## PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 6

Report No. 53005-81-RPT-052 Revision 0 February 10, 2019 – February 28, 2019

**Prepared for:** 

Washington River Protection Solutions, LLC P.O. Box 850 Richland, WA 99352

## Subcontract 53005, Release 81

Prepared by: TerraGraphics Environmental Engineering, Inc. 2926 E. Ainsworth Pasco, WA 99301



## **Approval Form**

Prepared by:

Willing

Date: 09/24/2019

Tyler Williams

**Reviewed by:** 

\_\_\_\_\_Date: 09/24/2019 Matthew Erickson, Ph.D.

Approved by:

ala

Rich Westberg

**TerraGraphics** 

\_\_\_\_\_Date:\_\_\_\_09/24/2019

# **Record of Revision**

Revision	Date	Pages/Sections Changed	Brief Description
0	09/2019	All	Original Issue.

# **Table of Contents**

1.0	DESC	RIPTION OF TESTS CONDUCTED	1
2.0		SUREMENT SYSTEM DESIGN	
2	.1 Sa	mpling Methods	2
	2.1.1	Design of Sampling System	2
2	.2 In	strumentation and Methods Used	3
	2.2.1	Proton Transfer Reaction – Mass Spectrometer	3
	2.2.2	Carbon Dioxide Monitor	5
	2.2.3	Ammonia Monitor	6
	2.2.4	Weather Station	6
2	.3 Co	onfirmatory Measurements (if Applicable)	7
3.0	CALI	BRATION METHODS AND CALIBRATION GASES USED	8
4.0	MEAS	SUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR	9
-	4.1.1	Proton Transfer Reaction – Mass Spectrometer	9
	4.1.2	Carbon Dioxide Monitor	
	4.1.3	Ammonia Monitor	
	4.1.4	Weather Station	
4	.2 M	ethod Detection Limit Study	
5.0	TEST	RESULTS	10
5		scussion of Maintenance Activities and Observations	
5		w Proton Transfer Reaction – Mass Spectrometer Zero/Span Check	-
-		linder	11
6.0	OUAI	JTY ASSESSMENT	15
6		ssons Learned – DR19-006	
7.0	CONC	CLUSION AND RECOMMENDATIONS	16
8.0	REFE	RENCES	17

# Appendices

Appendix A Deficiency Report

# Figures

Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.	4
Figure 5-1. Toluene Span Using the VOC Cylinder at ~40 sccm VOC Flow Diluted by ~2000 sccm Zero Air.	
Figure 5-2. Toluene Multi-point Calibration using the R&D Standard Showing the Average and Expected ppbv for 499 ppbv Within the Cylinder at ~40 sccm Flow Diluted by ~2000 sccm Zero Air.	13
Flow Diluted by ~2000 sccm Zero Air.	13

# Tables

Table 5-1. Mobile Laboratory Maintenance Activities	10
Table 5-2. Average Concentrations Resulting from Diluting R&D Standard Analytes	
Flowing at ~40 sccm with ~2000 sccm Zero Air along with the Ratio of these	
Averages to the Observed Average of Toluene.	14

# Acronyms and Abbreviations

-	
ASTM	ASTM International
COPC	Chemical of Potential Concern
DR	Deficiency Report
GPS	Global Positioning System
MDL	Method Detection Limit
MFC	Mass Flow Controller
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
NIOSH	National Institute for Occupational Safety and Health
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
PTR-TOF	Proton Transfer Reaction – Time of Flight
R&D	Research and Development
SME	Subject Matter Expert
TOF-MS	Time of Flight – Mass Spectrometer
VOC	Volatile Organic Compound

# **Executive Summary**

In support of the Hanford Vapor Monitoring, Detection, and Remediation Project, Washington River Protection Solutions, LLC has subsidized the implementation of a mobile vapor monitoring laboratory developed by TerraGraphics Environmental Engineering, Inc. (Statement of Work #306312, "Mobile Laboratory Services and Lease"). The contract secures services associated with the lease and operation of the Mobile Laboratory designed specifically for trace gas analysis based on the Proton Transfer Reaction – Mass Spectrometer and supplemental analytical instruments. Operation of the Mobile Laboratory will be at the discretion of Washington River Protection Solutions, LLC and will be conducted to support a variety of projects including continuing background studies, fugitive emissions, waste-disturbing activities, leading indicator studies, and general area sampling. Other applications of the Mobile Laboratory will be determined as needed by Washington River Protection Solutions, LLC.

