

Vapor Monitoring Detection System Weekly Report

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Abbreviations and Units

CH ₄	=	methane
CO	=	carbon monoxide
CO ₂	=	carbon dioxide
COPC	=	chemicals of potential concern
DRI	=	direct reading instrument
LEL	=	lower explosive limit
ND	=	not detected
NH ₃	=	ammonia
NO	=	nitric oxide
N ₂ O	=	nitrous oxide
NO ₂	=	nitrogen dioxide
O ₃	=	ozone
OEL	=	occupational exposure limit
OP-FTIR	=	open path Fourier transform infrared spectrometer ¹
OSHA	=	Occupational Safety and Health Administration
PEL	=	permissible exposure limit
ppb	=	parts per billion
ppm	=	parts per million
UV-DOAS	=	ultraviolet differential optical absorption spectrometer ²
VMDS	=	vapor monitoring detection system
VOC	=	volatile organic compounds, which include both volatile and semi-volatile compounds

VMDS Instruments

505	=	RAE MeshGuard (NH ₃ sensors)
506A	=	OP-FTIR Multipath (measures 24 analytes)
506B	=	OP-FTIR Single-path (measures 24 analytes)
508A	=	UV-DOAS (measures 26 analytes)
512	=	Gastronics (NH ₃ , VOC, and N ₂ O sensors)

¹ OP-FTIR Fact Sheet: <http://hanfordvapors.com/wp-content/uploads/2016/10/OP-FTIR-fact-sheet.pdf>

² UV-DOAS Quick Sheet: <http://hanfordvapors.com/wp-content/uploads/2016/10/UV-DOAS-Fact-Sheet.pdf>

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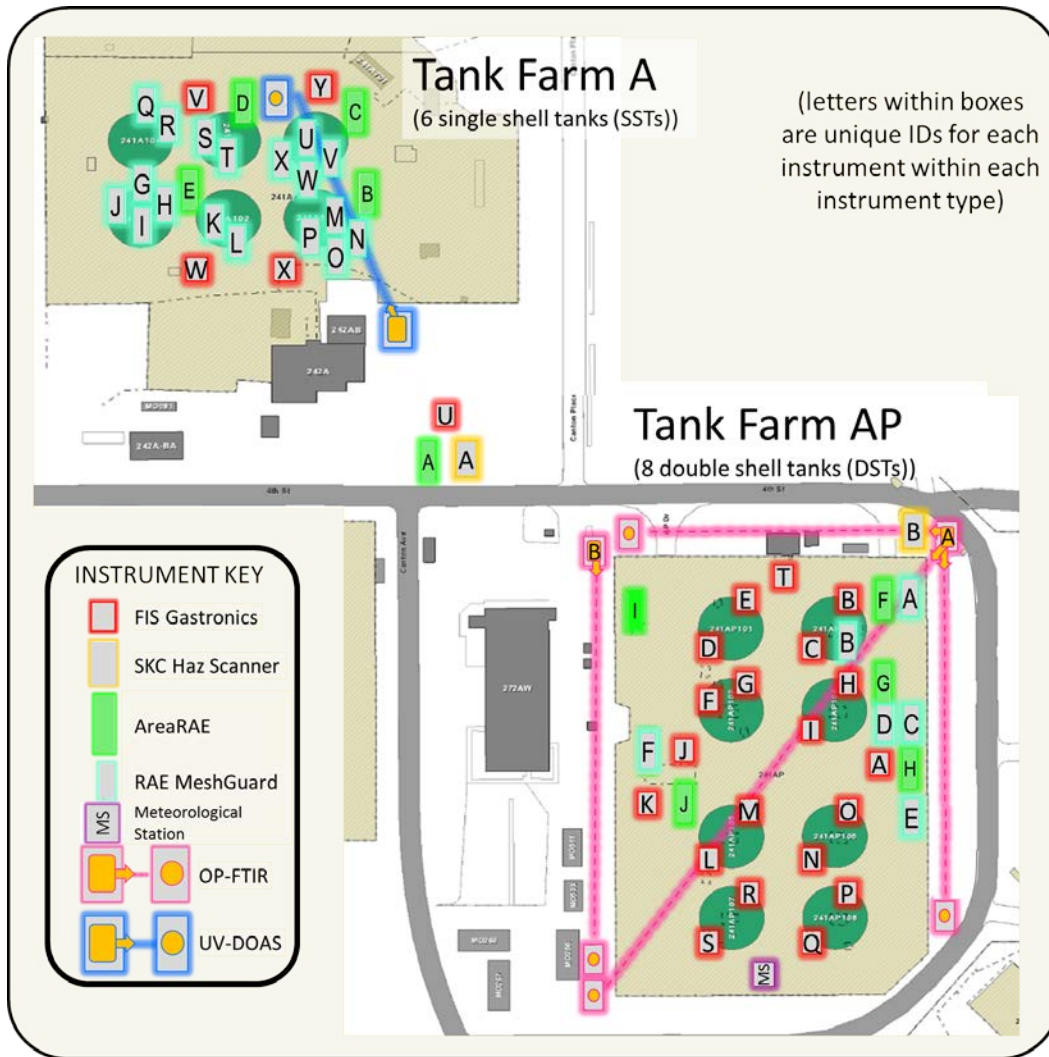
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Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (1/18/2017 at 6:00 a.m. through 1/25/2017 at 6:00 a.m.) using direct reading vapor detection instruments, the open path Fourier transform infrared spectrometer (OP-FTIR), and the ultraviolet differential optical absorption spectrometer (UV-DOAS).

