

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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Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (3/8/2017 at 6:00 a.m. through 3/15/2017 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 typically 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. The sampling locations for pilot-scale testing is shown on Figure 1.

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 accurate regarding the quantification of chemical 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 spectrographic instruments (OP-FTIR and UV-DOAS), each analyte has a specific reference spectrum, which represents the absorption characteristics for that chemical in the IR or UV spectral regions. Reference spectra for each analyte are stored in a library that specifies which absorption features are analyzed, how that analysis is performed, and reporting threshold values. Revisions to the library are periodically performed to improve accuracy of analysis for analytes; spectrographic instruments reporting for the VMDS project are still in the iterative optimization process and periodic changes to the library are being performed. Revisions to the library may result in the identification of a compound not previously thought to be present, or conversely determine that a previously reported analyte was not actually present. Identification of an analyte is dependent on the analytical method (UV or IR), library used, concentration, other chemical compounds present [chemicals present can interfere/overlap with each other at key locations; typically those having the same functional groups (e.g., methane or ketone groups) – the library is optimized to minimize these interferences], and many other factors.

The direct read instruments located within AP and A Tank Farms include the RAE MeshGuard (505) sensors for detecting NH₃ and the Gastronics (512) units with sensors for detecting NH₃ and VOCs.

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Summary for 3/8/2017 through 3/15/2017

The following sections summarize data reporting for vapor monitoring and detection instruments at AP and A Tank Farms for the 3/8/2017 through 3/15/2017 period. Instruments at AP Tank Farm include open path FTIR instruments (multi-path and single path) and the RAE MeshGuard and Gastronics direct reading instruments. Instruments at A Tank Farm include UV-DOAS and RAE MeshGuard and Gastronics direct reading instruments. No waste retrieval activities occurred during this reporting period.

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AP TANK FARM

OP-FTIR

During the week in review, instrument 506A did not report data to the OSI PI System. The instrument was shut down the previous week to convert the power source from a generator to shore power.

Instrument 506B detected nitrous oxide (N₂O), methane (CH₄), and ammonia (NH₃). Power was restored to the system at ~1:00 pm, 3/9/2017. The 506B OP-FTIR sensor experienced a disturbance in data acquisition between 12:15 and 01:45 a.m. on 3/10/2017; the disturbance was likely due to atmospheric conditions and high humidity. This instrument experienced another interruption on 3/13/2017 when detected values for methane and nitrous oxide fell to near zero, likely as a result of rainy conditions that interfered with instrument operations.

Most compounds detected by the 506B instrument are typically present in air at detectable levels. Consistency in measured values for these compounds indicates that the OP-FTIR unit is effectively measuring composition of the gas components within its path. Specific instrument information is reported in Table 1 and Figure 1 below.

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

Chemical	506A: OP-FTIR Multipath (ppm)	506B: OP-FTIR Single (ppm)
Nitrous Oxide*	NR	0.234 – 0.392 ^a
Ammonia*	NR	ND – 0.063
Methane	NR	1.15 – 1.80 ^a
1-3-Butadiene*	NR	ND
1-Butanol*	NR	ND
2-Hexanone*	NR	ND
3-Buten-2-one*	NR	ND
Acetaldehyde*	NR	ND
Acetonitrile*	NR	ND
Benzene*	NR	ND
Butanal*	NR	ND
Butyl Nitrite*	NR	ND
Ethylamine*	NR	ND
Formaldehyde*	NR	ND
Furan*	NR	ND
Methanol*	NR	ND
Methyl Isocyanate*	NR	ND
Methyl Nitrite*	NR	ND
N-Nitrosodiethylamine*	NR	ND
N-Nitrosodimethylamine*	NR	ND
N-Nitrosomorpholine*	NR	ND

