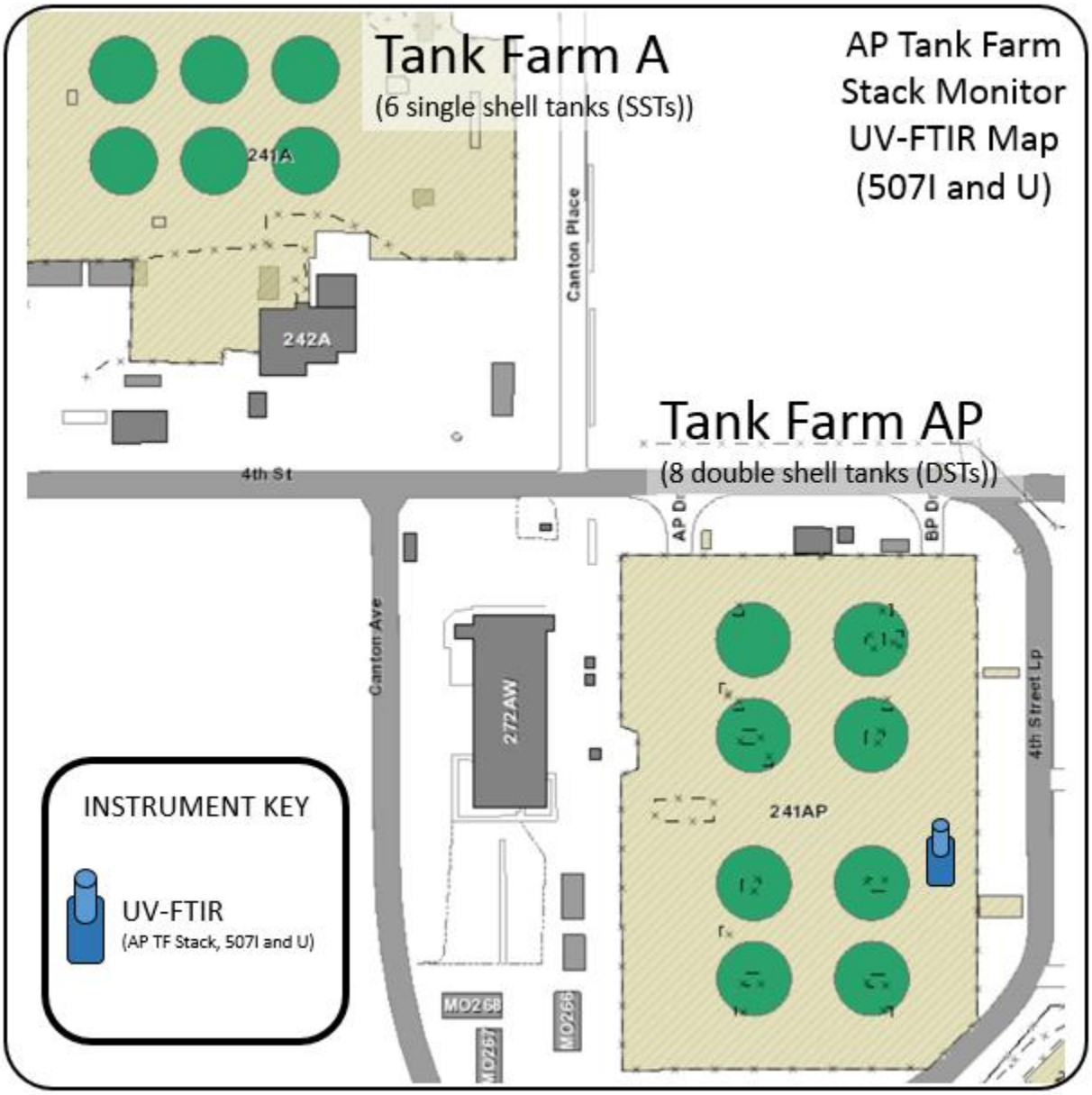
Vapor Monitoring Detection System Weekly Report – AP Tank Farm Stack Monitoring