Pilot-scale testing is focused on evaluating component integration and functionality. Data shown may include results for calibration and calibration check (bump test) tests performed to verify sensors are functioning; these tests are visible in the data as spikes. Any alarms occurring during pilot-scale testing are taken to be actual events and the appropriate actions/notifications are undertaken.

Sampling Location –A & AP-Tank Farms (map below)



The spectrometer instruments (OP-FTIR and UV-DOAS) provide real-time multi-gas measurement (qualitative and quantitative) of gases. Even though the instrument is very

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accurate regarding the quantification of compounds, reported results cannot be directly calculated into a concentration for a specific location, this is due to its sample size – an open path between two points. The sample path is defined by the location of the emitter and the reflector which may be tens to hundreds of meters apart. Therefore data from these instrument types will not be directly compared to Occupational Safety and Health Administration (OSHA) Occupational Exposure Limits (OELs) and Action Levels, but used to determine concentrations of compounds along the path of the instrument's beam.

For the spectrometer instruments, each analyte has a specific predetermined IR and/or UV trace which represents the model for that chemical. The detection and reporting of that chemical is based on evaluation of the R-squared (R^2) values (coefficient of determination) calculated by comparing the detection trace to the model trace for that chemical. R^2 is a statistical value representing the "percent of variance explained" by evaluating the detected trace with the model trace, or an estimate of how well the two traces match. R^2 values range from 0 to 1 with higher values indicating a better fit. R^2 values are dependent on spectroscopy method (UV-DOAS or OP-FTIR) sample concentration, chemical compounds [chemicals present can interfere/overlap with each other at key locations; typically those having the same functional groups (e.g., methane or ketone groups)], and many other factors. Typically the trigger used for reporting is an R^2 value of greater than or equal to 0.5; some compounds may have different trigger levels based on optimization of the analysis method using AP and A Tank Farm data.

The direct read instruments located within AP and A Tank Farms include the RAE MeshGuard (505) sensors for detecting NH_3 and the Gastronics (512) units with sensors for detecting NH_3 , VOCs and N_2O . The N_2O sensors on the 512 instruments have been difficult to keep in calibration and the N_2O data will remain suspect until the stability of the sensor and calibration can be confirmed.

1/18/2017 through 1/25/2017 Summary

During the current reporting week, waste retrieval activities at tank AY-102 (to AP Farm) was suspended until the late evening of 1/24/2017 due to a variety of reasons. No anomalies in response to the waste retrieval activities were reported with any instruments reviewed here.

AP TANK FARM

OP-FTIR

During the week in review, instrument 506A detected nitrous oxide (N_2O) and methane (CH_4) near the end of the week. Nitrous oxide and CH_4 are typically found in the atmosphere at background levels of approximately 0.330 ppm for N_2O and 1.80 ppm for CH_4 ³. The 506A instrument went off-line due to generator issues early on 1/18/2017, resulting in the instrument locking up and OSI PI reporting invalid constant values for both N_2O and CH_4 from 1/18/2017 to 1/23/2017. Instrument 506A was restored on 1/23/2017, but then went off-line again on

³ Climate Change Indicators: Atmospheric Concentration of Greenhouse Gases: <https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases>

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1/24/2017 and reported invalid constant values (see Figure 1). Instrument 506B did not report any data during this week because it also went off-line due to generator issues early on 1/18/2017.