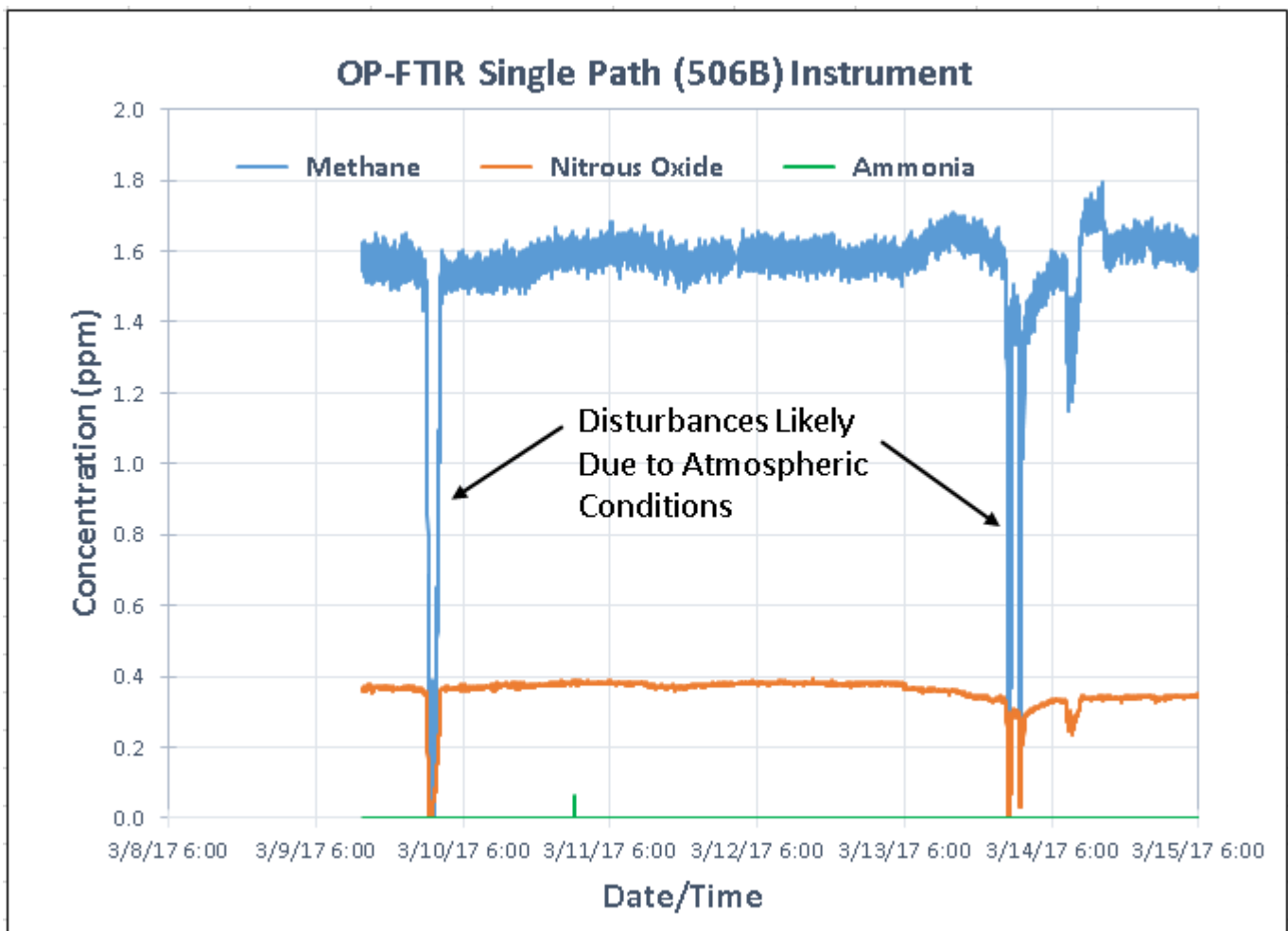
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Chemical	506A: OP-FTIR Multipath (ppm)	506B: OP-FTIR Single (ppm)
Propanenitrile*	NR	ND
Pyridine*	NR	ND
Tributyle Phosphate*	NR	ND

Notes: (a) Disrupted data not included in the table for these compounds
 *Chemical is on COPC list
 ND – Not detected by instrument (reporting non-detects is based on reference spectra stored in a library, which is revised periodically to improve analysis accuracy)
 NR – Not reported to OSI PI

Figure 2. Chemical Compounds Detected by the OP-FTIR (506B) Instrument.



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 Farm are 505A, B, C, D, and F. The RAE MeshGuard sensors have been offline since 2/5/2017 due to communication

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software errors. No calibrations or calibration checks were performed on the MeshGuard sensors and no NH₃ data were reported to the OSI PI System during this week (Table 2).

