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NUCON Vapor Abatement Unit Performance on Hanford Tank Farm Chemicals of Potential Concern

September 2018 – Rev. 0

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

Pacific Northwest National Laboratory (PNNL) assessed the performance of a NUCON International, Inc., Vapor Abatement Unit (VAU) prototype for the reduction of Hanford tank farm vapors associated chemicals of potential concern (COPCs). The engineering-scale test was conducted in compliance with the *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)* test plan at PNNL in Richland, WA.[1] Performance testing started on May 4, 2018, and continued through June 13, 2018.

NUCON developed a novel toxic vapor thermal oxidation technology, known as the NUCON VAU (see Figure S.1). In deployment, it is envisioned that the VAU will pull gas from the headspace of a single-shell tank (SST) and treat it through a sequential series of activated carbon, diesel engine combustion (diesel generator), and exhaust aftertreatment (oxidation catalyst and particulate filter). The VAU prototype in this test included a 15 kVA diesel generator with a nominal inlet flowrate of 50 cfm. Under study in this test was the diesel generator and exhaust aftertreatment; i.e., MERSORB® was not included because it is a mature commercial product with a high Technology Readiness Level and large body of knowledge regarding COPC removal performance.

Figure S.1. Engineering-Scale Prototype of NUCON Vapor Abatement Unit

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[1] Rappe KG. 2018. *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)*. Test Plan TP-71248-01, Rev. 0, April 2018, Pacific Northwest National Laboratory, Richland, Washington.

Eleven COPCs were chosen for testing to represent 59 of the 61 identified COPCs (less elemental mercury and dimethyl mercury).[1] The test COPCs are shown in Table S.1, and were chosen either due to (i) their frequency and/or significant concentrations found in Hanford high-level waste SST vapor emissions, or (ii) their use as a surrogate to represent a class of COPC compounds, or both. Testing performed on each COPC can be summarized as follows:

- Test 1 – Validation of analytical readiness in the VAU exhaust.
- Test 2 – Determination of the COPC concentration in select locations of the VAU with the COPC supplied to the engine inlet at 200% the Hanford Tank Farm Occupational Exposure Limits ($_{\mathrm{HTF}}$OEL) as shown in Table S.1.
- Test 3 – Determination of the COPC concentration in select locations of the VAU with the COPC supplied at a higher concentration (performed only for NDMA, furan, ammonia, and nitrous oxide), also shown in Table S.1.

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[1] The data to complete a preliminary assessment of MERSORB® performance was provided in the MERSORB® Mercury Adsorbents Bulletin 11B28-2012, *MERSORB® Mercury Adsorbents Design and Performance Characteristics,* by NUCON International Columbus, Ohio. MERSORB® has also been evaluated for removal of dimethyl mercury and was selected as the best available control technology for mercury abatement (both elemental mercury and dimethyl mercury) in the AP stack (*Evaluation of Best Available Control Technology for Toxics (tBACT) Double Shell Tank Farms Primary Ventilation Systems Supporting Waste Transfer Operations*. RPP-ENV-46679, Rev. 0, prepared by Washington River Protection Solutions for the U.S. Department of Energy, Office of River Protection, Richland, Washington).

Table S.1. Summary of Chemicals of Potential Concern and Targeted Test Concentrations

CAS	Name	Maximum[1] Conc. SWIHD/TWINS (COPC or surrogate)	200% $_{\text{HTF}}$OEL[a] Test	High Concentration Test	Analytical Method
75-07-0	Acetaldehyde	39 ppm	50 ppm	– [b]	PTR-MS
75-05-8	Acetonitrile	18.8 ppm	40 ppm	– [b]	PTR-MS
71-43-2	Benzene	0.189 ppm	1 ppm	– [b]	PTR-MS
107-12-0	Propanenitrile	0.78 ppm	12 ppm	– [b]	PTR-MS
106-99-0	1,3-Butadiene	3.38 ppm	3.4 ppm[c]	– [c]	PTR-MS
50-00-0	Formaldehyde	0.157 ppm	0.6 ppm	– [b]	PTR-MS
108-47-4	2,4-Dimethylpyridine	0.147 ppm	1 ppm	– [b]	PTR-MS
62-75-9	N-Nitrosodimethylamine	0.0621 ppm	0.0006 ppm	0.062 ppm	PTR-MS
110-00-9	Furan	0.721 ppm[c]	0.002 ppm	0.017 ppm	PTR-MS
7664-41-7	Ammonia	2,502 ppm[d]	50 ppm	630 ppm	FTIR
10024-97-2	Nitrous Oxide	831 ppm	100 ppm	831 ppm	FTIR

[a] Hanford tank farm occupational exposure limit ($_{\text{HTF}}$OEL)

[b] No maximum concentration test required since the testing conditions at 200% OEL already bounded the high concentration test conditions.