Compounds detected by the 506A instrument are typically present in background air at detectable levels. This information indicates that the OP-FTIR unit is effectively measuring composition of the gas components within its path. Compounds identified are reported in Table 1 and Figure 1 below.

Table 1. Chemical Species Detected on Open Path FTIRs at AP Tank Farm.

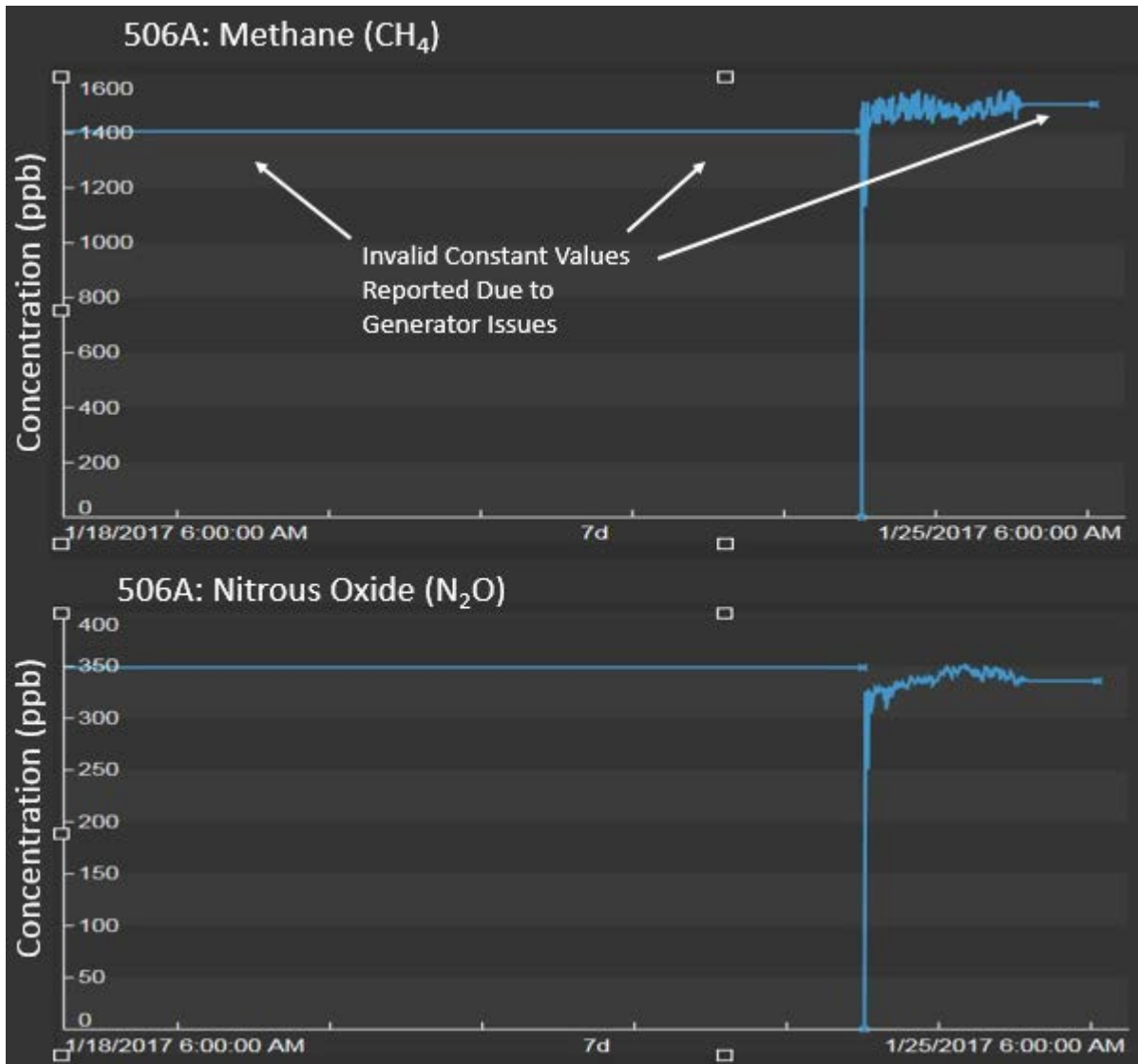
Chemical Compound	506A: OP-FTIR Multipath (ppm)	506B: OP-FTIR Single Path (ppm)
Nitrous Oxide*	0.31 – 0.35 ^a	NR
Ammonia*	ND	NR
Methane	1.43 – 1.56 ^a	NR
1-3-Butadiene*	ND	NR
1-Butanol*	ND	NR
2-Hexanone*	ND	NR
3-Buten-2-one*	ND	NR
Acetaldehyde*	ND	NR
Acetonitrile*	ND	NR
Benzene*	ND	NR
Butanal*	ND	NR
Butyl Nitrite*	ND	NR
Ethylamine*	ND	NR
Formaldehyde*	ND	NR
Furan*	ND	NR
Methanol*	ND	NR
Methyl Isocyanate*	ND	NR
Methyl Nitrite*	ND	NR
N-Nitrosodiethylamine*	ND	NR
N-Nitrosodimethylamine*	ND	NR
N-Nitrosomorpholine*	ND	NR
Propanenitrile*	ND	NR
Pyridine*	ND	NR
Tributyle Phosphate*	ND	NR