Table 2. AP 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: None Calibration/check tests: None 	25	12.5	1 – 50

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 the A Tank farm. Calibrations were performed on instruments 512A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, Q, R, T, and U during this week (3/13/2017 and 3/14/2017) and all these instruments passed calibration (i.e., within 10% of the test gas concentration for VOC). No ammonia was detected by Gastronics instruments that were in calibration and reporting this week. Ten of the units reported non-detectable levels of VOC. Seven units reported VOC at <2 ppm and no units reported VOCs ≥2 ppm (Table 3). A total VOC limit of 2 ppm currently is employed by the Industrial Hygiene Program Technical Basis³. N₂O sensors are suspect and no data are reported. Only instruments that are reporting to OSI PI and in calibration are reported on here.

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

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	No ammonia reported on any instrument	25	12.5	1 – 500
VOC (ppm)	<ul style="list-style-type: none"> Out of Calibration*: None Instruments that reported VOC non-detections: 512D, F, H, J, K, M, N, Q, R, and S Instruments that reported a maximum value of <2 ppm: 512A, B, G, I, L, T, and U 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.

³ 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

Ammonia, nitric oxide (NO), ozone (O₃), benzene (C₆H₆), toluene (MeC₆H₅), and p-Xylene (pXy) were reported by the instrument during the period under review (Table 4). Many of these are typically found in detectable quantities in air⁴. Toluene has a permissible exposure limit (PEL) of 200 ppm⁵ and is in ambient air concentrations in urban areas of the United States at approximately 0.003 ppm⁶. Xylene (including p-isomers of xylene) has a PEL of 100 ppm⁷ and ambient air concentrations of mixed xylenes in urban areas of the United States range from 0.0007ppm to 0.088ppm (at 25°, 1 atm)⁸. Analyte concentrations are reported in Table 4 and Figure 3 below.

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

Chemical	508A: UV-DOAS (ppm)	Chemical	508A: UV-DOAS (ppm)
Ammonia*	ND – 0.078	Methyl Nitrite*	ND
Nitric Oxide	ND – 0.129	Pyridine*	ND
Ozone	0.020 – 0.113 ^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 – 0.009	o-Xylene	ND
Butanal*	ND	p-Xylene	ND – 0.014
Ethylamine*	ND	Styrene	ND
Formaldehyde*	ND	Sulfur Dioxide	ND
Furan*	ND	Toluene	ND – 0.063
Mercury*	ND		

Notes: (a) Isolated spikes to zero do not follow the general trend, therefore these spikes are not included in the table

*Chemical is on COPC list

ND – Not detected by instrument (reporting non-detects is based on reference spectra stored in a library, which is revised periodically to improve analysis accuracy)

⁴ Air Composition from “The Engineering ToolBox”: http://www.engineeringtoolbox.com/air-composition-d_212.html

⁵ OSHA: https://www.osha.gov/SLTC/toluene/exposure_limits.html

⁶ EPA: <https://www.epa.gov/sites/production/files/2016-09/documents/toluene.pdf>

