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EMISSION TEST REPORT

Title                    TEST REPORT FOR THE VERIFICATION OF  
HYDROGEN CHLORIDE AND CHLORINE EMISSIONS

Report Date            May 17, 2016

Test Date(s)          April 19-20, 2016

Facility Information	
Name:	PVS TECHNOLOGIES, INC.
Street Address:	10900 Harper Avenue
City, County:	Detroit, Wayne
Phone:	(313) 571-1100

Facility Permit Information			
SRN:	B2371	Permit No.:	152-15

Testing Contractor	
Company:	Derenzo Environmental Services
Mailing Address:	39395 Schoolcraft Rd. Livonia, MI 48150
Phone:	(734) 464-3880
Project No.:	1601051

EMISSION TEST REPORT  
FOR THE VERIFICATION OF  
HYDROGEN CHLORIDE AND CHLORINE EMISSIONS

PVS TECHNOLOGIES, INC.  
DETROIT, MICHIGAN

**1.0 INTRODUCTION**

Derenzo Environmental Services (DES) was contracted by PVS Technologies, Inc. (PVS Technologies) for the determination of hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) emissions from the exhaust of two separate packed tower scrubber systems controlling emissions from liquid ferric chloride (LFC) production processes at its Detroit, Michigan facility.

Testing was performed in accordance with the requirements of Michigan Department of Environmental Quality - Air Quality Division (MDEQ-AQD) Permit to Install No. 152-15 for both the Reduction Process and the Chlorine Process.

Potential HCl emissions in the Reduction Process are controlled with a single-stage packed tower scrubber that exhausts through stack SVK-127. Permit No. 152-15 specifies that *Within 180 days after permit issuance, the permittee shall verify hydrogen chloride emission rates from FGREDUCTION by testing ... If the initial test is performed with a caustic scrubbing solution, then a subsequent test shall be performed within 180 days of switching the scrubbing solution to water.*

Potential chlorine (Cl<sub>2</sub>) emissions in the Chlorine Process are controlled with a two-stage packed tower scrubber that exhausts through stack SVK-501-502. Permit No. 152-15 specifies that *Within 180 days after permit issuance or an alternate timeline as agreed to in writing by the District Supervisor, the permittee shall verify chlorine emission rates from FGCHLORINE.*

The emission testing was performed on April 19-20, 2016 by Derenzo Environmental Services personnel Blake Beddow and Jason Logan. Mr. Matthew Hehn with PVS Technologies provided assistance and process coordination. The testing was witnessed by MDEQ-AQD personnel Mr. Thomas Maza and Mr. Jonathan Lamb.

Questions regarding this report should be directed to:

Blake Beddow  
Environmental Consultant  
Derenzo Environmental Services  
39395 Schoolcraft Rd  
Livonia MI 48150  
(734) 464-3880

Matthew Hehn  
Chemical Engineer  
PVS Technologies, Inc.  
10900 Harper Avenue  
Detroit, MI 48213  
(313) 571-1100 x4211

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**Report Certification**

This test report was prepared by DES based on field sampling data collected by DES. PVS Technologies representatives or employees provided facility process data and have approved this test report for submittal to the MDEQ-AQD.

I certify that the testing was conducted in accordance with the specified test methods and submitted test plan unless otherwise specified in this report. I believe the information provided in this report and its attachments are true, accurate, and complete.

Report Prepared By:

Reviewed By:



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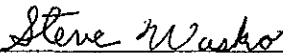
Blake Beddow  
Environmental Consultant  
Derenzo Environmental Services

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Robert L. Harvey, P.E.  
General Manager  
Derenzo Environmental Services

I certify that the facility and emission units were operated at maximum routine operating conditions for the test event. Based on information and belief formed after reasonable inquiry, the statements and information in this report are true, accurate and complete.

Responsible Official Certification:



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Steve Wasko  
Plant Manager  
PVS Technologies, Inc.

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**2.0 TEST RESULTS SUMMARY**

Emission testing was performed for the Reduction Process (FGREDUCTION) downstream of the single stage packed tower scrubber system (EUK-127), and for the Chlorine Process (FGCHLORINE) downstream of the two-stage packed tower scrubber system (EUK-501-502). A summary of the average measured HCl exhaust concentration for FGREDUCTION and chlorine exhaust concentrations for FGCHLORINE are presented in Table 2.1 below. Measured exhaust gas flowrate, sample train data, and HCl and chlorine concentrations for each one-hour test period are presented at the end of this report in Table 6.1 and 6.2.

