

OP-FTIR Weekly Summary

11/09/16 6:00 – 11/16/16 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 10s to 100s 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 (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 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. Results presented here are for compounds having an R^2 value of greater than or equal to 0.5.

During the week in review, instrument 506A detected nitrous oxide (N_2O), methane (CH_4), 1-3 butadiene, 1-butanol, and methanol. A recurring pattern of simultaneous N_2O and CH_4 spikes was noted again this week. The 1-3 butadiene R^2 value is typically below the reporting threshold of 0.5, but in a few instances the R^2 value was 0.5 or above and the detected peak concentration of 1-3 butadiene was 0.21 ppm. However, no detections were found which would indicate that an OEL of 1 ppm was exceeded. Values reported for 1-butanol and methanol both occurred during time periods where the nitrous oxide and methane observations were atypical. Additional analysis is needed for confirmation of 1-butanol and methanol during these time periods.

Instrument 506B detected N_2O , CH_4 , 1-butanol, and methyl nitrite. Concentrations of N_2O and CH_4 are consistent with values reported by instrument A for the week. Values reported for 1-butanol and methyl nitrite both occurred during time periods where the nitrous oxide and methane observations were atypical. Additional analysis is needed for confirmation of 1-butanol and methanol during these time periods.

The compounds detected by both instruments during most of the week are typically present in air at detectable levels (including 1-3 butadiene²). During those time

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

² EPA: <https://www.epa.gov/sites/production/files/2016-08/documents/13-butadiene.pdf>

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periods the OP-FTIR units were effectively measuring composition of the gas components within its path.

During the periods when the nitrous oxide and methane concentrations were suppressed (atypical), 1-butanol, methanol, and methyl nitrite were reported. All three, 1-butanol, methanol, and methyl nitrite, are on the COPC list with OEL limits of 20 ppm, 200 ppm, and 0.1 ppm respectively. The atypical time periods correspond with fog. Fog, condensed atmospheric water vapor, scatters and distorts the OP-FTIR spectrum - a different background spectrum should be used for measurement and processing using classical least squares regression.³ Troubleshooting is necessary to determine the impact of fog on the OP-FTIR system and define operational expectations during conditions of background interference.

Specific instrument information is reported below.

November 9th – November 16th 2016 Instrument Notes:

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

Chemical	506A: OP-FTIR Multipath	506B: OP-FTIR Single
Nitrous Oxide*	ND – 0.461 ppm ^a	ND – 0.403 ppm
Ammonia*	ND	ND
Methane	ND – 2.7 ppm ^a	ND – 1.9 ppm
1-3-Butadiene*	ND – 0.211 ppm ^b	ND
1-Butanol*	ND – 3.1 ppm ^c	ND – 2.0 ppm ^c
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 – 0.207 ppm ^c	ND
Methyl Isocyanate*	ND	ND
Methyl Nitrite*	ND	ND – 0.283 ppm ^c
N-Nitrosodiethylamine*	ND	ND
N-Nitrosodimethylamine*	ND	ND

³ "Detection of chemical agents in the atmosphere by open-path FT-IR spectroscopy under conditions of background interference: II. Fog and rain": <https://www.ncbi.nlm.nih.gov/pubmed/20414770>

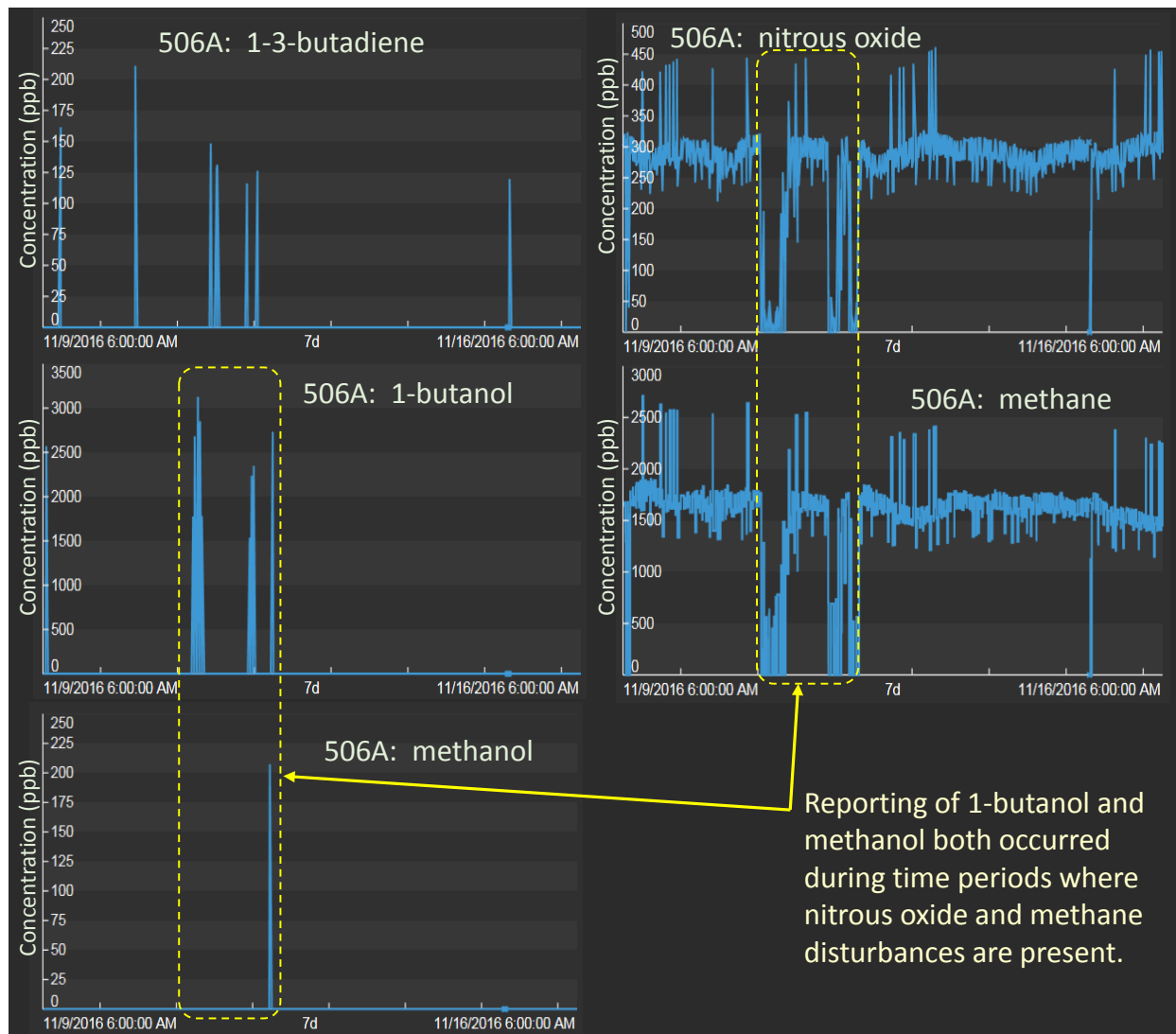
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Chemical	506A: OP-FTIR Multipath	506B: OP-FTIR Single
N-Nitrosomorpholine*	ND	ND
Propanenitrile*	ND	ND
Pyridine*	ND	ND
Tributyle Phosphate*	ND	ND