Notes: *Chemical is on COPC list
 ND – Not detected by instrument (i.e., either value reported was 0 or <R² limit)
 NR – Not reported
 (a) Disturbed data not included in the table for these compounds

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Figure 1. OP-FTIR (506A) Plot of CH₄ and N₂O.



AP Tank Farm Direct Reading Instruments

Instruments located between A and AP Tank Farm, are included.

RAE MeshGuards (505 - NH₃): The 505 sensors located in AP Tank Farms include: 505A, B, C, D, E, and F. No NH₃ was detected by the RAE MeshGuards in AP Tank Farm during this week.

Table 2. AP Tank Farm RAE MeshGuard (505) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
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NH ₃ (ppm)	<ul style="list-style-type: none"> Instruments reporting: 505A, C, D, and F Out of calibration*: None No ammonia detected 	25	12.5	1 – 50
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* Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are considered in calibration and reported here.

Gastronics (512 - NH₃, VOCs, N₂O) – Units located in AP Tank Farm include: 512A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, and T. Unit 512U is located between AP Tank Farm and A Tank Farm. Instruments 512B, C, D, E, F, G, H, I, J, L, M, N, O, P, Q, R, T, and U were calibrated during this week (1/23/17 – 1/24/17) and all these instruments were within 10% of the 100 ppm (NH₃) and 50 ppm (VOC) test gas concentrations. Unit 512A could not be calibrated because the power supply was too low.

No ammonia was detected by Gastronics instruments that were in calibration and reporting during time frames when waste transfers were underway. No VOCs were detected by instruments 512B, E, F, and L. Units 512C, D, H, I, K, N, O, Q, R, T, and U reported VOCs <2 ppm (0.2 to 0.8 ppm). No units reported VOCs ≥2 ppm. A total VOC limit of 2 ppm currently is employed by the Industrial Hygiene Program Technical Basis⁴. Only instruments that are reporting to the OSI PI system and in calibration are reported here. The N₂O sensors on the 512 instruments have been difficult to keep in calibration and the N₂O data will remain suspect until the stability of the sensor and calibration can be confirmed.

Table 3. AP Tank Farm Gastronics (512) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	No ammonia detected	25	12.5	1 – 500
VOC (ppm)	<ul style="list-style-type: none"> Out of calibration*: None Instruments that reported no VOCs detected: 512B, E, F, and L Instruments that reported a maximum value of <2 ppm: 512C, D, H, I, K, N, O, Q, R, T, and U Instruments that reported maximum values ≥2 ppm: None 	N/A	2	0 – 1000

* NH₃/VOC: Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are reported here.