This report of Month 6 operations spans the calendar month of February 2019, specifically February 10, 2019, through February 28, 2019. The first nine days of February 2019 were included in 53005-81-RPT-048, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report* – *Month 5*, as those days were part of continuous monitoring that had begun in January 2019. The remainder of the month of February 2019 was focused on maintenance tasks to support proper function of instrumentation in the Mobile Laboratory.

During Month 6, Mobile Laboratory operators received continuous training and performed maintenance, modifications, verifications, and calibration activities on the Mobile Laboratory instrumentation.

## **1.0 DESCRIPTION OF TESTS CONDUCTED**

During Month 6, spanning the dates of February 10, 2019, to February 28, 2019, the Mobile Laboratory (ML) performed a variety of activities to support proper function of the instruments within the ML. These duties include calibrations, troubleshooting, verifications and testing. Description of activities that were conducted are as follows:

- Week 28
  - Operator Self-Study, Maintenance, and Modifications
- Week 29
  - Report Contribution, Maintenance, and Modifications
- Week 30
  - Maintenance, Modifications, and Testing

Section 5.0 of this report provides further details for the specific activities completed in Month 6. This report is structured based on reporting requirements, as defined in the original statement of work (SOW) 306312, "Mobile Laboratory Services and Lease."

#### 2.0 MEASUREMENT SYSTEM DESIGN

This section describes the sampling methods, instrumentation, and confirmatory measurements used during this monitoring period.

#### 2.1 Sampling Methods

The following sections detail the sampling methods utilized during the monitoring periods that occurred in Month 6.

## 2.1.1 Design of Sampling System

The ML is housed in a Chevrolet<sup>®1</sup> 4500 14' Box Truck equipped with a 5.2L diesel engine. The box has been fully insulated to allow the ML to maintain comfortable working temperatures for the operators and the instrumentation. The ML has the option of utilizing either shore power or onboard diesel generator power for operation of the instruments. During Month 6, while the ML was located at the TerraGraphics warehouse in Pasco, WA, shore power was utilized. The ML was powered by the generator at all deployed locations during Month 6. When deployed for monitoring, the ML used both the mast and the side port to perform air sampling.

The layout of the ML and the sampling system is shown in the following drawings:

- 66409-18-ML-003, *Sampling Manifold Sketch*; and
- 66409-18-ML-004, *Mobile Lab Schematics*.

## 2.1.1.1 Proton Transfer Reaction – Mass Spectrometer Sampling

Proton Transfer Reaction – Time of Flight (PTR-TOF) 6000 X2 is the latest IONICON<sup>®2</sup> trace Volatile Organic Compound (VOC) analyzer. The PTR-TOF 6000 X2 is used to quantify chemicals of potential concern (COPCs) from the sampled air. The sampled air enters the Proton Transfer Reaction – Mass Spectrometer (PTR-MS) drift tube. In the drift tube, VOCs undergo chemical ionization via a fast proton transfer reaction using hydronium as the reagent ion. The hydronium ions are produced from water vapor via a series of reactions in a hollow cathode ion source. The proton transfer reactions with hydronium ions is a soft ionization method and VOC fragmentation is minimal for most compounds. These ionized compounds and hydronium travel through the drift tube to the transfer lens system, subsequently entering the Time of Flight – Mass Spectrometer (TOF-MS) where they are separated by mass and detected. The signal from the TOF-MS is used to identify the VOCs based on their mass, as well as to calculate individual compound concentration based on the ratio of compound signal to hydronium signal.

<sup>&</sup>lt;sup>1</sup> Chevrolet is a registered trademark of General Motors, LLC, Detroit, Michigan.

<sup>&</sup>lt;sup>2</sup> IONICON is a registered trademark of Ionicon Analytik Gesellschaft m.b.H., Innsbruck, Austria.

## 2.1.1.2 DAQFactory Sampling

DAQFactory<sup>®3</sup> is a data acquisition and automation software from AzeoTech that allows users to design custom applications with control and automatic output settings. In the ML, DAQFactory controls the sampling system through valves and flow controllers for the LI-COR<sup>®4</sup> CO<sub>2</sub> monitor, Picarro Ammonia Analyzer, Airmar<sup>®5</sup> Weather Station, and the PTR-TOF.