Revision 0: Initial Release of Report

2/22/2017 6:00 – 3/1/2017 6:00

AP-Tank Farm Stack Monitor (north is up)



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Abbreviations and Units

CH_4	=	methane
COPC	=	chemicals of potential concern
FTIR	=	Fourier transform infrared spectrometer
IDMS	=	Integrated Document Management System
IR	=	infrared
ND	=	not detected
NH_3	=	ammonia
NO	=	nitric oxide
N_2O	=	nitrous oxide
OEL	=	occupational exposure limit
OSHA	=	Occupational Safety and Health Administration
PEL	=	permissible exposure limit
ppb	=	parts per billion
ppm	=	parts per million
UV	=	ultraviolet
UV-DOAS	=	ultraviolet differential optical absorption spectrometer
UV-FTIR	=	ultraviolet - Fourier transform infrared (representing both analytical elements of the instrument, the UV and IR modules)
VMDS	=	vapor monitoring detection system

VMDS Instruments

507	=	ultraviolet - Fourier transform infrared (UV-FTIR) AP Farm Stack
507I	=	FTIR AP Farm Stack
507U	=	UV-DOAS AP Farm Stack

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Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (2/22/2017 at 6:00 a.m. through 3/1/2017 at 6:00 a.m.) using the AP-Farm stack monitor[1]. This instrument is a dual channel FTIR/UV-DOAS spectrometer that provides real-time multi-gas measurement (qualitative and quantitative) of gases. The concentrations detected for the 507I (FTIR) and 507U (UV-DOAS) shall be reported separately. The implementation method for this instrument allows for very accurate identification and quantification of compounds found in the AP-Farm exhauster stack.

Chemical compounds found in the stack are not representative of what is found in the work environment, so their concentrations are not reviewed against Occupational Exposure Limits (OELs) or other limits implemented in work environments. This review focuses on chemicals present, patterns, and observations during waste disturbing activities.

Pilot-scale testing is focused on evaluating component integration and functionality. Data shown may include results for calibration and calibration check (bump test) performed to verify sensors are functioning; these tests are visible in the data as spikes. Raw spectra (data) may need to be reprocessed and reviewed as understanding of the particular instruments being used as part of the VMDS pilot test are deployed and the company's ability to align the instruments with the overall objectives of the pilot test improves.

For the stack monitor, 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 an instrument software library (library) that specifies which absorption features are analyzed, how analysis is performed, and reporting criteria. Revisions to the library are periodically performed to improve accuracy of analysis for analytes; the optimization of the library is iterative 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 depends on the analytical method (UV or IR), the library used, analyte concentration, other chemical compounds present, and other factors. The compounds present can interfere/overlap with the analyte spectral signature, especially for compounds having the same functional groups (e.g., methyl or ketone groups). Work is ongoing to optimize the library and minimize these interferences.

[1] AP-Farm Stack Monitor Fact Sheet: https://hanfordvapors.com/wp-content/uploads/2016/11/UV-FTIR-Fact-Sheet.pdf

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2/22/2017 through 3/1/2017 Summary

There were no retrieval or waste disturbing activities during the reporting period. Following replacement of the IR (507I) module on 1/30/2017, the software was re-installed, but the library loaded to the software was not updated with the appropriate reporting thresholds and spectral ranges. As a result, the 507I data for many of the chemical compounds were reported as large positive and negative values that are considered erroneous. Ammonia and nitrous oxide have typically been detected by the 507I instrument in the past, but ammonia and nitrous oxide data reported this week are considered erroneous because the reporting thresholds were not correctly applied. Therefore, data and graphs are not included for 507I.

