0430 | 0.0421 | 0.0516 | 0.0456 |
| Pressure - Ps ("Hg) | 29.3 | 29.3 | 29.3 | 29.3 |
| Average Stack Velocity -Vs (ft/sec) | 43.5 | 43.4 | 43.5 | 43.4 |
| Area of Stack (ft2) | 12.6 | 12.6 | 12.6 | 12.6 |
| **Exhaust Gas Flowrate** | | | | |
| Flowrate $ft^3$(Actual) | 32,768 | 32,681 | 32,768 | 32,739 |
| Flowrate $ft^3$ (Standard Wet) | 22,649 | 22,113 | 22,064 | 22,276 |
| Flowrate $ft^3$ (Standard Dry) | 21,676 | 21,181 | 20,924 | 21,260 |
| Flowrate $m^3$ (standard dry) | 614 | 600 | 593 | 602 |
| **Total Ammonia Weight (ug)** | | | | |
| Total | 70 | 72 | 28 | 57 |
| **Total Ammonia Concentration** | | | | |
| lb/1000 lb (wet) | 0.000 | 0.000 | 0.000 | 0.000 |
| lb/1000 lb (dry) | 0.000 | 0.000 | 0.000 | 0.000 |
| mg/dscm (dry) | 0.0 | 0.0 | 0.0 | 0.0 |
| PPM (dry) | 0.1 | 0.1 | 0.0 | 0.1 |
| **Total Ammonia Emission Rate** | | | | |
| lb/ hr | 0.004 | 0.004 | 0.001 | 0.003 |

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**Table 4**
**NH3 Emission Rates**

| **Company** | **Corteva** | | | |
|---|---|---|---|---|
| **Source Designation** | **TTU 870** | | | |
| **Test Date** | **1/27/2020** | **1/27/2020** | **1/27/2020** | |
| | | | | |
| **Meter/Nozzle Information** | P-1 | P-2 | P-3 | Average |
| Meter Temperature Tm (F) | 73.3 | 73.6 | 74.0 | 73.6 |
| Meter Pressure - Pm (in. Hg) | 29.4 | 29.4 | 29.4 | 29.4 |
| Measured Sample Volume (Vm) | 43.9 | 44.9 | 43.8 | 44.2 |
| Sample Volume (Vm-Std ft3) | 43.2 | 44.2 | 43.0 | 43.4 |
| Sample Volume (Vm-Std m3) | 1.22 | 1.25 | 1.22 | 1.23 |
| Condensate Volume (Vw-std) | 1.415 | 1.603 | 1.745 | 1.587 |
| Gas Density (Ps(std) lbs/ft3) (wet) | 0.0742 | 0.0741 | 0.0739 | 0.0741 |
| Gas Density (Ps(std) lbs/ft3) (dry) | 0.0751 | 0.0751 | 0.0751 | 0.0751 |
| Total weight of sampled gas (m g lbs) (wet) | 3.31 | 3.39 | 3.31 | 3.34 |
| Total weight of sampled gas (m g lbs) (dry) | 3.24 | 3.31 | 3.23 | 3.26 |
| Nozzle Size - An (sq. ft.) | 0.000491 | 0.000504 | 0.000491 | 0.000495 |
| Isokinetic Variation - I | 99.5 | 100.2 | 101.1 | 100.3 |
| **Stack Data** | | | | |
| Average Stack Temperature - Ts (F) | 153.3 | 151.0 | 150.8 | 151.7 |
| Molecular Weight Stack Gas- dry (Md) | 29.0 | 29.0 | 29.0 | 29.0 |
| Molecular Weight Stack Gas-wet (Ms) | 28.7 | 28.7 | 28.6 | 28.6 |
| Stack Gas Specific Gravity (Gs) | 0.990 | 0.989 | 0.988 | 0.989 |
| Percent Moisture (Bws) | 3.28 | 3.50 | 3.90 | 3.56 |
| Water Vapor Volume (fraction) | 0.0317 | 0.0350 | 0.0390 | 0.0352 |
| Pressure - Ps ("Hg) | 29.3 | 29.3 | 29.3 | 29.3 |
| Average Stack Velocity -Vs (ft/sec) | 28.9 | 28.6 | 28.4 | 28.7 |
| Area of Stack (ft2) | 19.4 | 19.4 | 19.4 | 19.4 |
| **Exhaust Gas Flowrate** | | | | |
| Flowrate $ft^3$(Actual) | 33,621 | 33,241 | 33,071 | 33,311 |
| Flowrate $ft^3$ (Standard Wet) | 28,308 | 28,096 | 27,960 | 28,121 |
| Flowrate $ft^3$ (Standard Dry) | 27,380 | 27,112 | 26,870 | 27,121 |
| Flowrate $m^3$ (standard dry) | 775 | 768 | 761 | 768 |
| **Total Ammonia Weight (ug)** | | | | |
| Total | 1,275 | 1,778 | 1,940 | 1,664 |
| **Total Ammonia Concentration** | | | | |
| lb/1000 lb (wet) | 0.001 | 0.001 | 0.001 | 0.001 |
| lb/1000 lb (dry) | 0.001 | 0.001 | 0.001 | 0.001 |
| mg/dscm (dry) | 1.0 | 1.4 | 1.6 | 1.4 |
| PPM (dry) | 1.5 | 2.0 | 2.3 | 1.9 |
| **Total Ammonia Emission Rate** | | | | |
| lb/ hr | 0.107 | 0.145 | 0.161 | 0.138 |

