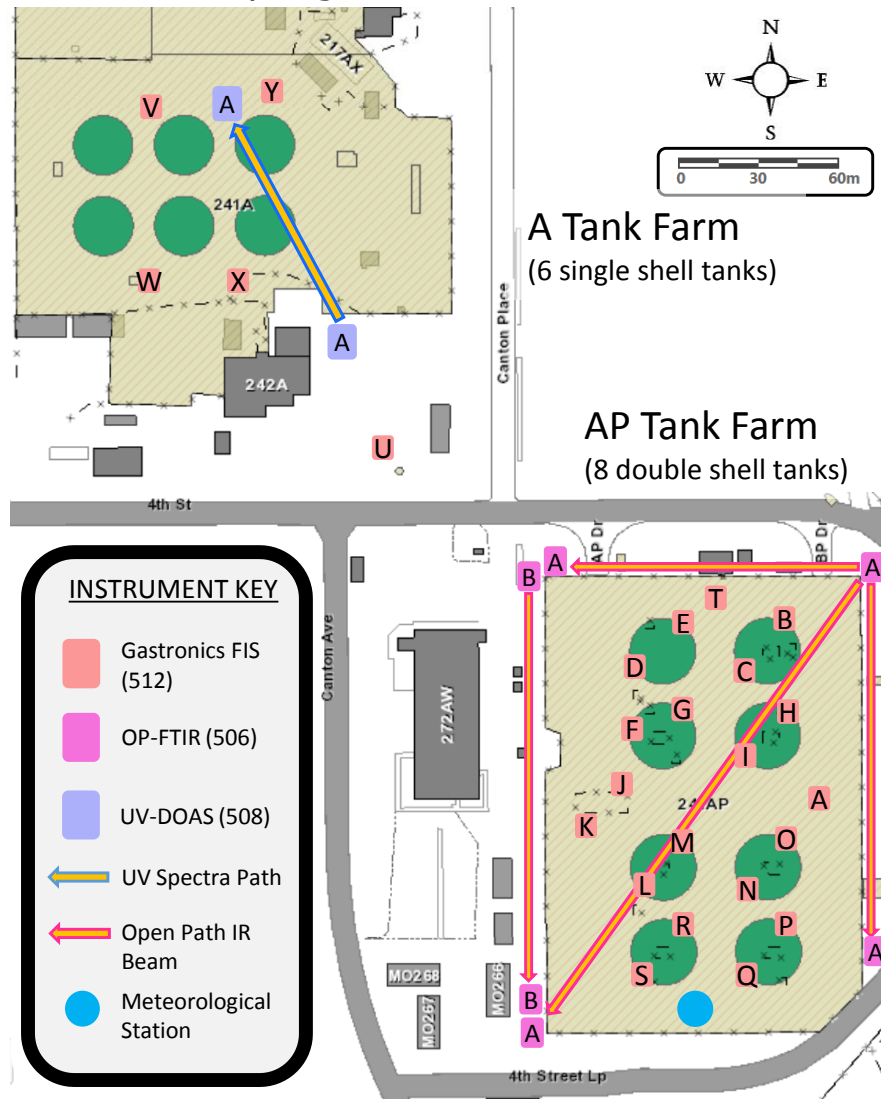


Vapor Monitoring and Detection System Weekly Report – A and AP Tank Farm Field Instrument Report

Revision 0 – Initial Release of Report

3/29/2017 6:00 – 4/5/2017 6:00

Instrument/Sampling Locations – A and AP Tank Farms



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Abbreviations and Units

| | | |
|------------------|---|---|
| CH ₄ | = | methane |
| COPC | = | chemicals of potential concern |
| DRI | = | direct reading instrument |
| FIS | = | fixed instrument skid |
| IR | = | infrared |
| ND | = | not detected |
| NH ₃ | = | ammonia |
| NO | = | nitric oxide |
| N ₂ O | = | nitrous oxide |
| NO ₂ | = | nitrogen dioxide |
| 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 | = | ultraviolet |
| UV-DOAS | = | ultraviolet differential optical absorption spectrometer ² |
| VMDS | = | vapor monitoring and detection system |
| VOC | = | volatile organic compounds, which include both volatile and semi-volatile compounds |

VMDS Instruments

| | | |
|------|---|--|
| 506A | = | OP-FTIR Multi-Path |
| 506B | = | OP-FTIR Single-Path |
| 508A | = | UV-DOAS |
| 512 | = | FIS Gastronics Direct Reading Instrument |

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 (3/29/2017 at 6:00 a.m. through 4/5/2017 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. 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.