The measured HCl content in the FGREDUCTION exhaust gas (SVK-127) was determined to be below the method detection limit (i.e., was 'non-detect') and the calculated emission rate at the detection limit is less than the allowable emission rate of 1.03 pph. The measured Cl<sub>2</sub> content in FGCHLORINE exhaust gas (SVK-501-502) is less than the allowable limit of 1 ppmv and the calculated emission rate is less than 0.022 pph as specified in MDEQ-AQD Permit to Install No. 152-15. Emission calculations are presented in Appendix A.

A Method 26A HCl audit sample was analyzed with the test samples according to the USEPA Stationary Source Audit Sample (SSAS) Program. Additional information is provided in Section 6.0 of this report.

Process operating data are presented in Section 6.0 and Tables 6.1 and 6.2 of this report.

Table 2.1 Summary of average measured emissions

Process	FGREDUCTION	FGCHLORINE
Stack ID	SVK-127	SVK-501-502
Measured Pollutant	HCl	Cl <sub>2</sub>
Emission Rate (pph)	< 0.002	< 0.001
Permit Limit (pph)	1.03	0.022
Emission Conc. (ppmv)	< 0.23	0.09
Permit Limit (ppmv)	N/A	1.00

### **3.0 PROCESS DESCRIPTION**

PVS Technologies operates a facility in Detroit, Wayne County that produces LFC that is primarily used as a flocculent for water treatment and as an etchant for manufacturing printed circuit boards. The PVS facility consists of two primary process units; the Reduction Process (FGREDUCTION) and the Chlorine Process (FGCHLORINE).

The Reduction Process produces ferrous chloride ( $\text{FeCl}_2$  or iron (II) chloride) from the reaction of iron and hydrochloric acid (HCl). The ferrous chloride is filtered and reacted with chlorine to produce ferric chloride ( $\text{FeCl}_3$  or iron (III) chloride) in the Chlorine Process. The finished product, liquid ferric chloride (LFC), is used as a flocculent for water treatment and as an etchant for manufacturing printed circuit boards..

Potential HCl emissions from the Reduction Process are controlled with a single-stage packed tower scrubber that exhausts through stack SVK-127. Potential  $\text{Cl}_2$  emissions in the Chlorine Process are controlled with a two-stage packed tower scrubber that exhausts through stack SVK-501-502. The reduction process scrubbing solution is water, while the chlorine process scrubbing solution is composed of ferrous chloride.

### **4.0 TESTING AND ANALYSIS**

The emission testing was conducted using appropriate USEPA stationary source test methods as presented in the test protocol submitted to the MDEQ-AQD dated February 16, 2016. This section provides a summary of the test methods and procedures.

Field measurement data sheets are presented in Appendix B.

#### **4.1 Sample and Velocity Traverse**

USEPA Method 1, *Sample and Velocity Traverses for Stationary Sources*, was used to determine the number of traverse points required for testing the source. Based on flow disturbance data, sampling ports were installed in the exhaust stacks to meet the criteria for a "representative measurement" location. Pollutant sample and exhaust gas velocity traverse points were identified based on the criteria in USEPA Method 1.

Appendix D provides a schematic of the traverse and sampling locations.

#### **4.2 Stack Gas Velocity and Volumetric Flowrate**

USEPA Method 2, *Determination of Stack Gas Velocity and Volumetric Flowrate*, was used to determine the average gas velocity. Average velocity pressure measurements of the exhaust gas were made using a Stausscheibe (Type S) Pitot tube connected to an oil manometer capable of reading pressures from 0.0 to 10 inches water column. Concurrent temperature measurements of the exhaust gas were made with a type-K thermocouple attached to the Pitot tube. Cyclonic flow

determinations were conducted on the exhaust stack and the null angle was determined to be less than 20° on average.

#### **4.3 Determination of Molecular Weight**

The gas collected by the emission control system is primarily in-plant air. Carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) samples were collected and analyzed using a Fyrite® combustion gas analyzer. Samples were taken for the determination of CO<sub>2</sub> and O<sub>2</sub> during each test period. The average O<sub>2</sub> and CO<sub>2</sub> concentrations measured during the testing were 20.9% and 0% respectively.

