# 40 CFR 63 Subpart MMM Site-Specific Test Plan National Emission Standards for Hazardous Air Pollutants for Pesticide Active Ingredient Production, 40 CFR 63 Subpart MMM T-1001 Caustic Scrubber

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DOW CHEMICAL U.S.A. MICHIGAN OPERATIONS MIDLAND, MICHIGAN

### 1.0 INTRODUCTION

# 1.1 Summary of Test Program

This site-specific test report describes the test procedures performed on the T-1001 Caustic Scrubber at the 948 Unit, owned and operated by The Dow Chemical Company, Michigan Operations, Midland, Michigan.

The 2,4 D process (948 Unit) has a Group 1 HCl/Cl<sub>2</sub> vent subject to the process vent provisions for HCl/Cl<sub>2</sub> under the Pesticide Active Ingredient Production (PAIP) MACT, 40 CFR 63 Subpart MMM, 63.1362(b)(3)(ii).

Under normal conditions, the primary control device for this process vent is the 963 TTU and associated halogen scrubber system (FG963TTU) which has been demonstrated by a performance test to meet the both the organic HAP and  $HCI/Cl_2$  emission reduction requirements in the PAIP MACT.

T-1001 is considered a cascaded  $HCI/Cl_2$  control device prior to the TTU. Per the Title V EU12b air permit, the 2,4-D vent is allowed to bypass the TTU and vent directly to the atmosphere through condenser E-1002 for a maximum of 20 days per year. During these bypass times, the T-1001 caustic scrubber serves as the sole  $HCI/Cl_2$  control device and will comply with the 20 ppmv outlet concentration limit under §63.1362(b)(3)(ii). As a  $HCI/Cl_2$  control device, T-1001 must be tested to demonstrate compliance with the process vent provisions for  $HCI/Cl_2$  under PAIP MACT, in accordance with §§63.1365(a)(6), (b), (c)(1)(v).

All testing was performed according to the procedures detailed in 40 CFR 63 Subpart MMM and Subpart A. The testing was conducted by personnel from The Dow Chemical Company. Pollutants measured were Hydrogen Chloride (HCl) and Chlorine (Cl<sub>2</sub>).

The following table summarizes the pertinent data for this compliance test:

Responsible Groups	<ul> <li>The Dow Chemical Company</li> <li>Michigan Department of Environmental Quality (MDEQ)</li> <li>Environmental Protection Agency (EPA)</li> </ul>
Applicable Regulations	40 CFR Part 63, Subpart MMM (PAI MACT)
Industry / Plant	Dow AgroSciences 948 Building     Phenoxy Herbicide Process Unit
Plant Location	The Dow Chemical Company Midland, Michigan, 48667
Sample Points	T-1001 Caustic Scrubber Outlet
Pollutants To Be Measured	<ul> <li>HCl</li> <li>Cl<sub>2</sub></li> </ul>
Proposed Test Dates	• March 26 <sup>th</sup> , 2014

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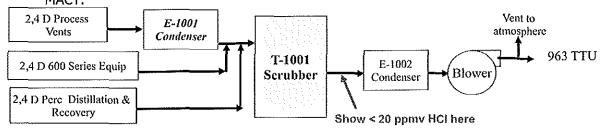
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# 2.0 PLANT AND SAMPLING LOCATION DESCRIPTION

# 2.1 Facility Description

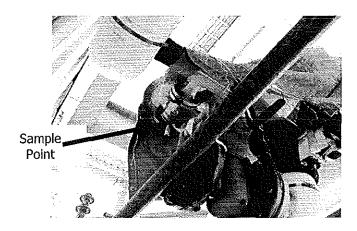
The Phenoxy Herbicide Process Unit manufactures 2,4-D for use in the pesticide market. The process unit begins with a batch reaction and is followed by a continuous recovery system. The 2,4 D process has a Group 1  $HCI/CI_2$  vent under the PAIP MACT.

Under normal conditions, the primary treatment for this vent is accomplished by the 963 TTU and associated halogen scrubber system which has been demonstrated by a performance test to meet the both the organic HAP and  $HCI/Cl_2$  emission reduction requirements in the PAIP MACT. T-1001 is considered a cascaded  $HCI/Cl_2$  control device prior to the TTU. Per the Title V EU12b air permit, the 2,4-D vent is allowed to bypass the TTU and vent directly to the atmosphere out of E-1002 for a maximum of 20 days per year. During these bypass times, the T-1001 caustic scrubber serves as the sole  $HCI/Cl_2$  control device. As a  $HCI/Cl_2$  control device, T-1001 must be performance tested to demonstrate compliance with the process vent provisions for  $HCI/Cl_2$  under PAIP MACT.