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 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 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.

The direct read instruments located within AP and A Tank Farms include the Fixed Instrument Skid (FIS) Gastronics (512) units with sensors for detecting NH₃ and VOCs.

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Summary for 3/29/2017 through 4/5/2017

The following sections summarize data reporting for vapor monitoring and detection instruments at AP and A Tank Farms for the 3/29/2017 through 4/5/2017 period. Instruments at AP Tank Farm include open path FTIR instruments (multi-path and single-path) and the FIS Gastronics direct reading instruments. Instruments at A Tank Farm include the UV-DOAS spectrographic instrument and the FIS Gastronics direct reading instruments. No waste retrieval activities occurred during this reporting period.

AP TANK FARM

AP Tank Farm OP-FTIR Instruments

During the week in review, instrument 506A reported nitrous oxide (N₂O), methane (CH₄), and ammonia (NH₃) (Table 1). Nitrous oxide and methane are typically found in the atmosphere at background levels of approximately 0.33 ppm for N₂O and 1.8 ppm for CH₄³⁴. Ammonia was detected on 4/3/2017 and 4/4/2017 and ranged from non-detect to 0.12 ppm. The instrument's software locked up between 11:28 on 3/30/2017 and 6:05 on 4/3/2017 and did not report new data for methane and nitrous oxide, but only reported the last value during this period (Figure 1). At 6:07 on 4/3/2017, the instrument resumed reporting data after the onboard PC was rebooted. At 13:30 on 4/4/2017, the OP-FTIR instrument was temporarily shut down for base and tower modifications.

Single-path instrument 506B detected N₂O, CH₄, and NH₃ during this week (Table 1). Ammonia was detected on 3/31/2017 and 4/1/2017 and ranged from non-detect to 0.12 ppm. Between 11:10 on 4/3/2017 and 12:32 on 4/4/2017, the instrument's software locked up and did not report new data for methane and nitrous oxide (Figure 2). The instrument's software was restarted and the instrument resumed reporting valid data from 12:32 on 4/4/2017 through the reporting period.

Most compounds detected by both instruments are typically present in air at detectable levels. Consistency in measured values for these compounds indicates that the OP-FTIR units are effectively measuring composition of the gas components within its path. Specific instrument information is reported in Table 1 and Figures 1 and 2 below.

³ Air Composition from "The Engineering ToolBox": http://www.engineeringtoolbox.com/air-composition-d_212.html

⁴ 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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Table 1. Chemical Species Detected^a on Open Path FTIRs at AP Tank Farm.

| Chemical | 506A: OP-FTIR Multi-Path (ppm) | 506B: OP-FTIR Single-Path (ppm) |
|-------------------------|--------------------------------|---------------------------------|
| Nitrous Oxide* | 0.033 – 0.44 ^b | 0.32 – 0.38 ^b |
| Ammonia* | ND – 0.12 | ND – 0.12 |
| Methane | 1.1 – 2.5 ^b | 1.4 – 1.7 ^b |
| 1,3-Butadiene* | ND | ND |
| 1-Butanol* | ND | ND |
| 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 |
| 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 |
| Tributyl Phosphate* | ND | ND |

Notes: (a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.
 (b) Methane and nitrous oxide values associated with the instrument software locking up are not included in table
 *Chemical is on COPC list
 ND – Not detected