#### **4.4 Determination of Moisture Content**

USEPA Method 4, *Determination of Moisture Content in Stack Gases*, was used to determine the moisture content of the exhaust for each test period. Exhaust gas moisture was collected in chilled impingers (as part of the USEPA Method 26A sample train) and determined gravimetrically.

#### **4.5 Hydrogen Chloride Emission Measurements (USEPA Method 26A)**

USEPA Method 26A, *Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method*, was used to measure the HCl emissions exhausted from the Reduction Process scrubber (SVK-127). A dry gas metering console and leak-free vacuum pump was used to draw exhaust gas at an isokinetic rate through a Method 26A sampling train. The Method 26A HCl sampling train consisted of a:

1. Borosilicate-glass nozzle,
2. Heated stainless steel probe with glass probe liner, heated filter holder with a quartz filter,
3. Glass connections to the first impinger,
4. Set of five Greenberg-Smith (GS) impingers with the first and the second standard GS impingers each containing 100 milliliters (ml) of 0.1 Normal Sulfuric Acid (0.1 N H<sub>2</sub>SO<sub>4</sub>), the third modified GS impinger left empty (knockout impinger), and a fourth modified GS impinger containing approximately 300 grams of a silica gel desiccant with glass fiber.

At the conclusion of the sampling period, impinger contents were weighed and transferred to a sample bottle. The first and second impingers along with connecting glassware were rinsed with water, and the rinse was added to the sample bottle. The rinse and impinger solutions were sent to a third-party laboratory (Bureau Veritas, Novi MI) for HCl analysis by ion chromatography.

#### **4.6 Chlorine Emission Measurements (USEPA Method 26A)**

USEPA Method 26A, *Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method*, was also used to measure Cl<sub>2</sub> emissions exhausted from the Chlorine Process scrubber (SVK 501-502).

The Method 26A chlorine sampling train consisted of:

1. Borosilicate-glass nozzle,
2. Heated stainless steel probe with glass probe liner, heated filter holder with a quartz filter,
3. Glass connections to the first impinger,
4. Set of five Greenberg-Smith (GS) impingers with the first and the second standard GS impingers each containing 100 milliliters (ml) of 0.1 Normal Sulfuric Acid (0.1 N H<sub>2</sub>SO<sub>4</sub>), the third and fourth modified GS impingers both containing 100 milliliters (ml) of 0.1 Normal Sodium Hydroxide (0.1 N NaOH), and a fifth modified GS impinger containing approximately 300 grams of a silica gel desiccant with glass fiber.

At the conclusion of the sampling period, the impingers were weighed and the contents of the third and fourth impingers were transferred to a sample bottle. The third and fourth impingers were rinsed with water and the rinses were added to the sample bottle. Sodium thiosulfate was added to the sample bottle (25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume in dry standard cubic meters, dscm, of stack gas sampled, which is equivalent to 0.7 mg/ppm-dscf). Based on the expected Cl<sub>2</sub> concentration, 26 to 28 mg of sodium thiosulfate added to the sample container following each test run.

The rinse and impinger solutions were sent to a third-party laboratory (Bureau Veritas, Novi MI) for total chlorine analysis by ion chromatography.

## **5.0 QUALITY ASSURANCE/QUALITY CONTROL**

USEPA Quality Assurance/Quality Control (QA/QC) procedures were followed during the emissions testing program. The following information is a general overview of the QA/QC requirements of the test program. Specific information for these procedures are presented in the USEPA test methods in 40 CFR Part 60, Appendix A.

### **5.1 Exhaust Gas Properties and Flowrate**

In accordance with the USEPA Methods 1-4, the following QA/QC activities were performed:

- Prior to arriving onsite, the instruments used during the source testing to measure the exhaust gas properties, such as the barometer, pyrometer, and Pitot tube are calibrated and documented to specifications in the sampling methods. Calibration and inspection sheets are presented in Appendix C.
- During isokinetic sampling, the exposed space of the sample port opening, between the probe and the port wall, was covered in order to minimize influence of ambient conditions on velocity pressure readings.

- Prior to the sampling event, the velocity measurement assembly (Pitot tube, flexible line, and inclined manometer) was leak checked through both the positive and negative side of the Pitot at a velocity pressure equal to or greater than 3 inches water column.