## 2.2 Instrumentation and Methods Used

The following sections detail the instrumentation and methods utilized during the monitoring periods that occurred in Month 6.

## 2.2.1 Proton Transfer Reaction – Mass Spectrometer

Measurements performed by the ML during Fiscal Year 2018 utilized the IONICON PTR-TOF 6000 X2 system. The mass resolution of the PTR-TOF 6000 is sufficient to resolve some COPCs with high confidence (i.e., furan from isoprene) while other compounds have interferences which can potentially compromise their reliable detection and quantification. A full discussion of the reliability of COPC detection and quantification as performed by a PTR-TOF 4000, an instrument with less resolution, can be found in *Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study*, September 2017. A brief summary of the instrument and its underlying chemistry that leads to the sensitive detection of vapor components will be provided herein. The general layout of the instrument is shown in Figure 2-1.

<sup>&</sup>lt;sup>3</sup> DAQFactory is a registered trademark of Azeotech, Inc., Ashland, Oregon.

<sup>&</sup>lt;sup>4</sup> LI-COR is a registered trademark of LI-COR, Inc., Lincoln, Nebraska.

<sup>&</sup>lt;sup>5</sup> Airmar is a registered trademark of Airmar Technology Corporation, Milford, New Hampshire.

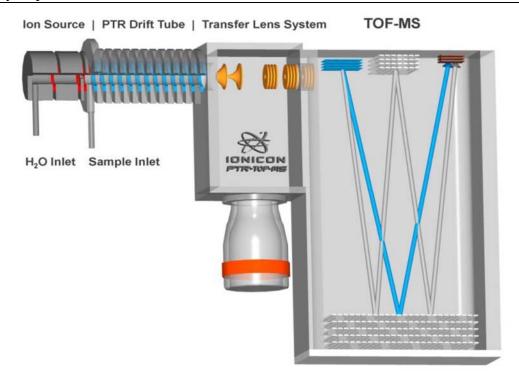


Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

The VOCs are measured by chemical ionization, where the reagent ion  $H_3O^+$  ionizes organics via a fast proton transfer reaction (R1).

$$R + H_3O^+ \rightarrow RH^+ + H_2O \tag{R1}$$

These reactions are normally non-dissociative, although there are some compounds that fragment to smaller ions upon protonation. The reaction takes place in a drift tube where the sample air stream reacts with  $H_3O^+$  ions produced by a hollow cathode ion source. The number of ions counted per second for the reagent ion and protonated sample ion are monitored and used for the determination of estimated concentrations according to Equation 1.

$$[R] = \frac{1}{kt} \left( \frac{I_{RH+}}{I_{H3O+}} \right) \frac{\mathcal{E}_{RH+}}{\mathcal{E}_{H3O+}}$$
(1)

where k is the ion-molecule rate constant (molecules cm<sup>-3</sup> s<sup>-1</sup>), t is the reaction time (~ 100 microseconds), I<sub>RH+</sub> and I<sub>H3O+</sub> are the respective ion count rates, and  $\mathcal{E}_{RH+}$  and  $\mathcal{E}_{H3O+}$  are the ion transmission efficiencies through the TOF. It is important to note that estimated concentrations of compounds can be determined directly from Equation 1 (the "kinetic approach" to quantification). There is no need for the analysis of authentic standards and the generation of calibration curves. The system is essentially self-correcting as all measurements are made with respect to the ion count rate of the reagent ion.

The mixing ratio X of the organic R in the sample air is then determined by:

$$X_R (ppbV) = \frac{[R]}{[AIR]_{drift}} \times 1 \times 10^9$$
<sup>(2)</sup>

where [AIR] is the number density of air (molecules/cm<sup>3</sup>) in the drift tube given the drift tube pressure (typically ~ 2.4 mbar) and temperature (typically ~ 50°C).

The PTR-MS technology has been used in numerous applications around the world with hundreds of peer-reviewed publications appearing in the literature over the past 20 years. Even though the technology is widely used in the research arena and has proven to be indispensable for many applications, there is no standard method among the United States regulatory agencies such as the U.S. Environmental Protection Agency, American Society for Testing and Materials (ASTM)<sup>®6</sup>, and National Institute for Occupational Safety and Health (NIOSH)<sup>®7</sup>. The end user of the technology is expected to provide the "best practice" in its use by adhering to established operational parameters governed by the scope of the project and the nature of the sample(s) to be measured.