⁴ RPP-22491, Rev 1, "Industrial Hygiene Chemical Vapor Technical Basis": <http://hanfordvapors.com/wp-content/uploads/2016/10/Industrial-Hygiene-Chemical-Vapor-Technical-Basis-RPP-22491 - Rev 1.pdf>

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A TANK FARM

UV-DOAS

While sampling during the period under review ammonia (NH₃), nitric oxide (NO), ozone (O₃), and p-xylene were reported and detected by the instrument. Many of these are typically found in detectable quantities in background air⁵. Noisy ozone data were observed during times of high relative humidity (Figure 2), indicating the instrument ozone readings can become disturbed during weather events (e.g., fog, rainfall). P-xylene peaks of 0.013 ppm and 0.011 ppm were detected on 1/19/2017 and 1/22/2017, respectively. The PEL for p-xylene⁶ is 100 ppm. No other chemical species were detected during this monitoring period. Specific instrument information is reported in Table 4 and Figure 2 below.

Table 4. Chemical Species Detected on UV-DOAS at A Tank Farm

Chemical Compound	508A: UV-DOAS (ppm)	Chemical Compound	508A: UV-DOAS (ppm)
Ammonia*	ND – 0.033	Methyl Nitrite*	ND
Nitric Oxide	ND – 0.077	Pyridine*	ND
Ozone	0.031 – 0.11 ^a	1-2-4 Trimethylbenzene	ND
1-3 Butadiene*	ND	1-3-5 Trimethylbenzene	ND
2-Methyl-2-butenal*	ND	Ethylbenzene	ND
2-Methylfuran*	ND	m-Xylene	ND
Acetaldehyde*	ND	Nitrogen Dioxide	ND
Benzene*	ND	o-Xylene	ND
Butanal*	ND	p-Xylene	ND – 0.013
Ethylamine*	ND	Styrene	ND
Formaldehyde*	ND	Sulfur Dioxide	ND
Furan*	ND	Toluene	ND
Mercury*	ND		

Notes: *Chemical is on COPC list

ND – Not detected by instrument (either value reported was 0 or <R² limit)

(a) Disturbed data not included in the table for this compound

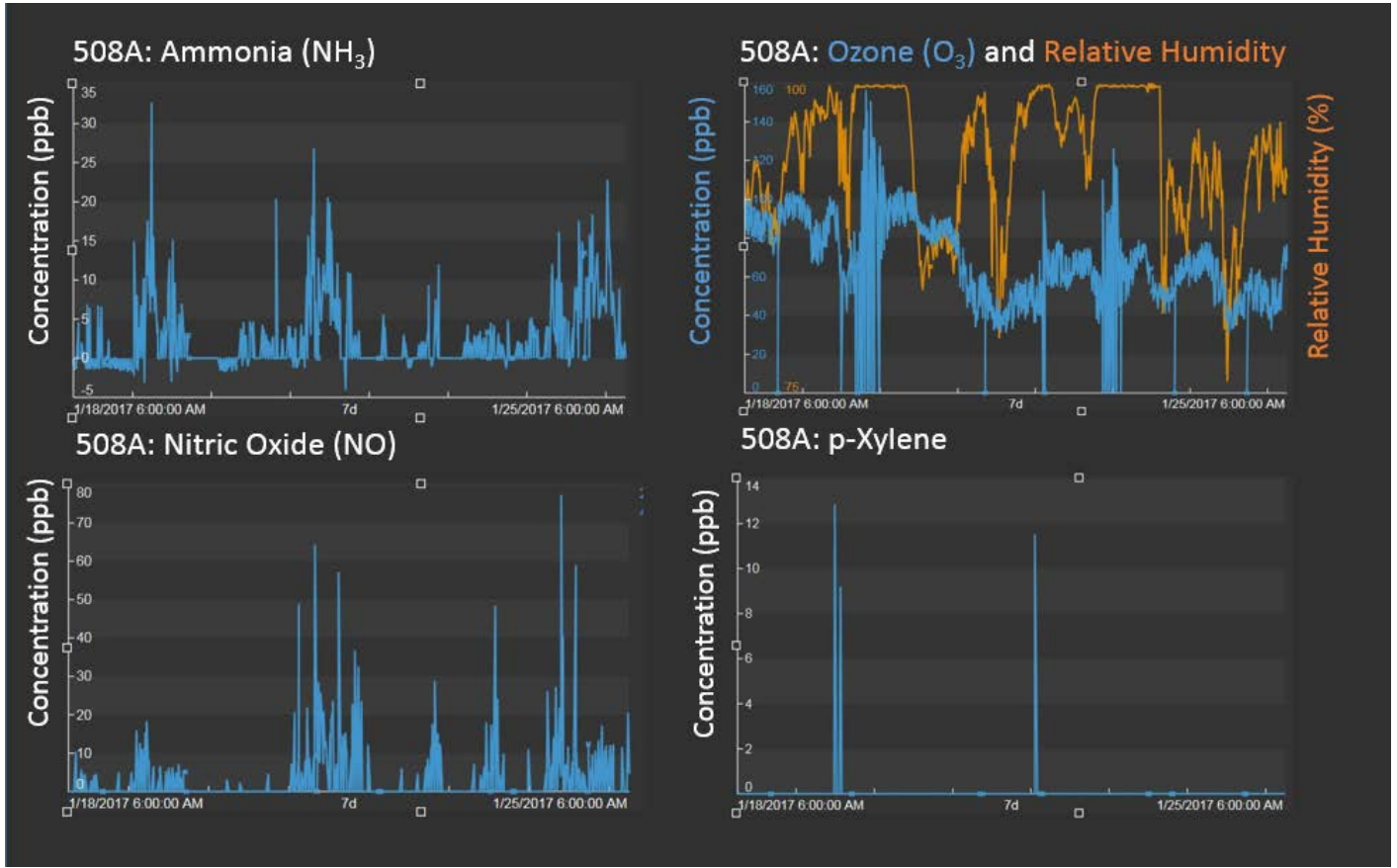
⁵ Air Composition from “The Engineering ToolBox”: http://www.engineeringtoolbox.com/air-composition-d_212.html