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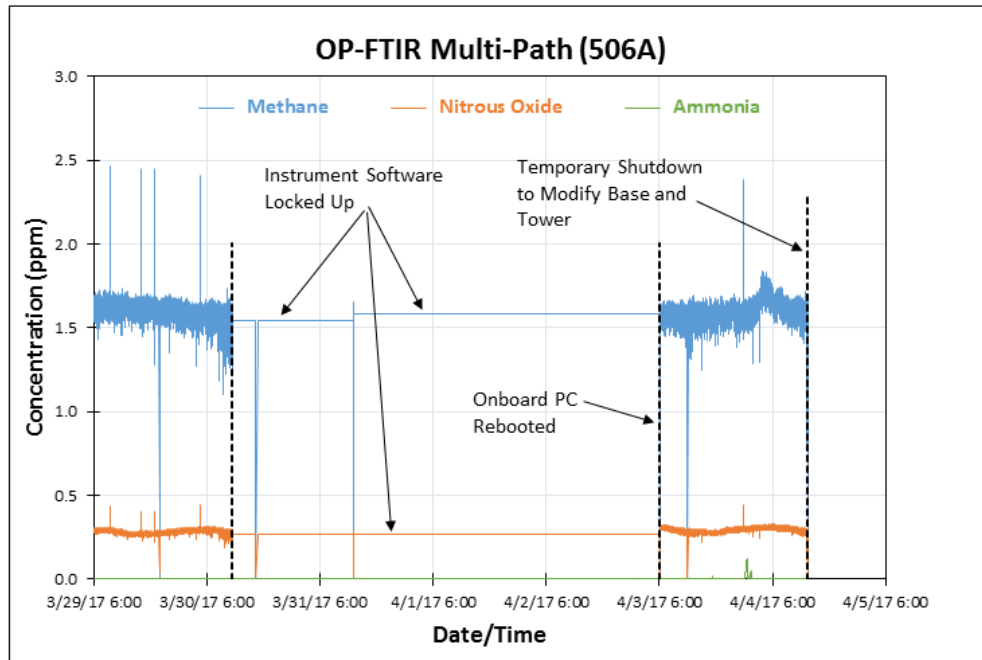


Figure 1. Chemical Compounds Detected by the OP-FTIR Multi-Path (506A) Instrument.

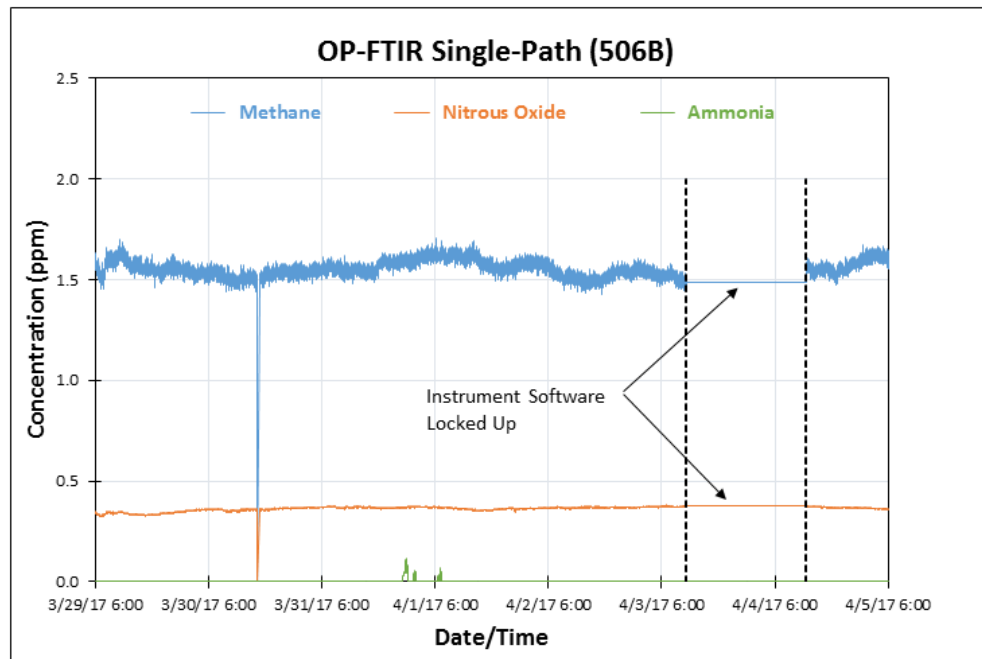


Figure 2. Chemical Compounds Detected by the OP-FTIR Single-Path (506B) Instrument.

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AP Tank Farm Direct Reading Instruments

Instruments located between AP and A tank farms are included.

Gastronics FIS (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. Calibration checks were performed on all of these 512 instruments on 4/3/2017 and 512R was the only NH₃ sensor out of calibration. No ammonia was detected by Gastronics instruments that were in calibration and reporting this week. Regarding VOC sensors, instruments 512C, E, I, J, O, S, and U passed calibration checks. Four of the 512 units reported non-detectable levels of VOC. One unit reported VOC at <2 ppm and no units reported VOCs ≥2 ppm (Table 2). Two units (512C and 512I) reported VOC values <2 ppm, but these are residual values associated with bump tests performed on 4/3/2017. A total VOC action limit of 2 ppm currently is prescribed by Fact Sheet EH-09-001⁵. The N₂O sensors do not hold calibration and are not reported on. Only instruments that are reporting to OSI PI and pass calibration are reported on here.