#### 2.2.2 Carbon Dioxide Monitor

Carbon dioxide is not a COPC; however, monitoring CO<sub>2</sub> is necessary for correlation of vapor signals to combustion processes or other sources. There are numerous combustion sources near the sampling sites of the background study including diesel and gas generators, all-terrain vehicles with no catalytic converters, and diesel and gasoline vehicles. These contribute VOCs to the vapor burden and are readily observed by the PTR-MS. It is necessary to distinguish these VOCs from tank farm related emissions resulting from normal work-related activities.

The CO<sub>2</sub> monitor used in the TerraGraphics ML was the LI-COR Model 840A. The Li840A is an absolute, non-dispersive infrared gas analyzer based upon a single path, dual wavelength infrared detection system. It is a low-maintenance, high performance monitoring solution that gives accurate, stable readings over a wide range of environmental conditions. It has a range of 0-20,000 ppm (0-2%), low power consumption (4W after power-up), and 1-second signal averaging to allow for real-time source apportionment (i.e., monitoring vehicle exhaust or other combustion sources on-the-fly). The instrument operates on a gas flow of less than 1 liter per minute.

It is interfaced to the ML's internal gas manifold at the same location as the PTR-MS sampling port to ensure that both instruments are simultaneously measuring the same source. The data from the  $CO_2$  monitor are used to predict when VOC measurements from the PTR-MS come from combustion sources.

The CO<sub>2</sub> monitor used during the background study was operated using a factory calibration. Periodic checks of the unit were made with zero air and ambient background air [ambient atmospheric CO<sub>2</sub> levels are approximately 400 parts per million (ppm)], and a certified

<sup>&</sup>lt;sup>6</sup> ASTM is a registered trademark of American Society for Testing and Materials, West Conshohocken, Pennsylvania.

<sup>&</sup>lt;sup>7</sup> NIOSH is a registered trademark of U.S. Department of Health and Human Services, Bethesda, Maryland.

reference standard to ensure continued system operation. The system has a continuous direct readout which can be displayed on the DAQFactory monitor in real time to aid in real-time decision making by the field analysts.

#### 2.2.3 Ammonia Monitor

Ammonia is a compound on the COPC list of particular importance. It is believed to be associated with all high-level waste storage tanks on the Hanford Site. The global average background for ammonia is between 5-7 parts per billion by volume (ppbv). Previous studies of ammonia levels on the Hanford Site indicate the expected measurement range should be in the low ppbv range. Although relatively easy to measure at the parts per million by volume (ppmv) level, its measurement at the low ppbv level with high temporal resolution is not trivial. The purpose of measuring trace levels of NH<sub>3</sub> is the correlation of vapor data from the PTR-MS to actual tank emissions. A measured vapor plume containing elevated COPCs with the same time correlation as an ammonia plume is reasonable evidence of a tank emission.

The ammonia monitor used was a Picarro Model G2103 that is capable of measuring NH<sub>3</sub> with parts per trillion by volume (pptv) sensitivity. It is a sophisticated time-based measurement system that uses a laser to quantify spectral features of gas phase molecules in an optical cavity. It is based on cavity ring down spectroscopy. Gas phase spectroscopy measurements are subject to temperature and pressure fluctuations. The Picarro system features a  $\pm 0.005^{\circ}$ C temperature stability and  $\pm 0.0002$  atm pressure stability to ensure low noise and high accuracy measurements. Sample flow rate to the instrument was provided by an external pump at 0.8 liters per minute at 760 Torr.

The analyzer is interfaced to the ML main sample stream to ensure the instrument measured the same gas sample as the PTR-MS and CO<sub>2</sub> monitor. The system outputs real-time data to a monitor, records data to its internal computer, and uses the ML Wi-Fi connection to automatically synchronize to a clock service. Daily data sets are retrieved and backed up similar to the other data collection instruments.

## 2.2.4 Weather Station

The weather station used in the ML is an Airmar 200WX-IPx7 with a control unit mounted in the server cabinet and the transducer mounted on the sampling mast located above the roof of the van. Real-time display of the output is visible on the DAQFactory monitor to aid field analysts in making sampling decisions in the field. The output data are fed to the server with a clock time-stamp that is synchronized to the other monitoring systems in the ML. The functions and outputs of the station include:

- Apparent wind speed and angle,
- True wind speed and angle,
- Air temperature,
- Barometric pressure,

- 2D Magnetic compass heading,
- Heading relative to true north, and
- Global positioning system (GPS).