## **5.2 Isokinetic sampling**

The QA/QC guidelines practiced during the Method 26A testing include:

- Prior to their use in the field, the sampling nozzle, glass liner, impingers, and all connecting glassware were cleaned in accordance with the guidelines in USEPA Method 26A.
- A three-point calibration measurement was performed on the glass nozzle used in the performance of the isokinetic testing. This field calibration sheet is presented in Appendix C.
- The Nutech Model 2010 sampling console was calibrated prior to and after the testing program. This calibration uses the critical orifice calibration technique presented in USEPA Method 5. Meter calibration sheets are presented in Appendix C.
- The digital pyrometer in the Nutech metering console was calibrated using a NIST traceable Omega<sup>®</sup> Model CL 23A temperature calibrator.
- Prior to each test run, the sampling train was assembled and leak-checked at the sampling site by plugging the inlet to the probe and pulling a vacuum of approximately 10 in. Hg. At the conclusion of each test run, the sampling train was leak-checked by drawing a vacuum equal to or greater than the highest vacuum measured during the test run.
- The calculated isokinetic variation for each one hour test period is within the method allowance, +/-10% of the isokinetic sampling rate, as required by USEPA Method 26A and 5.
- Blank samples of DI rinse water, 0.1 N NaOH, and 0.1 N H<sub>2</sub>SO<sub>4</sub> absorbing solutions used in the compliance testing were obtained and submitted to the laboratory for analysis in the same manner as each of the HCl and Cl<sub>2</sub> test samples.
- A Method 26A HCl audit sample was analyzed with the test samples according to the SSAS Program. The laboratory analytical report is provided in Appendix G; the ERA Waters (SSAS provider) report is provided in Appendix H. A discussion of the SSAS results is provided in Section 6.3 of this report.



## **6.0 MEASUREMENT RESULTS**

### **6.1 HCl and Cl<sub>2</sub> Concentrations and Emission Rates**

The analyte concentration in several of the test samples (combined impinger contents and rinses) were below the method detection limit. These non-detect values are reported as less than (<) the detection limit and emission calculations were performed using the laboratory's reported detection limit.

The average measured HCl concentration in the FGREDUCTION SVK-127 scrubber exhaust was less than 0.35 milligrams per dry standard cubic meter (mg/dscm). The average measured exhaust gas flowrate from the SVK-127 scrubber control device was 1,285 dry standard cubic feet per minute (dscfm), which results in a calculated HCl mass emission rate of less than 0.002 pounds per hour (pph).

The average measured Cl<sub>2</sub> concentration in the FGCHLORINE SVK-501-502 scrubber exhaust was 0.27 mg/dscm or 0.09 ppmvd. The average measured exhaust gas flowrate from the SVK-501-502 scrubber control device was 357 dry standard cubic feet per minute (dscfm), which results in a calculated Cl<sub>2</sub> mass emission rate of less than 0.001 pph.

Table 6.1 presents the emission concentrations, sample volumes, and measured exhaust gas properties for the three HCl test runs conducted on the Reduction Process scrubber exhaust. Table 6.2 presents the data for the three Cl<sub>2</sub> test runs conducted on the Chlorine Process scrubber exhaust.

### **6.2 Monitoring Parameters**

The liquid flowrate (GPM), pressure drop (in. H<sub>2</sub>O) to each scrubber was recorded during the testing events. The scrubber solution conductance (millisiemens, mS) was recorded for the single-stage scrubber (EUK-127), and the reduction potential of the scrubber solution (millivolts, mV) was recorded for the two-stage scrubber (EUK-501-502) during each test period. Chlorine concentration (ppmv) in the scrubber exhaust was recorded by the facility's permanently installed monitor in Stack SVK-501-502. Daily production data were recorded for the production facility including dry tons of ferric chloride and number of batches produced.

Process data are presented with the test results in Tables 6.1 and 6.2.

Appendix F contains data sheets provided by PVS Technologies representatives.

### **6.3 Variations from Normal Sampling Procedures or Operating Conditions**

Both FGREDUCTION and FGCHLORINE operated normally and no variations from the normal operating conditions occurred during the testing program.

The contract laboratory, Bureau Veritas, performed the audit sample analysis according to the SSAS Program and reported an HCl concentration that exceeded the acceptance limits range (400 mg/L which was greater than 110% of the certified value of 225 mg/L). Analysis of the test impinger samples indicated non-detect at a reporting limit of 340 micrograms per liter ( $\mu\text{g/L}$ , or 0.34 mg/L). The calculated in-stack HCl concentration using the laboratory reporting limit is less than 0.35 mg/m<sup>3</sup> of exhaust gas, which correlates to a calculated emission rate of 0.002 pph HCl. This value is less than 0.2% of the permit limit for EUREDUCATION HCl emissions (1.03 pph). Therefore, while the laboratory did not satisfy the SSAS performance evaluation requirements it is our opinion that the analysis is adequate to demonstrate compliance based on the large difference between the measured value and the applicable emission limit.