The UV-DOAS (507U) was operating normally during the reporting period. Table 1 shows that ammonia concentrations ranged from 37 to 46 ppm (typical AP stack readings), mercury concentrations ranged from 0.06 to 0.093 ppb and m-xylene from non-detect to 0.081 ppm. The low readings of ammonia concentrations measured with the 507U on 2/27/2017 and 2/28/2017 were due to the instrumentation set up on the non-operating stack after operations changed the stack at approximately 09:00 on 2/27/2017 (Figure 1). The instrumentation was in line with the operating stack at approximately 15:00 on 2/28/2017. The elevated ammonia concentrations between approximately 13:30 to 16:30 on 2/23/2017 are due to calibration and configuration activities performed by Cerex on the spectrometer. The mercury concentrations were within typical levels observed when no waste activities occur (Figure 2). Figure 3 shows individual observances of m-xylene from 507U during the reporting period; concentrations are in line with what can be seen in urban areas[2]. Table 2 shows the reporting time of the stack monitors. Both the 507I and the 507U reported to OSI PI for 100% of the reporting period, although the data from 507I are considered erroneous and 507U data has been reprocessed.

The collection of 507U data for this reporting week preceded library changes performed on 3/8/2017. Data reported here has been reprocessed with the new library to aid in correct identification of constituents, such as mercury. The reprocessed data with the optimized library improves performance regarding false-positive and false-negative readings of compounds reported to OSI PI[3]. The data were reprocessed and the output data is stored in the Integrated Document Management System (IDMS).

[2] EPA Xylenes: https://www.epa.gov/sites/production/files/2016-09/documents/xylenes.pdf

[3] OSI PI System is a data visualization software package from OSIsoft.

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Table 1. Chemical Species Detected[a] in the AP Tank Farm Stack by Method

Chemical	507I FTIR (ppm)	Chemical	507U[a] UV-DOAS (ppm)
Ammonia*	N/A	Ammonia*	37 - 46
Nitrous Oxide*	N/A	Nitric Oxide	ND
Methane	N/A	1,3-Butadiene*	ND
1,3-Butadiene*	N/A	2-Methyl-2-butenal*	ND
1-Butanol*	N/A	2-Methylfuran*	ND
2-Hexanone*	N/A	Acetaldehyde*	ND
3-Buten-2-one*	N/A	Benzene*	ND
Acetaldehyde*	N/A	Butanal*	ND
Acetonitrile*	N/A	Ethylamine*	ND
Benzene*	N/A	Formaldehyde*	ND
Butanal*	N/A	Furan*	ND
Butyl Nitrite*	N/A	Mercury*	0.000060 – 0.000093
Ethylamine*	N/A	Methyl Nitrite*	ND
Formaldehyde*	N/A	Pyridine*	ND
Furan*	N/A	1,2,4 Trimethylbenzene	ND
Methanol*	N/A	1,3,5 Trimethylbenzene	ND
Methyl Isocyanate*	N/A	Ethylbenzene	ND
Methyl Nitrite*	N/A	m-Xylene	ND – 0.081
N-Nitrosodiethylamine*	N/A	Nitrogen Dioxide	ND
N-Nitrosodimethylamine*	N/A	o-Xylene	ND
N-Nitrosomorpholine*	N/A	p-Xylene	ND
Propanenitrile*	N/A	Styrene	ND
Pyridine*	N/A	Sulfur dioxide	ND
Tributyl Phosphate*	N/A	Toluene	ND

Notes:
a) Chemical concentration data was reprocessed and are different than reported in OSI PI
N/A) Not Applicable; the data reported into OSI PI by the instrument are considered suspect because the reporting thresholds were not correctly applied, see text above.
ND – Not detected
* Chemical is on COPC list