The weather station transmitted data continuously at 2-second intervals to DAQFactory.

## 2.3 Confirmatory Measurements (if Applicable)

No confirmatory samples were collected during Month 6.

## 3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Table 3-1, shown below, highlights the type, identification number, and expiration date for each gas standard cylinder employed by the ML for calibration purposes during Month 6.

## Table 3-1. Calibrated Gases in use During Month 6.

Cylinder	ID#	Exp. Date
Carbon Dioxide	77-401243203-1	07/13/2026
Ammonia	48-401233442-1	06/21/2019
Zero-air	Lot #: 2181802 (115421, C5438107, T-2768, 330-662, KI428)	06/29/2019
VOC	160-401380144-1	01/16/2020
1,3-butadiene	CC508261	03/06/2019

#### 4.0 MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR

The sections below discuss the measurement uncertainty associated with each instrument employed in the ML, as well as studies conducted to quantify the Method Detection Limits (MDLs) of the PTR-MS.

#### 4.1.1 **Proton Transfer Reaction – Mass Spectrometer**

All standards/zeroes performed by the field team to verify the accuracy of the instrument fell within acceptable administrative limits as described in 66409-RPT-004, *Mobile Laboratory Operation Procedure*.

#### 4.1.2 Carbon Dioxide Monitor

The LI-COR CO<sub>2</sub> analyzer had no specific errors associated within the timeframe covered in this monthly report. All standards/zeroes performed by the field team and reported in this summary to verify the accuracy of the instrument fell within acceptable administrative limits ( $\pm$  20%). The measurement accuracy of a properly calibrated instrument is listed in the LI-COR factory specifications as  $\pm$ 3% of reading.

#### 4.1.3 Ammonia Monitor

The Picarro G2103 Ammonia Monitor had no specific errors associated within the timeframe covered in this monthly report. Further detail regarding the errors associated with measuring ammonia using a Picarro instrument is discussed in *Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study*, September 2017. All standards/zeroes associated with data reported in this summary performed by the field team to verify the accuracy of the instrument fell within acceptable administrative limits ( $\pm$  20%). The measurement accuracy of a calibrated instrument listed in the Picarro factory specifications is  $\pm$ 5% of reading.

#### 4.1.4 Weather Station

The Airmar 200WX-IPx7 Weather Station had no specific errors associated within the timeframe covered in this monthly report. The Airmar 150 WX Weather Station is factory calibrated and is not user calibrated. The manual does not recommend periodic calibration. This is described in 66409-RPT-003, *Mobile Laboratory Operational Acceptance Testing Plan*.

#### 4.2 Method Detection Limit Study

No method detection limits (MDLs) were calculated during Month 6.

#### 5.0 TEST RESULTS

This section details the testing and maintenance tasks performed during this month's activities.

#### 5.1 Discussion of Maintenance Activities and Observations

During Month 6, there were 14 days spent on maintenance and testing-related activities for the ML. These activities included vehicle maintenance, modifications to the interior, and continuous training opportunities for ML operators.

Planned preventative and corrective maintenance were performed on the ML throughout the duration of Month 6 and are presented in Table 5-1.

Week	Date	Description	Activities/Observations
	02/10/2019	ML Maintenance	PTR-MS multi-point calibration.
	02/11/2019	ML Maintenance	Housekeeping tasks and Microsoft <sup>®8</sup> Windows <sup>®10</sup> updates.
28	02/12/2019	Continuous Training	Operator self-study of PTR-MS related papers and reports.
28	02/13/2019	Continuous Training	Operator self-study, conducted report reviews, and report comment resolution.
	02/14/2019	Continuous Training	Operator self-study, conducted report review, and report comment resolution.
	02/15/2019	Continuous Training	Operator self-study, conducted report reviews, and report comment resolution.
	02/19/2019	ML Maintenance	Installation of MFCs, setup of 208-ft heated line, testing of MFCs, instrument calibrations.
	02/20/2019	ML Modifications	Generator maintenance, DAQFactory programming, multipoint calibrations.
29	02/21/2019	ML Maintenance	PTR-MS Modbus <sup>®9</sup> software programming, new shelf constructed, testing of Circuit 21.
	02/22/2019	ML Maintenance	Sorbent sample reconfigured, VOC gas installed, PTR-MS Modbus software programming.
	02/25/2019	ML Maintenance and Modification	TPS installation.
20	02/26/2019	ML Maintenance and Modification	TPS maintenance, PTR-MS Modbus software programming, IONICON assistance.
30	02/27/2019	ML Maintenance and Modification	PTR-MS water bottle refilled, gas standard inventory, preparation for MFC acceptance testing.
	02/28/2019	ML Testing	MFC acceptance testing, R&D and VOC gas cylinder multipoint calibrations.