Table 6.1. Reduction Process (FGREDUCTION) Hydrogen Chloride Concentrations and Emission Rates, Stack SVK-127

Test No.	1	3	4	
Test Date	04/19/16	04/19/16	04/19/16	Test
Test Period (24-hr clock)	0930-1034	1117-1121	1251-1354	Avg.
<b>Scrubber Operating Parameters</b>				
Scrubber solution conductance (mS)	27.16	26.90	26.76	26.94
Scrubber liquid flow rate (GPM)	58	59	58	58
Pressure drop across scrubber (in. H <sub>2</sub> O)	1.5	1.5	1.5	1.5
<b>Exhaust Gas Composition</b>				
O <sub>2</sub> content (% vol)	20.9	20.9	20.9	20.9
CO <sub>2</sub> content (% vol)	0.0	0.0	0.0	0.0
Moisture (% vol)	7.7	7.2	8.1	7.7
<b>Exhaust Gas Flowrate</b>				
Standard conditions (scfm)	1,487	1,396	1,291	1,391
Dry basis (dscfm)	1,372	1,295	1,187	1,285
<b>HCl Concentrations and Emission Rates</b>				
Sample volume (dscm)	1.04	0.96	0.95	0.98
HCl lab weight (mg)	< 0.34	< 0.34	< 0.34	< 0.34
HCl concentration (mg/m <sup>3</sup> )	< 0.33	< 0.35	< 0.36	< 0.35
HCl concentration (ppmvd)	< 0.22	< 0.23	< 0.24	< 0.23
HCl emissions (pph)	< 0.002	< 0.002	< 0.002	< 0.002
<i>HCl permit limit (pph)</i>				<b>1.03</b>

Table 6.2. Chlorine Process (FGCHLORINE) Chlorine Concentrations and Emission Rates,  
Stack SVK-501-502

Test No.	1	2	3	
Test Date	04/20/16	04/20/16	04/20/16	Test
Test Period (24-hr clock)	111-1216	1328-1432	1520-1622	Avg.
<b>EUK-501 Scrubber Operating Parameters</b>				
Scrubber solution Redox Potential (mV)	475	474	474	474
Liquid flow rate to scrubber (GPM)	49	50	50	50
Pressure drop across scrubber (in. H <sub>2</sub> O)	0.15	0.15	0.15	0.15
<b>EUK-502 Scrubber Operating Parameters</b>				
Scrubber solution Redox Potential (mV)	419	419	420	419
Liquid flow rate to scrubber (GPM)	42	41	41	41
Pressure drop across scrubber (in. H <sub>2</sub> O)	0.0	0.0	0.00	0.0
Scrubber exhaust Cl <sub>2</sub> monitor (ppm)	-0.5	-0.5	-0.5	-0.5
<b>Exhaust Gas Composition</b>				
O <sub>2</sub> Content (% vol)	20.9	20.9	20.9	20.9
CO <sub>2</sub> Content (% vol)	0.0	0.0	0.0	0.0
Moisture (% vol)	2.4	2.3	2.1	2.3
<b>Exhaust Gas Flowrate</b>				
Standard conditions (scfm)	382	338	378	366
Dry basis (dscfm)	373	330	370	357
<b>Cl<sub>2</sub> Concentrations and Emission Rates</b>				
Sample volume (dscm)	1.11	0.99	1.09	1.06
Cl <sub>2</sub> lab weight (mg)	< 0.27	0.32	< 0.27	0.29
Cl <sub>2</sub> concentration (mg/m <sup>3</sup> )	< 0.24	0.32	< 0.25	0.27
Cl <sub>2</sub> concentration (ppmvd)	< 0.08	0.11	< 0.08	0.09
Cl <sub>2</sub> permit limit (ppmvd)				<b>1.00</b>
Cl <sub>2</sub> emissions (pph)	< 0.001	< 0.001	< 0.001	< 0.001
Cl <sub>2</sub> permit limit (pph)				<b>0.022</b>