Notes: *Chemical is on COPC list
 a – Peaks to maximum and minimum observed values occur at the same time
 b – Additional analysis needed for confirmation of chemical identification
 c – Multiple peaks observed on during data disturbances, additional analysis needed for confirmation of chemical identification
 ND – Not detected by instrument (i.e., either value reported was 0 or R² value is <0.5)

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



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

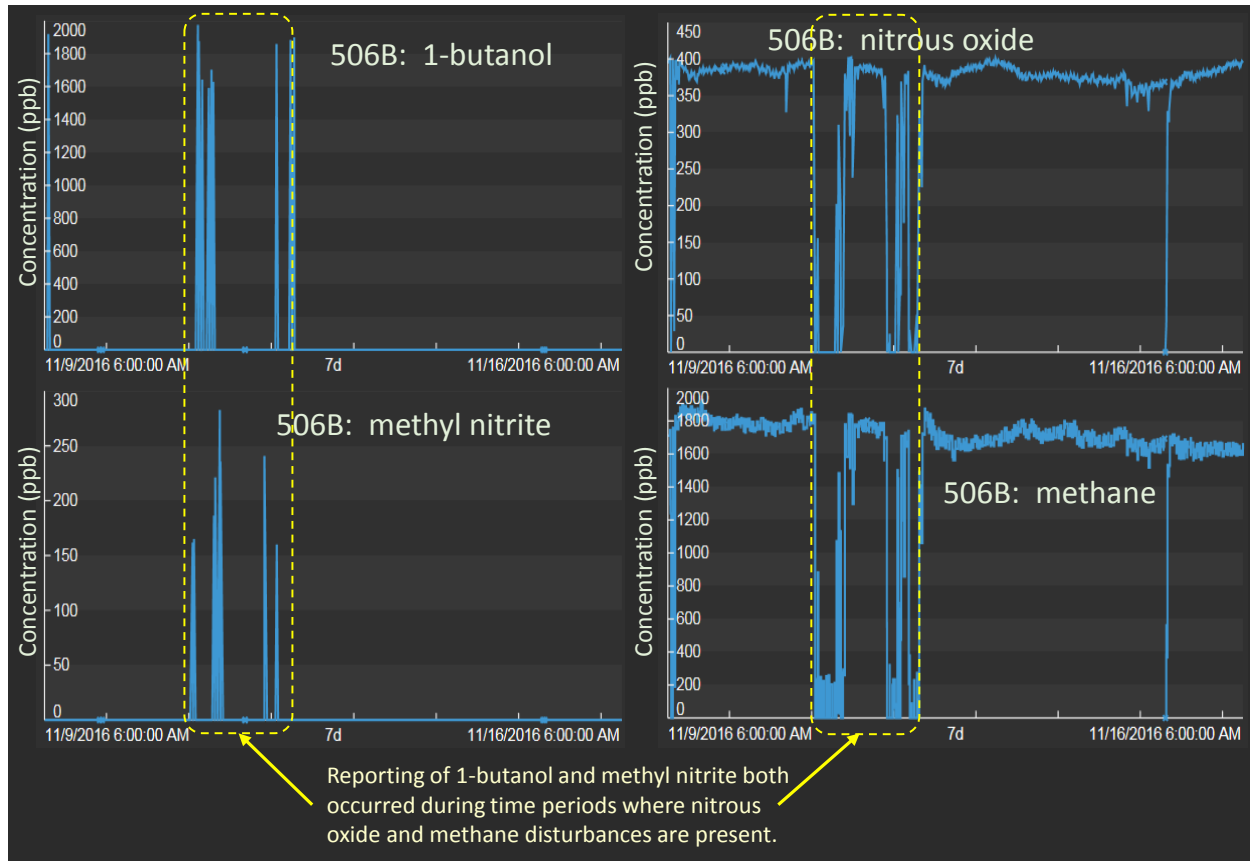


Table 2. OP-FTIR Instrument Time Reporting^a.

Instrument	Comments
506A	The instrument was reported 100% of the time.
506B	The instrument was reporting 100% of the time.

Notes: a) % down is based on review of data from OSI PI⁴

⁴ OSI PI is a data visualization software package from [OSIsoft](http://www.osisoft.com).