#### Table 5-1. Mobile Laboratory Maintenance Activities.

Although adverse weather conditions delayed the completion of the various maintenance-related tasks in the ML, it allowed operators to expand their knowledge of the PTR-MS and its capabilities. Thus far, operators have performed numerous monitoring campaigns providing hands-on experience with operating the instrument, but with the reading and studying of scientific papers on the subject, their overall understanding of the instrumentation was vastly

<sup>&</sup>lt;sup>8</sup> Microsoft and Windows are registered trademarks of Microsoft Corporation in the United States and other countries.

<sup>&</sup>lt;sup>9</sup> Modbus is a registered trademark of Schneider Electric USA, Inc., Palatine, Illinois.

improved. The purpose of these self-study activities is to ensure operators are capable of independently identifying potential vapor sources during monitoring and perform troubleshooting when anomalies occur.

Operators were also utilized in the comment resolution process for reports. Through this process, operators learned the importance of providing detailed logbook notes and observations. The goal of the ML Team is to allow operators to become cross-trained in all aspects of the vapor project, lessening the opportunity for single points of failure. These continuous training activities were documented in the operator's Indoctrination and Training Record maintained by the TerraGraphics Quality Assurance department.

## 5.2 New Proton Transfer Reaction – Mass Spectrometer Zero/Span Check Cylinder

The last day the VOC cylinder (CC483181) – Part No. X20NI99C15A0000 Certificate of Authenticity validity was February 28, 2019, and the ML transitioned to a new VOC cylinder (FF56465) – Part No. X05NI99C33A0029 for zero/span checks. The old VOC cylinder (CC483181) – Part No. X20NI99C15A0000 will now be referred to as the Research and Development (R&D) standard and the new VOC cylinder (FF56465) – Part No. X05NI99C33A0029 will be referred to as the VOC standard. Figure 5-1 shows a time-series of toluene when sampling from the VOC cylinder (FF56465) – Part No. X05NI99C33A0029 along with the expected level of toluene output from the zero/calibration box (CZ-MHE-001). The expected concentration is calculated by taking the concentration within the tank (549 ppbv) and multiplying it by the dilution factor determined by the flows of the VOC and zero mass flow controllers (MFCs). The dilution factor is determined by dividing the VOC flow (~40 sccm) by the sum of the zero (~2000 sccm) and VOC flows (~40 sccm). This comes out to be:

549 ppbv \* 40 sccm / (2000 sccm + 40 sccm) = 10.76 ppbv expected

Taking the average toluene when the signal is stable from Figure 5-1 results in approximately 10.85 ppbv, which is within 1% of the expected ppbv. This demonstrates that the VOC cylinder produces desired results and will work well for performing zero/span checks until it expires on January 16, 2020.

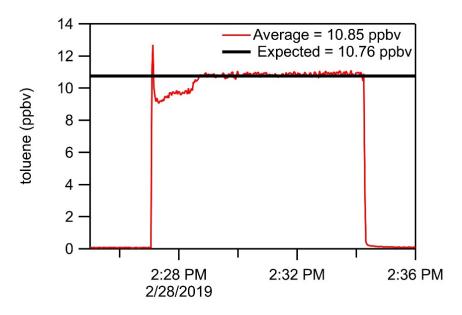
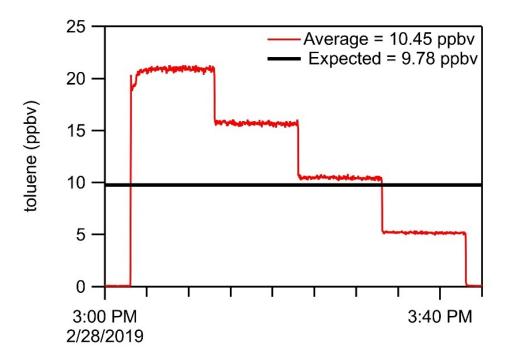
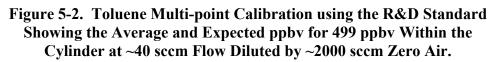


Figure 5-1. Toluene Span Using the VOC Cylinder at ~40 sccm VOC Flow Diluted by ~2000 sccm Zero Air.