[c] Due to comparatively similar values for 1,3-butadiene for 200% OEL concentration and the maximum applicable observed concentration, it was decided to increase the concentration of 1,3-butadiene employed in the 200% OEL to be inclusive of both values.

PTR-MS = proton transfer reaction mass spectrometer instrument; FTIR = Fourier-transform infrared spectroscopy instrument.

The target criteria for analytical readiness in Test 1 was to detect each of the COPCs at or below 10% of their respective $_{\text{HTF}}$OELs in a relatively complex diesel exhaust matrix. This also ensured the ability to detect down to the exhaust purification target for each COPC in subsequent tests 2 and 3. This test is of particular importance for the ultra-trace level (<1 ppb) detection and quantification of NDMA and furan that was required of the analytical system. Target criteria for VAU performance in tests 2 and 3 were defined as (i) COPC destruction/removal efficiency (DRE) ≥ 95%, and (ii) exhaust purified to an outlet concentration of ≤ 10% $_{\text{HTF}}$OEL for each COPC.

Results of the NUCON VAU tests are shown in Table S.2. These results can be summarized as follows:

- **Eight of the eleven COPCs successfully achieved all of the VAU target removal (i.e., DRE) and purification performance (i.e., % OEL) criteria, including acetaldehyde, acetonitrile, benzene, propanenitrile, 1,3-butadiene, 2,4-dimethylpyridine, furan, and ammonia.**
- **Only nitrous oxide did not meet any target performance (removal or purification) criteria for any of its tests. However, it was consistently reduced by >72% in the engine.**
- **The VAU achieved target removal for NDMA at high concentration, and reduced NDMA exhaust concentration to a very low level in that test. However, it failed to reach target performance metrics for NDMA at 200% OEL. The accuracy of the ultra-trace analysis required for <50% OEL NDMA measurement is likely a factor in these results governing**

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[1] Mahoney et.al. 2018. *Maximum Concentration Values Review for Use in NUCON Vapor Abatement Unit Testing*. RPT-71248-001, Rev. 0; PNNL-27368, Pacific Northwest National Laboratory, Richland, Washington.

VAU perceived performance. This is because these measurements are at the limit of analytical capability for NDMA detection, and the estimated error associated with those measurements is of similar order of magnitude to the NDMA concentration values.

- **Formaldehyde removal and purification results were controlled by a persistent exhaust background level that was not increased by COPC injection. In other words, the VAU successfully reduced incoming formaldehyde to pre-existing exhaust levels.**

Table S.2. Summary of NUCON VAU Destruction Efficiencies and Exhaust Concentrations as % OEL

COPC	Detection Validation	COPC Removal & Purification Performance			
		200% OEL		High Concentration Test	
		DRE	[Exhaust] % OEL	DRE	[Exhaust] % OEL
Acetaldehyde	9.7%	99.6%	1.1%	-[e]	-[e]
Acetonitrile	10.4%	>99.9%	0.1%	-[e]	-[e]
Benzene	2.9%	97.3%	4.7%	-[e]	-[e]
Propanenitrile	1.3%	>99.9%	0.2%	-[e]	-[e]
1,3-Butadiene	9.3%	99.7%	2.6%	-[e]	-[e]
Formaldehyde[a]	10.1%	45.7%	242%	-[e]	-[e]
2,4-Dimethylpyridine	-[d]	99.3%	1.4%	-[e]	-[e]
NDMA[b,c]	49.6%	55.6%	50.4%	>99.9%	13.9%
Furan[c]	4.9%	99.3%	1.7%	99.8%	3.5%
Ammonia	7.9%	98.7%	2.8%	>99.9%	1.3%
Nitous Oxide	5.8%	72.7%	57.9%	69.5%	521%

[a] The inlet background in the 200% OEL injection test was >250% OEL

[b] Prohibitively high background in the exhaust at m/Z 74 prevented 10% OEL detection validation