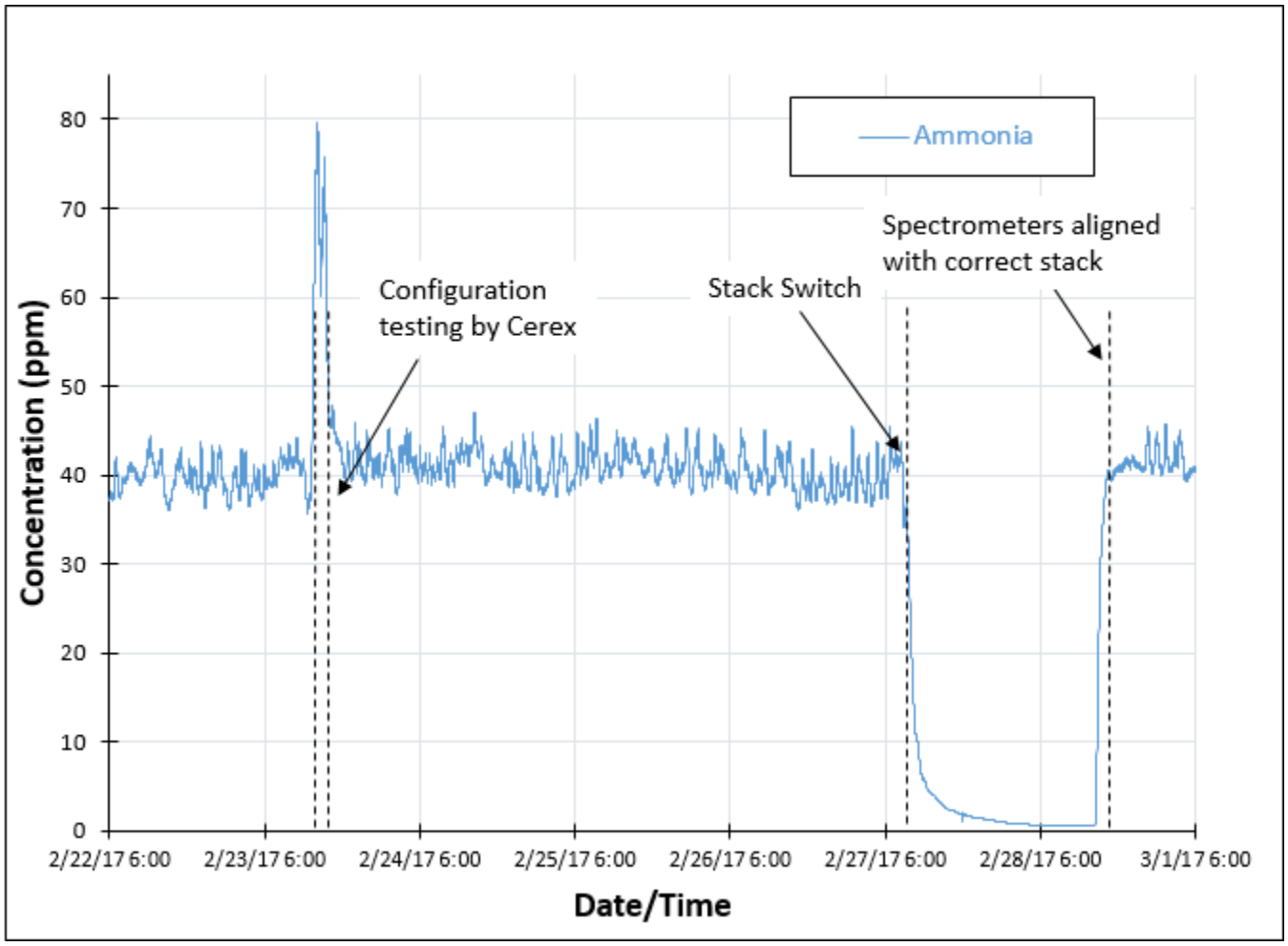

Figure 1. UV-DOAS (507U) Ammonia Data Review.
(Note that concentration units are ppm)