⁶ OSHA: https://www.osha.gov/dts/chemicalsampling/data/CH_276400.html

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Figure 2. Concentrations of Chemicals Detected by UV-DOAS (508A). Note Noisy Ozone Readings during Times of High Relative Humidity Measured by the Coastal Meteorological Station at AP Tank Farm (510A).



A Tank Farm Direct Reading Instruments

RAE MeshGuard (505 - NH₃) – Sensors located in A Tank Farms include: 505G, H, I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, and X. No NH₃ was detected by the RAE MeshGuards in A Tank Farm during this week.

Table 5. A Tank Farm RAE MeshGuard (505) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	<ul style="list-style-type: none"> • Instruments reporting: 505H, I, J, K, M, M, N, O, P, Q, R, S, T, U, V, W, and X • Out of calibration*: None • No ammonia detected 	25	12.5	1 – 50

* Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are considered in calibration and reported here.

Gastronics (512 - NH₃, VOCs, N₂O) – Units located in A Tank Farm include: 512V, W, X, and Y. Instruments V, W, and X were calibrated during this week and were within 10% of the 100 ppm

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(NH₃) and 50 ppm (VOC) test gas concentrations. Instrument 512Y could not be calibrated because the power supply was too low. None of the calibrated units reported VOC or ammonia data during this week. The N₂O sensors on the 512 instruments have been difficult to keep in calibration and the N₂O data will remain suspect until the stability of the sensor and calibration can be confirmed.

Table 6. A Tank Farm Gastronics (512) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	No ammonia reported	25	12.5	1 – 500
VOC (ppm)	<ul style="list-style-type: none"> • Out of calibration*: None • Instruments that reported no VOCs detected: None • Instruments that reported a maximum value of <2 ppm: None • Instruments that reported maximum values ≥2 ppm: None 	N/A	2	0 – 1000

* VOC: Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are reported here.

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Time reporting is calculated using the time that sensors are reporting to OSI PI System⁷ for each instrument.

Table 7. RAE MeshGuard (505) and Gastronics (512) % Time Reporting^a.

Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting
505A	91	505N	97	512B	95	512N	58
505B	0	505O	98	512C	68	512O	73
505C	95	505P	99	512D	91	512P	0
505D	90	505Q	99	512E	91	512Q	48
505E	0	505R	29	512F	97	512R	45
505F	90	505S	8	512G	0	512S	0
505G	0	505T	99	512H	95	512T	74
505H	98	505U	98	512I	96	512U	>99
505I	98	505V	99	512J	0	512V	0
505J	99	505W	98	512K	28	512W	0
505K	27	505X	99	512L	0	512X	0
505L	0	512A	72 ^a	512M	0	512Y	0
505M	97						

(a) % time reporting based on NH₃.

Table 8. Spectrometer Instruments Time Reporting.

Instrument	% Time Reporting
506A	97
506B	0
508A	>99

⁷ OSI PI System is a data visualization software package from [OSIsoft](http://www.osisoft.com).