#### 2.2 Flue Gas Sampling Locations

The outlet of the T-1001 Scrubber has one sample point that is an acceptable sample location using EPA Method 26 methodology. The sample point selected is known to be "dry" and will be sufficient for  $HCI/CI_2$  concentration sampling. The sample point to be used for sampling is a 2" line with a flange that allowed  $HCI/CI_2$  sample concentrations to be collected.



# 3.0 SUMMARY AND DISCUSSION OF TEST RESULTS

# 3.1 Objectives and Test Matrix

The purpose of this test was to complete a performance test on the T-1001 vent to demonstrate compliance with PAIP MACT.

The specific objectives of the test were to:

- Determine the HCl/Cl<sub>2</sub> concentration emitted by the T-1001 scrubber vent to demonstrate compliance with the 20 ppmv outlet concentration limit under 63.1362(b)(3)(ii).
- Establish operating parameter limits for the T-1001 scrubber in accordance with 63.1366(b)(1)(ii) and (b)(3)(ii).

#### 3.2 Facility Operation

This test was performed under hypothetical peak case conditions for batch process vents in accordance with 63.1365(b)(11)(ii) using an emission profile by equipment under 63.1365(b)(11)(iii)(B) to simulate test conditions that, at a minimum, contain the highest total average hourly HAP load of emission that would be predicted to be vented to the control device. The emission profile by equipment must consist of emissions that meet or exceed the highest hourly HAP load that would be expected under actual processing conditions. The profile shall describe equipment configurations used to generate the emission events, volatility of materials processed in the equipment, and the rationale used to identify and characterize the emission events. The emissions may be based on using a compound more volatile than compounds actually used in the process(es), and the emissions may be generated from all equipment in the process(es) or only selected equipment.

See Section 7 for a description of the hypothetical worst case emission profile.

#### 3.3 Results

The scrubber was within the allowable limits for all species analyzed.

#### 3.4 Comments/Exceptions

- Tom Gasloli of the Michigan Department of Environmental Quality observed testing.
- As required, a Hydrogen Halides evaluation sample was submitted and found acceptable. The evaluation standard was provided by ERA. A final report provided by ERA can be found in the Analytical section of this report.

**TABLE 3.1: Emission Results** 

Sample Type	Test Method	Sampling Time (Min/Run)	Allowable Emission Rate	Actual Emission Rate*
Hydrogen Chloride (HCI)	EPA Method 26	60	N/A	0.3 ppmv
Chlorine (Cl <sub>2</sub> )	EPA Method 26	60	N/A	0.3 ppmv
HCI/CI2 combined	EPA Method 26	60	<20 ppmv	0.6 ppmv

<sup>\*</sup> Emissions based on average of three one-hour runs.

TABLE 3.2: Testing Run Data

PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
Run Date	3/26/2014	3/26/2014	3/26/2014	N/A
Run Times	1016/1116	1235/1335	1453/1553	N/A
Catch Wt. HCl in Outlet (ug)	82.6	< 13.2	24.5	40.1
Conc. HCl (ppmv)	0.590	< 0.097	0.176	0.288
Catch Wt. Cl2 in Outlet (ug)	62	108	77	82
Conc. Cl2 (ppmv)	0.228	0.409	0.283	0.307
Conc HCl and Cl2 (ppmv)	0.818	0.506	0.459	0.594

**TABLE 3.3: Operational Rates** 

TABLE 5:51 OPERATIONAL RATES						
PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE		
Run Date	3/26/2014	3/26/2014	3/26/2014	N/A		
Run Times	1016/1116	1235/1335	1453/1553	N/A		
Scrubber pH (once per day)	7.8	7.8	7.8	7.8		
T-1001 Recirculation Rate (GPM)	10.0	10.0	10.0	10.0		

# 4.0 SAMPLING AND ANALYTICAL PROCEDURES

#### 4.1 Test Methods

 $HCl/C_{l2}$  concentration was determined utilizing EPA Method 26. The sample point used is known to be "dry" and yielded an accurate concentration. Supplemental gases are sometimes added to this stream. All supplemental gases were turned off during sampling.

#### 4.2 Procedures

The EPA Method 26 sampling train was used to determine HCl and Cl<sub>2</sub> emissions. The average sampling rate for each run was approximately 3 liters/minute. Each test run was one hour in duration. The sampling train is described as follows:

- The first and second impinger consisted of 0.1N H2SO4
- The third and fourth impinger were 0.1N NaOH
- A fifth impinger was filled with silica gel to prevent water from getting to the dry gas meter.
- The two impingers containing sulfuric acid were analyzed for HCl by Ion Chromatography (EPA Method 26).
- The remaining two caustic impingers were analyzed for Chlorine by Ion Chromatography (EPA method 26) after the addition of sodium thiosulfate to react any hypochlorous acid to chloride.

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