Table 2. AP Tank Farm FIS Gastronics (512) Comments.

| Compound (units) | Comment | OEL | Action Level | Detection Range |
|-----------------------|---|-----|--------------|-------------------------|
| NH ₃ (ppm) | No ammonia reported on any instrument | 25 | 12 | 1 – 100 |
| VOC (ppm) | <ul style="list-style-type: none">Out of Calibration*: 512A, B, D, F, G, H, K, L, M, N, P, Q, R, and TInstruments that reported no VOCs detected: 512C, I, J, and SInstruments that reported a maximum value of <2 ppm: 512UInstruments that reported maximum values ≥2 ppm: None | N/A | 2 | 0.005 – 50 ⁶ |

* VOC: Only instruments reading within 10% of the calibration gas concentration⁷ during their most recent bump/calibration test are reported here.

⁵ [Fact Sheet for Action Limit for Volatile Organic Compounds, Washington River Protection Solutions, Richland, Washington: \\ap014\EnvironmentalHealth\Fact Sheets\EH-09-001 Turnback value for VOCs.pdf](#)

⁶ One-Page Fact Sheet for Gastronics Fixed Instrument Skid, Tank Farm Vapors Control Team, Version 1.0 2016/7/21 RBC.

⁷ Calibrating and Testing Direct-Reading Portable Gas Monitors: <https://www.osha.gov/dts/shib/shib093013.html>

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A TANK FARM

A Tank Farm UV-DOAS Instrument

Ammonia and nitric oxide (NO) were reported by the instrument during the period under review (Table 3). These compounds are typically found in detectable quantities in air⁸. Analyte concentrations are reported Table 3 and Figure 3 below.

Table 3. Chemical Species Detected^a on UV-DOAS at A Tank Farm

| Chemical | 508A: UV-DOAS (ppm) | Chemical | 508A: UV-DOAS (ppm) |
|---------------------|---------------------|------------------------|---------------------|
| Ammonia* | ND – 0.19 | Methyl Nitrite* | ND |
| Nitric Oxide | ND – 0.078 | Pyridine* | ND |
| 1,3-Butadiene* | ND | 1,2,4-Trimethylbenzene | ND |
| 2-Methyl-2-butenal* | ND | 1,3,5-Trimethylbenzene | ND |
| 2-Methylfuran* | ND | Ethylbenzene | ND |
| Acetaldehyde* | ND | m-Xylene | ND |
| Benzene* | ND | Nitrogen Dioxide | ND |
| Butanal* | ND | o-Xylene | ND |
| Ethylamine* | ND | p-Xylene | ND |
| Formaldehyde* | ND | Styrene | ND |
| Furan* | ND | Sulfur Dioxide | ND |
| Mercury* | ND | Toluene | ND |

Notes: (a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.

*Chemical is on COPC list

ND – Not detected

⁸ Air Composition from "The Engineering ToolBox": http://www.engineeringtoolbox.com/air-composition-d_212.html