Although the R&D standard (CC483181) – Part No. X20NI99C15A0000 is expired, it still provides a lot of value for testing. It contains a wider variety and range of analytes compared to the VOC standard which is limited to only benzene, toluene, p-xylene, and ethyl benzene. Continued use of the R&D standard will be accompanied by a zero/span check with the VOC standard. This will provide a comparison between the standards and provide a means of trend analysis for the constituents of the R&D standard. Figure 5-2 shows a multi-point calibration of toluene from the R&D standard, which contains 499 ppby toluene. The average toluene was calculated when the calibration and zero flows were the same as the VOC span which were ~40 sccm and ~2000 sccm, respectively. The resulting average was 10.45 ppbv and the expected was 9.78 ppbv showing a  $\sim$ 7% difference. For trend analysis of the R&D standard, it is important to create a dilution with the same flows as the VOC standard. If the flows remain constant over time, the only variable that could change would be the concentration within the tank. The objective of trend analysis is to track any change in the R&D standard compared to the VOC standard to verify the stability of the R&D standard components. If it is found that a compound within the R&D standard has changed, its use will be reevaluated. The ratio of the VOC standard to the R&D standard is 10.85 to 10.45 which equals ~1.04. This acts as the initial comparison for trend analysis and will be used as a metric for future comparisons.





Once the VOC to R&D ratio is established and is determined to be acceptable by the Subject Matter Expert (SME) or designee, it is important to check the other constituents of the R&D standard. This is done by comparing the ratio of an analyte to the ratio of toluene within the cylinder and is shown in Table 5-2. These ratios will be tracked over time to determine any changes by individual analytes. The analytes are not expected to decay within the tank at the same rate. If an analyte is shown to change beyond an acceptable range by the SME or designee, the use of that specific analyte will need to be reevaluated. If an analyte within the cylinder has reached a point of low reliability, it does not invalidate the information provided by the analytes that have shown to be within acceptable ranges.

Table 5-2. Average Concentrations Resulting from Diluting R&D Standard
Analytes Flowing at ~40 sccm with ~2000 sccm Zero Air along
with the Ratio of these Averages to the Observed Average of Toluene.

Analyte	MW	Average	Ratio
methanol	32	7.96	0.76
acetonitrile	41	8.54	0.82
acetaldehyde	44	19.98	1.91
1-butene	56	2.53	0.24
acetone	58	8.23	0.79
dimethylsulfide	62	8.31	0.80
furan	69	7.38	0.71
isoprene	69	3.51	0.34
methyl vinyl ketone + methacrolein	70	7.55	0.72
methyl ethyl ketone	72	7.52	0.72
benzene	78	10.23	0.98
diethylketone	86	6.70	0.64
toluene	92	10.45	1.00
3-hexanone	100	7.50	0.72
p-xylene	106	9.03	0.86
1,3,5-trimethylbenzene	120	9.67	0.93
1,2,3,5-tetramethylbenzene	134	7.08	0.68
alpha pinene	136	3.60	0.34

## 6.0 QUALITY ASSESSMENT

From February 10, 2019, to February 28, 2019, quality control procedures were followed by the TerraGraphics Vapor Team; Data Collection, and Data Processing. Data were collected and quality documents completed according to 66409-RPT-004. All data were accepted, processed and reported according to the Procedure 17124-DOE-HS-102, "Mobile Laboratory Data Processing – Analysis." All exceptions have been noted and any potential quality-affecting issues were resolved prior to report or are noted in this report. All potential quality-affecting deviations have been captured in Deficiency Reports (DRs) and are summarized below with some interpretation.

During the February 10, 2019, to February 28, 2019, maintenance period, there was one DR created. DR19-006 records the issue of an ineffective macro used in the processing of PTR-MS data from January 26, 2019.