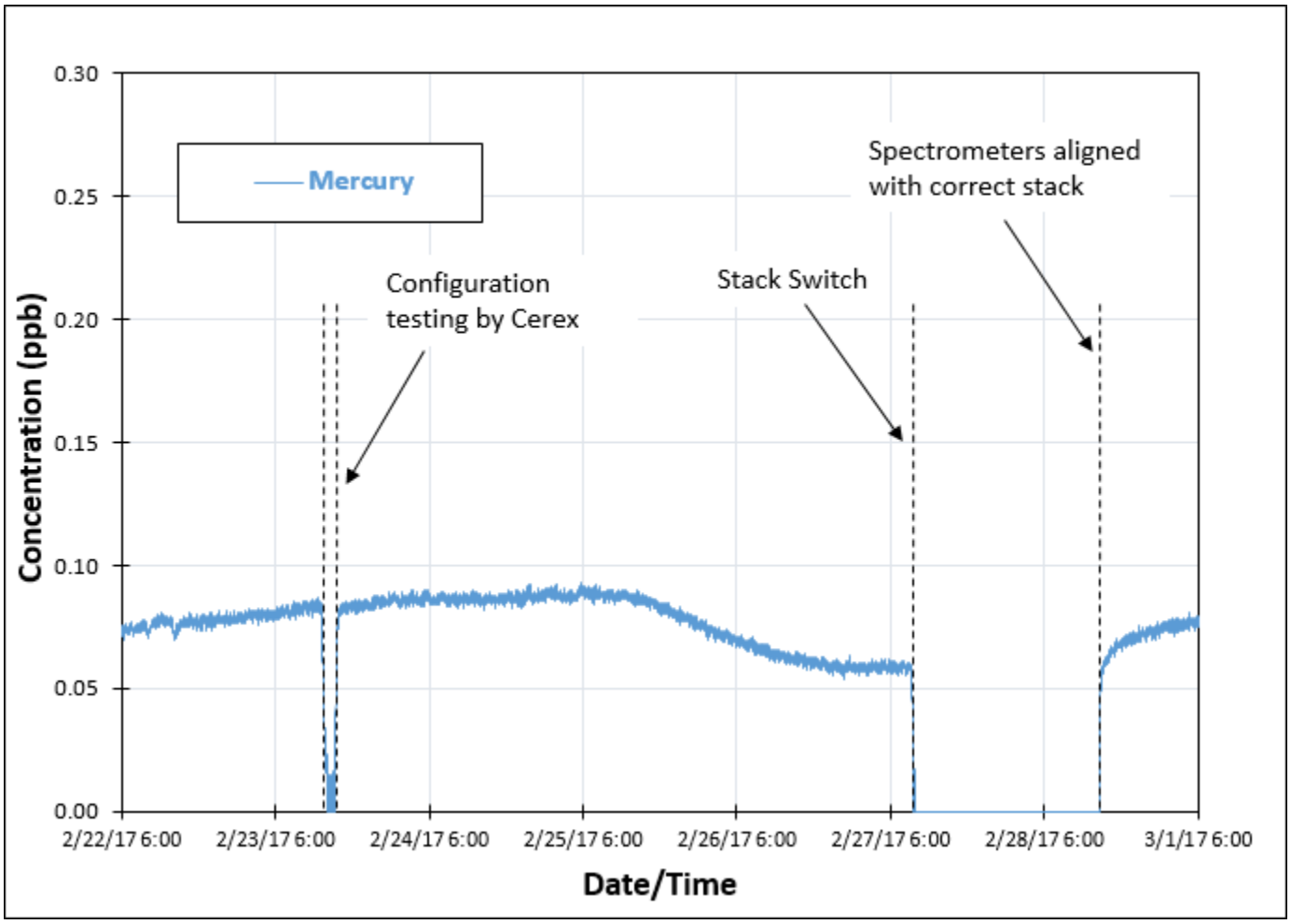

Figure 2. UV-DOAS (507U) Mercury Data Review.
(Note that concentration units are ppb)