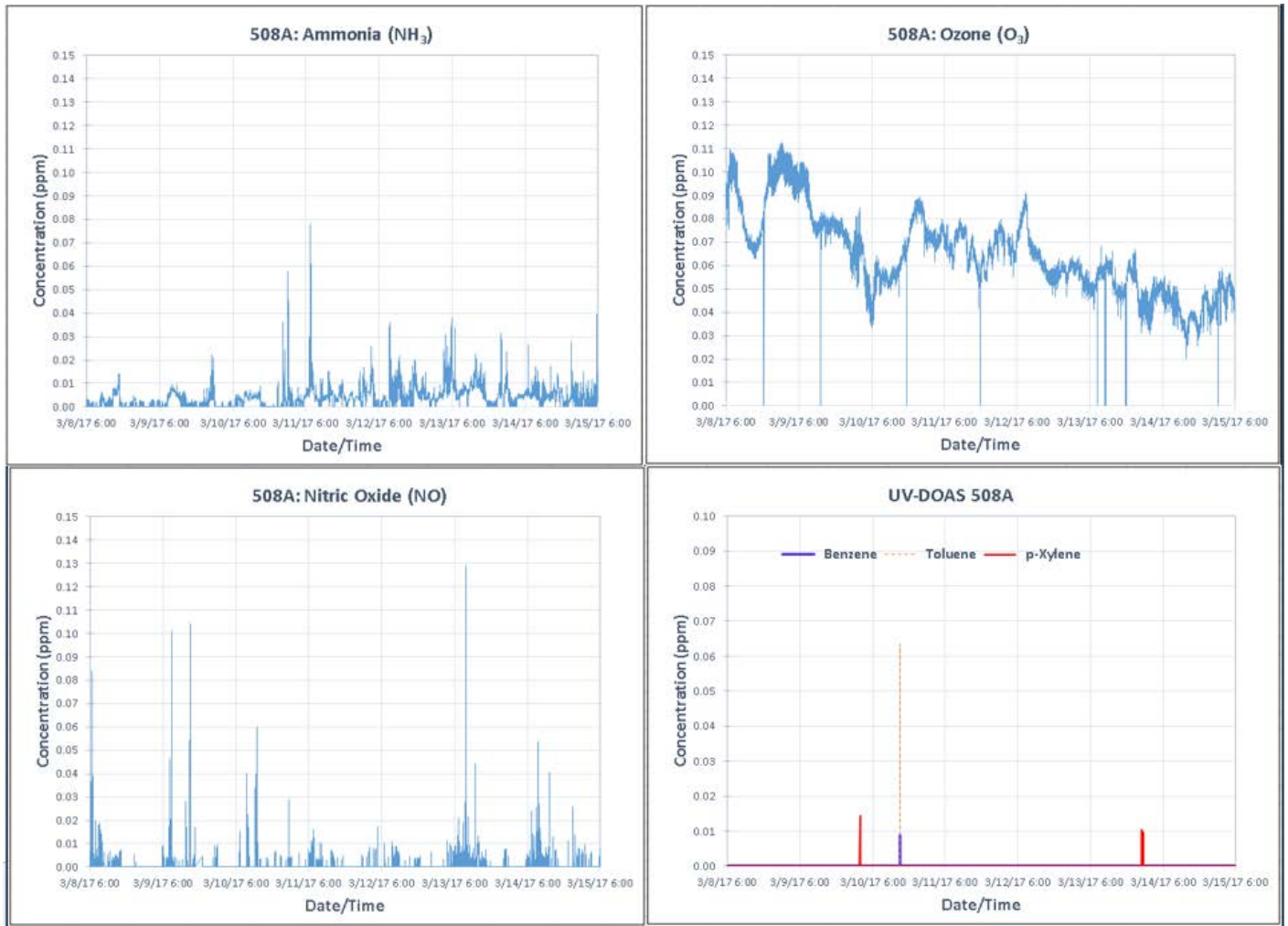
⁷ OSHA: https://www.osha.gov/dts/chemicalsampling/data/CH_276400.html

⁸ EPA: <https://www.epa.gov/sites/production/files/2016-09/documents/xylenes.pdf>

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Figure 1. Concentrations of Chemicals Detected by UV-DOAS (508A).



A Tank Farm Direct Reading Instruments

RAE MeshGuards (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. The RAE MeshGuard sensors have been offline since 2/5/2017 due to communication software errors. No calibrations or calibration checks were performed on the MeshGuard sensors and no NH₃ data were reported to the OSI PI System during this week (Table 5).

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: None Calibration/check tests: None 	25	12.5	1 – 50

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Gastronics (512 - NH₃, VOCs, N₂O): Units located in A Tank Farm include: 512V, W, X, and Y (Table 6). None of these instruments reported data during the week. Calibrations were performed on 512V, W, X, and Y during this week (3/14/2017) and all of them were within 10% of the test gas concentration for VOC.

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

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	No ammonia reported on any instrument	25	12.5	1 – 100
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	0.001 – 50.0

* 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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3/8/2017 – 3/15/2017 Instrument Operational Status:

Time reporting is calculated using the time sensors that are reporting to OSI PI System⁹ for each instrument (Tables 7 and 8).

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

Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting
505A	0	505N	0	512A	40	512N	44
505B	0	505O	0	512B	25	512O	0
505C	0	505P	0	512C	0	512P	0
505D	0	505Q	0	512D	0	512Q	63
505E	0	505R	0	512E	0	512R	24
505F	0	505S	0	512F	95	512S	0
505G	0	505T	0	512G	27	512T	70
505H	0	505U	0	512H	29	512U	>99
505I	0	505V	0	512I	41	512V	0
505J	0	505W	0	512J	7	512W	0
505K	0	505X	0	512K	68	512X	0
505L	0			512L	69	512Y	0
505M	0			512M	73		

(a) % time reporting based on NH₃.

Table 8. Spectrometer Instruments Time Reporting.

Instrument	% Time Reporting
506A	0
506B	81
508A	>99

⁹ OSI PI System is a data visualization software package from [OSIsoft](http://www.osisoft.com).