#### 6.1 Lessons Learned – DR19-006

On February 15, 2019, it was discovered that a macro used for removing non-reportable data in Igor Pro was removing an entire dataset. While processing data from January 26, 2019, a data analyst discovered that the macro responsible for applying NaNs (not-a-number) was displacing two columns and flagging all data from the dataset as non-reportable. To resolve this issue, all data exports will be loaded into Igor Pro with explicit column headers so that columns cannot be misidentified in the future.

## 7.0 CONCLUSION AND RECOMMENDATIONS

There were no on-site or off-site monitoring activities involving the ML during Month 6. The first ten days of the month were spent completing a 24-day continuous monitoring campaign. The combination of completing a rigorous background study campaign and upcoming area monitoring deployments resulted in the remainder of the month to be dedicated to maintenance tasks supporting the continued function of the ML.

The inclement weather over the next three weeks caused several delays to maintenance tasks and ML testing but provided operators the opportunity to fulfill continuous training through self-studying of PTR-MS related papers. Operators also assisted with generating report content and from this learned the importance of capturing details in the ML logbook during the collection of data.

The final day of Month 6 was dedicated to acceptance testing of newly calibrated MFCs and the verification of a new VOC gas standard for use in the ML. This day of testing yielded ideas for future testing in Month 7 and Month 8 such as: sample dilution testing, heated line testing, and sorbent system testing.

#### 8.0 **REFERENCES**

- 17124-DOE-HS-102, 2018, "Mobile Laboratory Data Processing Analysis," Revision 2, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-003, 2018, *Sampling Manifold Sketch*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-004, 2018, *Mobile Lab Schematics*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-003, 2018, *Mobile Laboratory Operational Acceptance Testing Plan*, Revision 0, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-004, 2019, *Mobile Laboratory Operational Procedure*, Revision 11, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study, September 2017, RJ Lee Group, Inc., Pasco, Washington.
- SOW 306312, 2018, "Mobile Laboratory Services and Lease," Revision 2, Washington River Protection Solutions, LLC, Richland, Washington.

## APPENDIX A

## **DEFICIENCY REPORT**

TerraGraphics

-

TerraGraphics	C	AUTHENTIC
DEFICIENCY REPORT	Ini	TERRACEAPHICS
Deficiency Report No.:		Page:
DR19-006		1 of 1
Driginator (Print Name):	Signature:	Date:
Anna Woehle	anna Wol	ale 02/19/2019
Project No./Title:		
3005-81 PTR-MS Data Processing	1	
AAA Reportable:	10 CFR 21 Reportal	
No Yes Description of Requirement that was Violated a		No Yes
CORR	ECTIVE ACTION	
ke "wave0, wave1, etc." <i>RenameWaves</i> " now explicitly calls out the c exible than relying on order to rename, but h lentifying a column.	column headers to be renar has the added benefit of nev	ned in the macro. This is less ver mis-labeling or mis-
ompletion Date: 02/19/2019		
eficiency Cause and Extent of Condition:		
his deficiency report documents this as a nalysis if Macros continue to be inconsist		
urther investigation showed that the name as: nis determination (TofSupply_MCPF_Act) w ifferent unrelated diagnostic trace. This mis-r 2/15/19.	as incorrectly assigned to	TofSupply_ReflBack_Act, a
he source of this error was determined to be olumn headers from the PTR-MS data export olumn headers in Igor were renamed based st olumns appeared in the 01/26 data (Automati accessive column headers to be displaced two ace used in " <i>ApplyNaNs</i> " to inadvertently fla hat caused the PTR data export to include the very dataset in which automation was used.	t from PTR-MS Viewer ( $R$ trictly on order in the View ion.RunNumber and Autor positions in the naming on all data from 01/26 as no	enameWaves). Previously, ver export. Two unaccounted-for nation.StepNumber), causing all order. This is what caused the on-reportable data. It is unclear

DEFICIE		KT				
Action to Preclue						
condition is cu	specific actions ide urrently being treat med to determine t rrence.	ted as an anon	naly. Should th	ne condition p	persist, f	urther analysis
Completion Date	: 02/19/2019					
Resp. Manager/T		Date:	QA Rep. (Pri		1	Date:
Rich Westberg	g // An	02/27/19	Heath Low	Buth	17	02/27/19
	V	) CL	OSURE	l	/	
	Notes (if applicable):					
None.						
QA Manager (Pr	int Name):		Signature: /	1	Date	2:
Heath Low			that	17	1.550.65	27/19
			1/	/		
			V			
			V			
			V			
			V			
			V			

TerraGraphics