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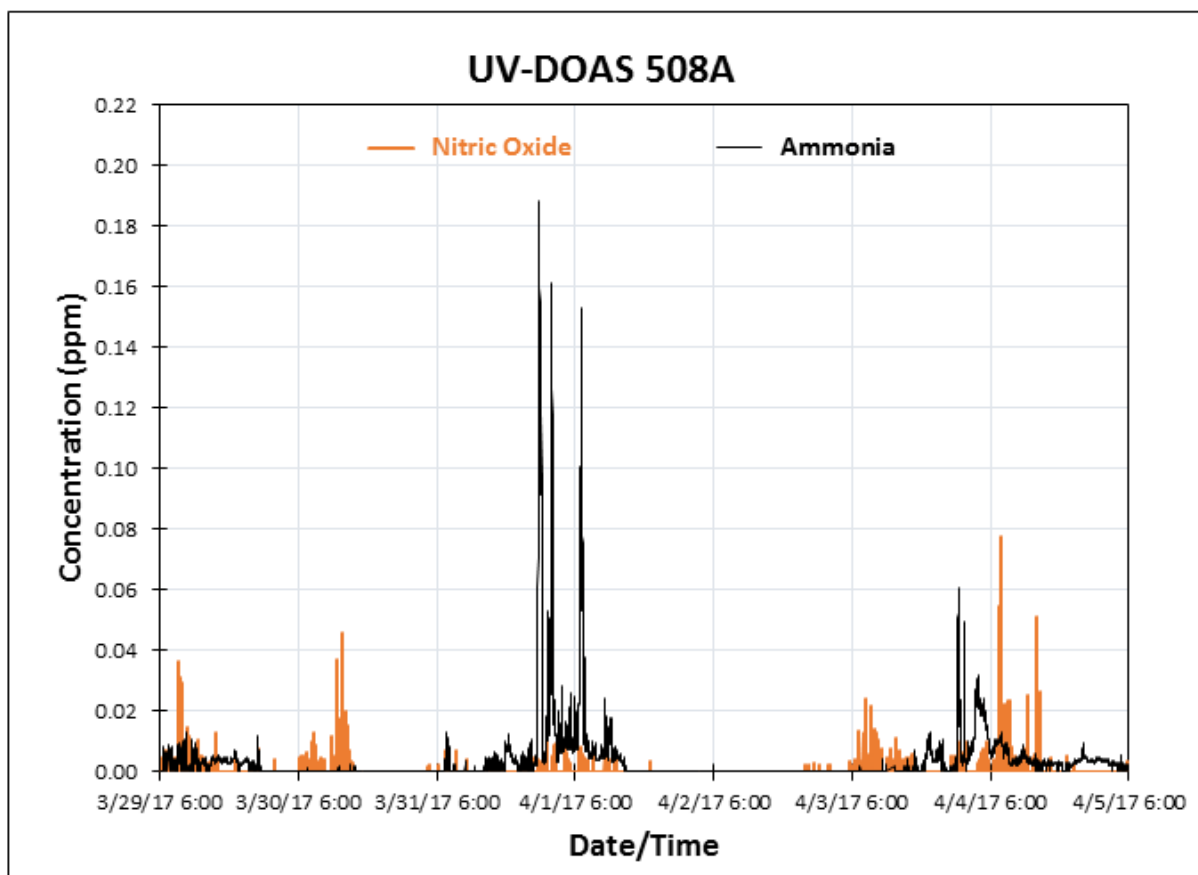


Figure 3. Chemical Compounds Detected by UV-DOAS (508A).

A Tank Farm Direct Reading Instruments

FIS Gastronics (512 - NH₃, VOCs, N₂O): Units located in A Tank Farm include: 512V, W, X, and Y (Table 4). Calibration checks were performed on all for instruments with all four passing ammonia calibration and three passing VOC calibration (512V, W and X). None of these instruments reported to OSI PI during the week.

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Table 4. A Tank Farm Gastronics (512) Comments.

| Compound (units) | Comment | OEL | Action Level | Detection Range |
|-----------------------|---|-----|--------------|-------------------------|
| NH ₃ (ppm) | Instruments did not report to OSI PI | 25 | 12 | 1 – 100 |
| VOC (ppm) | <ul style="list-style-type: none"> Out of Calibration*: 512Y Instruments did not report to OSI PI | N/A | 2 | 0.005 – 50 ⁹ |

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

3/29/2017 – 4/5/2017 Instrument Operational Status:

Time reporting is calculated using the time sensors that report to OSI PI System¹⁰ for each instrument (Tables 5 and 6).

Table 5. Gastronics Direct Reading Instruments (512) % Time Reporting^a.

| Instrument | % Time Reporting | Instrument | % Time Reporting |
|------------|------------------|------------|------------------|
| 512A | 46 | 512N | 63 |
| 512B | 26 | 512O | 0 |
| 512C | 27 | 512P | 13 |
| 512D | 23 | 512Q | 97 |
| 512E | 0 | 512R | <1 |
| 512F | 23 | 512S | 0 |
| 512G | 17 | 512T | 27 |
| 512H | 98 | 512U | 99 |
| 512I | 98 | 512V | 0 |
| 512J | <1 | 512W | 0 |
| 512K | 26 | 512X | 0 |
| 512L | 99 | 512Y | 0 |
| 512M | 26 | | |

a) % time reporting based on NH₃.

⁹ One-Page Fact Sheet for Gastronics Fixed Instrument Skid, Tank Farm Vapors Control Team, Version 1.0 2016/7/21 RBC.

¹⁰ OSI PI System is a data visualization software package from [OSIsoft](#).

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Table 6. Spectrometer Instruments Time Reporting.

| Instrument | % Time Reporting |
|-------------------|-------------------------|
| 506A | 36 ^a |
| 506B | 85 ^a |
| 508A | >99 |

(a) Instrument reporting time does not include time the instrument software locked up