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# Figures

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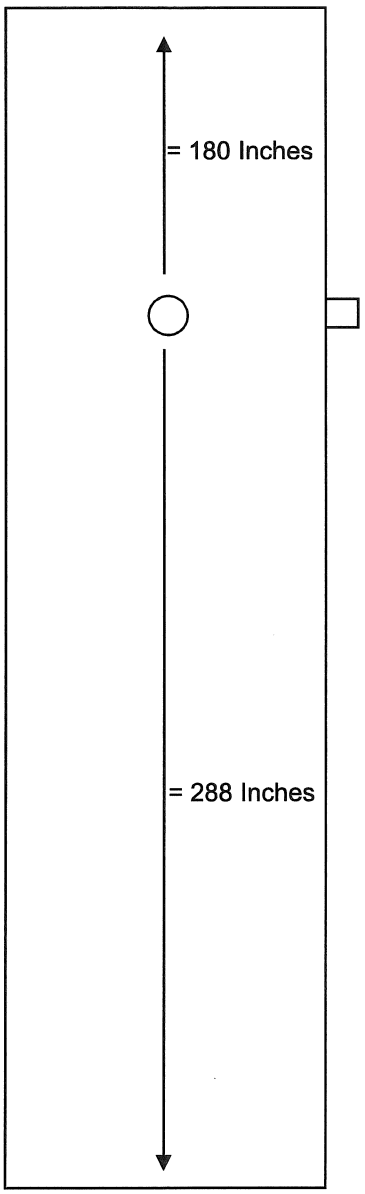
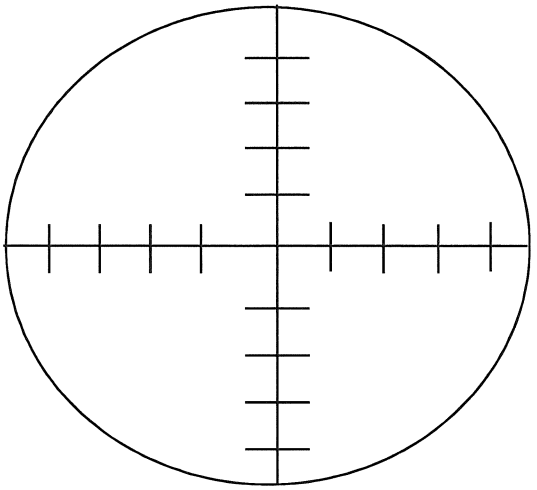
diameter = 48



Not to Scale

| Points | Distance " |
|---|---|
| 1 | 1.5 |
| 2 | 5.0 |
| 3 | 9.3 |
| 4 | 15.5 |
| 5 | 32.5 |
| 6 | 38.7 |
| 7 | 43.0 |
| 8 | 46.5 |

**Figure 1**

| | | |
|---|---|---|
| **Site:**<br>**TTU-865 Exhaust**<br>**Cortiva Agriscience**<br>**Harbor Beach, Michigan** | **Sampling Dates:**<br>**January 28, 2020** | **Montrose Air Quality Services, LLC**<br>**4949 Fernlee**<br>**Royal Oak, Michigan** |

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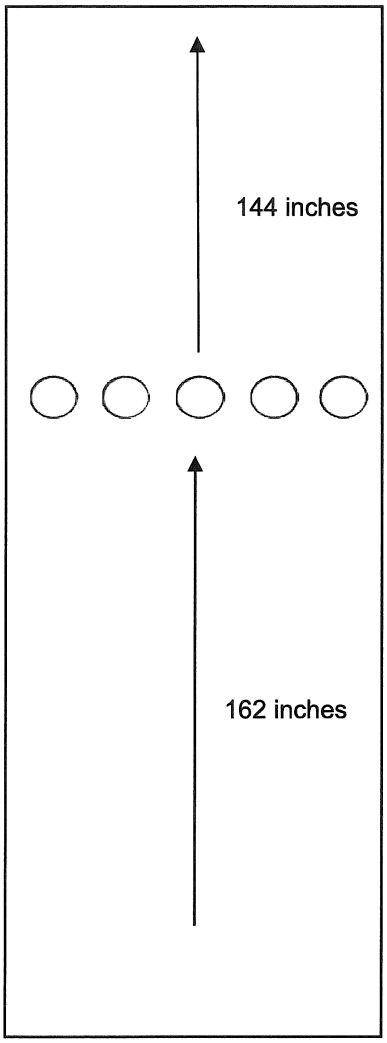
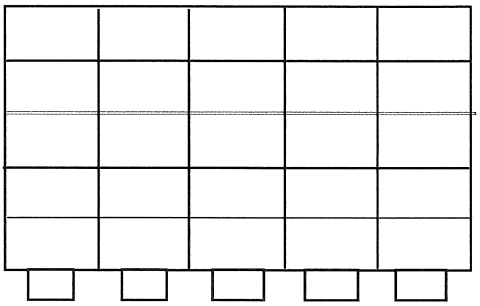
Stack Dimensions: 36 x 77.5



