01/11/17 6:00 - 01/18/17 6:00



The following information is for the time period from January 11th at 6:00am through January 18th at 6:00am. This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week for the open path Fourier transform infrared spectrometer (OP-FTIR). Pilot-scale testing is focused on evaluating component integration and functionality. Data shown may include results from calibration and bump tests performed verify instruments function; these tests result in data spikes.

Abbreviations:

 $\begin{array}{l} CH_4 = methane \\ NH_3 = ammonia \\ NO = nitric oxide \\ N_2O = nitrous oxide \\ NO_2 = nitrogen dioxide \\ OEL = occupational exposure limit \\ OP-FTIR = Open Path Fourier Transform Infrared Spectrometer \\ R^2 = R-squared \\ VMDS = Vapor Monitoring and Detection System \end{array}$

01/11/17 6:00 - 01/18/17 6:00

Weekly Summary: The OP-FTIR spectrometer provides real-time multi-gas measurement (qualitative and quantitative) of gases¹. Even though the instrument is very 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 Exposure Limits (OELs) and Action Levels, but used to determine concentrations of compounds along the path of the instrument's beam.

Each analyte has a specific predetermined infrared (IR) trace which represents the model for that chemical. The detection and reporting of that chemical is based on evaluation of the R-squared (R²) values (coefficient of determination) calculated by comparing the detection trace to the model trace for that chemical. R² 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. R² values range from 0 to 1 with higher values indicating a better fit. R² values for OP-FTIR data are dependent on 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 R² 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.

During the week in review, instrument 506A detected nitrous oxide (N₂O), ammonia (NH₃), and methane (CH₄). Nitrous oxide and CH₄ are typically found in the atmosphere at background levels of approximately 0.330 ppm for N₂O and 1.80 ppm for CH₄². A recurring pattern of simultaneous N₂O and CH₄ spikes on this instrument was noted again this week (see Figure 1). Unit 506A went off-line on the evening of 1/12/2017 due to generator issues and was restored the morning of 1/16/2017. Ammonia is not typically detected along the 506A paths, but three ammonia peaks were detected this week, with a peak concentration of 0.021 ppm on January 17th. This concentration is well below the OEL of 25 ppm for ammonia³.

Instrument 506B detected N₂O, CH₄, NH₃, 1-butanol (BuOH), and methanol (MeOH). Unit 506B went off-line due to generator issues at the same time as 506A, but was not restored until 1/17/2017. The single peaks of BuOH and MeOH occurred at the same time as one of the ammonia peaks detected by the 506A instrument on 1/17/2017. The Conference of Governmental Industrial Hygienists (ACGIH) TLV value for 1-butanol⁴ is 20 ppm.

¹ OP-FTIR Fact Sheet: <u>http://hanfordvapors.com/wp-content/uploads/2016/10/OP-FTIR-fact-sheet.pdf</u> ² Climate Change Indicators: Atmospheric Concentration of Greenhouse Gases: <u>https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases</u>

³ OSHA: <u>https://www.osha.gov/dts/chemicalsampling/data/CH_218300.html</u>

⁴ ACGIH information regarding 1-butanol: <u>https://www.osha.gov/dts/chemicalsampling/data/CH_222900.html</u>

01/11/17 6:00 - 01/18/17 6:00

Most compounds detected by both instruments are typically present in background air at detectable levels. This information indicates that the OP-FTIR units are effectively measuring composition of the gas components within its path. Specific instrument information is reported below.

Waste retrieval operations resumed on 1/12/2017 at 11:12 pm and sluicing operations were performed continuously for approximately 12 hours until the system was shut down on 1/13/2017. Operations were shut down due to low temperature measured in a waste transfer pit. Retrieval operations were restarted on 1/14/2017 at 10:36 pm and pumping continued intermittently until 1/15/2017 at 5:10 am, when operations were shut down for a few hours because the material balance exceeded the allowable level. Sluicing operations resumed on 1/15/2017 at 9:42 am and ran continuously until the system was intentionally shut down on 1/16/2017 at 3:17 am. The OP-FTIR instruments were off-line and did not report data during these waste retrieval activities.

01/11/17 6:00 - 01/18/17 6:00

January 11th – January 18th 2017 Instrument Notes:

Chemical	506A: OP-FTIR Multipath	506B: OP-FTIR Single
Nitrous Oxide*	0.28 – 0.55 ppm ^a	0.32 - 0.45 ppm ^a
Ammonia*	ND – 0.021 ppm	ND – 0.020 ppm
Methane	0.102 – 2.12 ppm ^a	1.50 – 1.97 ppm ^a
1-3-Butadiene*	ND	ND
1-Butanol*	ND	ND – 1.36 ppm
2-Hexanone*	ND	ND
3-Buten-2-one*	ND	ND
Acetaldehyde*	ND	ND
Acetonitrile*	ND	ND
Benzene*	ND	ND
Butanal*	ND	ND
Butyl Nitrite*	ND	ND
Ethylamine*	ND	ND
Formaldehyde*	ND	ND
Furan*	ND	ND
Methanol*	ND	ND – 0.30 ppm
Methyl Isocyanate*	ND	ND
Methyl Nitrite*	ND	ND
N-Nitrosodiethylamine*	ND	ND
N-Nitrosodimethylamine*	ND	ND
N-Nitrosomorpholine*	ND	ND
Propanenitrile*	ND	ND
Pyridine*	ND	ND
Tributyle Phosphate*	ND	ND

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

Notes: *Chemical is on COPC list

ND – Not detected by instrument (i.e., either value reported was 0 or R^2 value is <0.5)

(a) Disturbed data not included in the table for these compounds

01/11/17 6:00 - 01/18/17 6:00

Figure 1. OP-FTIR A (506A) Review. (Note that concentration units are ppb)



01/11/17 6:00 - 01/18/17 6:00



Figure 2. OP-FTIR B (506B) Review. (Note that concentration units are ppb)

01/11/17 6:00 - 01/18/17 6:00

Table 2. OP-FTIR Instrument Time Reporting^a.

Instrument	Comments	
506A	The instrument was reported 48% of the time.	
506B	The instrument was reporting 34% of the time.	

Notes: a) % down is based on data reported to OSI PI System⁵

⁵ OSI PI System is a data visualization software package from <u>OSIsoft</u>.