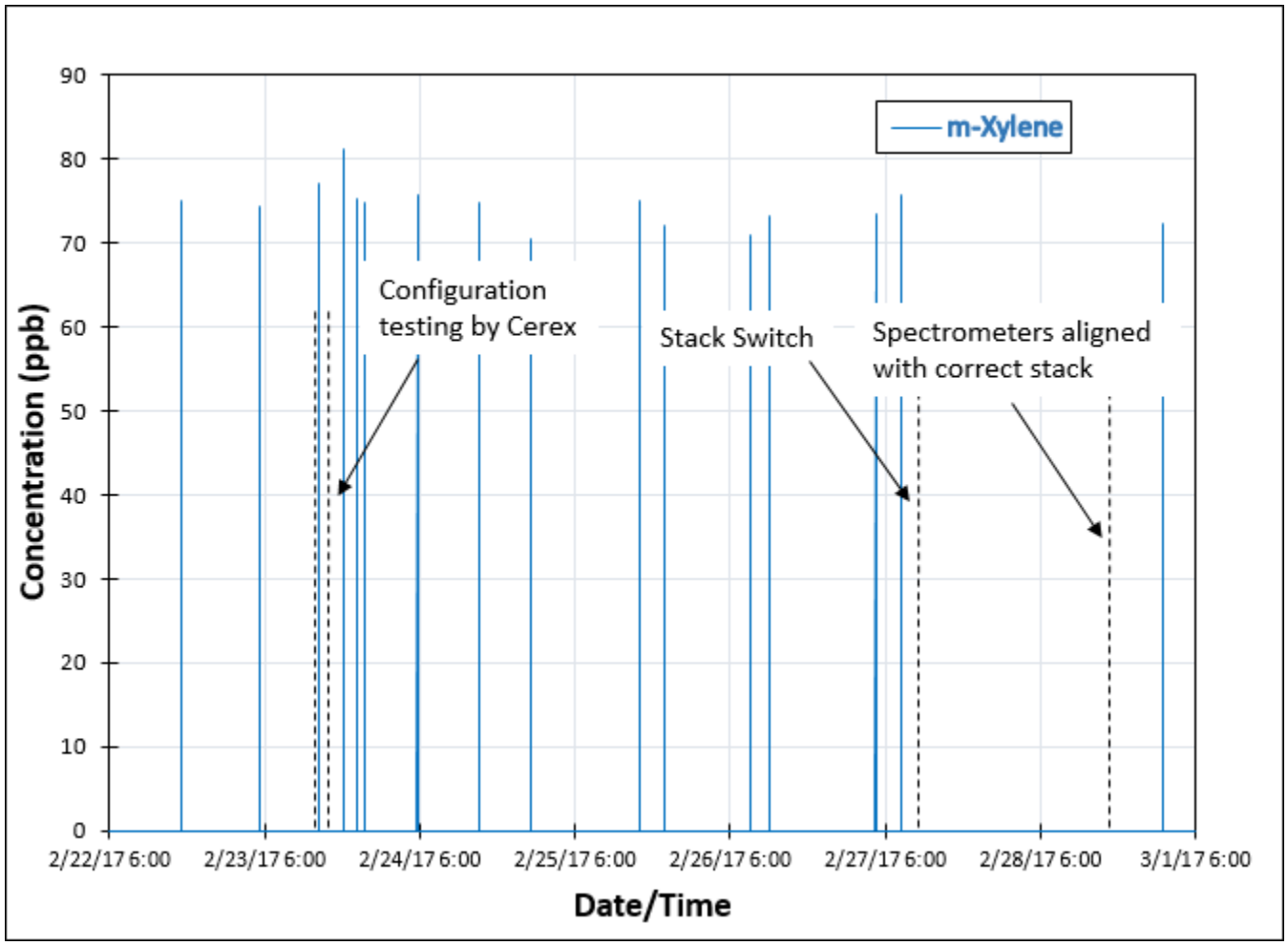

Figure 3. UV-DOAS (507U) m-Xylene Data Review.
(Note that concentration units are ppb)

Table 2. Stack Monitor Time Reporting.

Instrument	% Time Reporting
507I	100%
507U	100%

Notes: % time reporting is based on data reported to OSI PI System