Not to Scale

| Points | Distance " |
|---|---|
| 1 | 4.5 |
| 2 | 10.8 |
| 3 | 18.0 |
| 4 | 25.2 |
| 5 | 32.4 |

**Figure 2**

| | | |
|---|---|---|
| **Site:**<br>**TTU-870 Exhaust**<br>**Cortiva Agriscience**<br>**Harbor Beach, Michigan** | **Sampling Date:**<br>**January 27, 2020** | **Montrose Air Quality Services, LLC**<br>**4949 Fernlee**<br>**Royal Oak, Michigan** |

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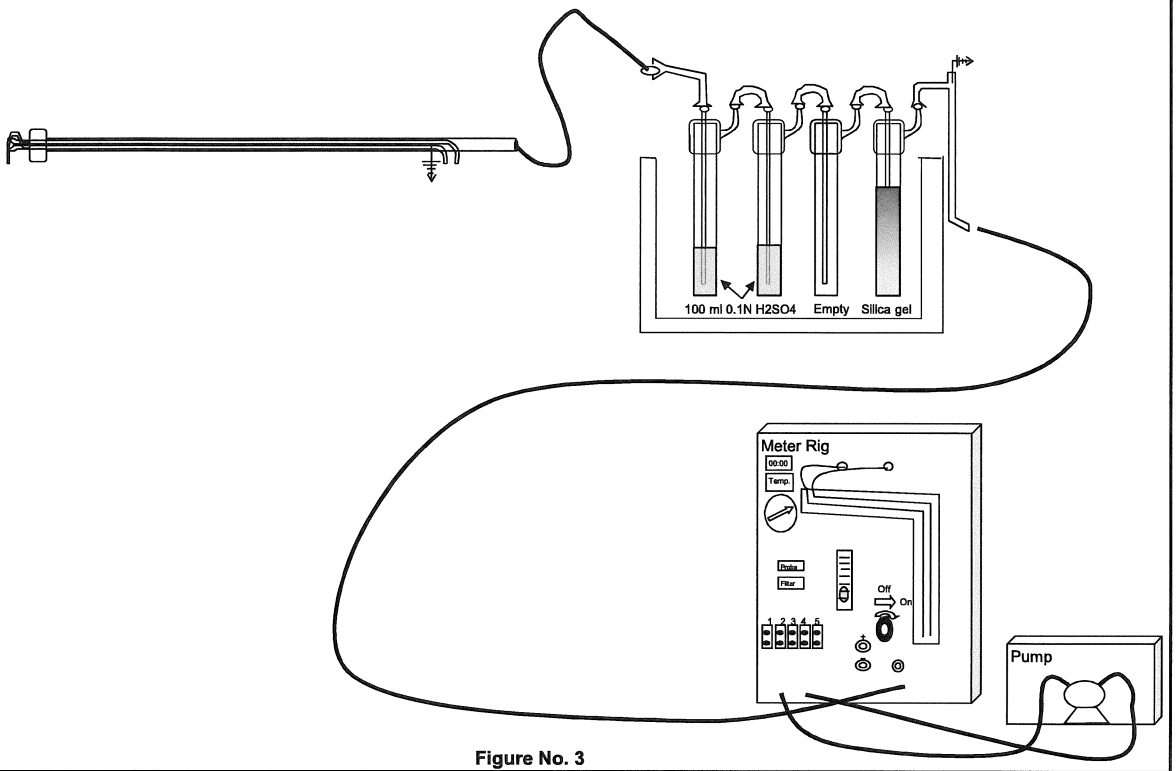


**Figure No. 3**

| | | |
|---|---|---|
| **Site:**<br>**USEPA CTM 027**<br>**Corteva Agriscience**<br>**Harbor Beach, Michigan** | **Sampling Date:**<br>**January 27-28, 2020** | **Montrose Air Quality Services, LLC**<br>**4949 Fernlee Avenue**<br>**Royal Oak, Michigan** |