[c] COPC results (removal & purification) reflect the combination of PTR-MS and TOFWERK ultra-high resolution VOCUS-PTR measurements; see Section 5.5.2 for additional detail and explanation

[d] 10% OEL detection validation was unsuccessful due to prohibitively long passivation time required. Test 3.2 indicated that the analytical system was capable of measuring ~1.4% OEL

[e] No test performed

During testing, gas samples were collected and analyzed before and after the applicable VAU components, including the diesel engine, the diesel oxidation catalyst (DOC), and the diesel particulate filter (DPF). This enabled determination of the contribution of each component to overall VAU performance. The DPF, although an extremely important device for the removal of noxious soot and ash from diesel engine exhaust, had very little impact on COPC concentrations. Conversely, testing revealed that the diesel engine was successful at reducing incoming COPC concentrations significantly for 9 of the 11 COPCs, excluding only formaldehyde and furan, which were conversely generated in the engine.

Testing also revealed that the DOC was a critical component for enabling the VAU to successfully meet the target criteria for 7 of the 1 COPCs, including acetaldehyde, acetonitrile, benzene, propanenitrile, 1,3-butadiene, furan, and ammonia. 2,4-Dimethylpyridine at 200% OEL and NDMA at high concentration were both removed at >95% DRE by the diesel engine alone; conversely, formaldehyde and furan, which were both generated by the engine in comparatively large quantities, were reduced solely by the oxidation

catalyst with high efficiency. Thus, both the diesel engine and catalytic converter contributed significantly to successful VAU performance for COPC removal and exhaust purification.

Acronyms and Abbreviations

200% OEL	two times the Hanford tank farm occupational exposure limit concentration
CAS	Chemical Abstract Service Registry Number
CI	chemical ionization
COPC	chemical of potential concern
DEP	diethylphthalate
DL	detection limit
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
DRE	destruction and removal efficiency
EPA	U.S. Environmental Protection Agency
FTIR	Fourier-transform infrared spectroscopy instrument
GC/MS	gas chromatography mass spectrometry instrument
HDI	How Do I…?
${}_{\text{HTF}}$OEL	Hanford tank farm occupational exposure limit
kVA	kilovolt-ampere
M&TE	measurement and testing equipment
NDMA	N-nitrosodimethylamine
NUCON	NUCON International, Inc.
OEL	occupational exposure limit concentration as established by the Hanford Tank Farm Operations Contractor Washington River Protection Solutions
ORP	Office of River Protection
PFD	process flow diagram
PID	photoionizer instrument detector
PLC	programmable logic controller
PNNL	Pacific Northwest National Laboratory
ppb	parts per billion (= 10^3·ppm)
ppm	parts per million
ppt	parts per trillion (= 10^6·ppm)
PTR-MS	proton transfer reaction mass spectrometer instrument
QA	quality assurance
scfm	standard cubic feet per minute
SST	single-shell tank (located in the Hanford tank farms)
SWIHD HS	Site-Wide Industrial Hygiene Database for Headspace
TWINS IH	Tank Waste Information Network System Industrial Hygiene database
TWINS HS	Tank Waste Information Network System Headspace database
USEPA	United States Environmental Protection Agency
VAU	vapor abatement unit or NUCON vapor abatement unit
VOC	volatile organic compound
WAI	Wastren Advantage, Inc.
WRPS	Washington River Protection Solutions

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1.0 Introduction

The purpose of the Pacific Northwest National Laboratory (PNNL) and NUCON International, Inc. (NUCON) testing was to assess the performance of the NUCON Vapor Abatement Unit (VAU) prototype with the diesel engine and control system update for the abatement of Hanford tank farm vapors. The *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)* test plan[1] covers the methodology and approach towards determining the abatement of 11 specific chemicals of potential concern (COPCs) when processed through the VAU.

NUCON has developed a novel toxic vapor thermal oxidation technology, known as the NUCON VAU. PNNL conducted an engineering-scale evaluation of the fate of COPCs passing through a NUCON VAU prototype. The purpose of the test is to evaluate the VAU vapor destruction efficiency for a selection of 11 COPCs that have been measured in Hanford high-level waste (HLW) single-shell tank (SST) passive breather vapor emissions. At this time, the NUCON VAU is expected to be used on passively ventilated SSTs.

1.1 Background

The Tank Vapor Assessment Team (Wilmarth 2014) identified the need to provide engineered controls to protect tank farm workers from toxic organic vapor emissions from Hanford HLW tanks. In response to this need, NUCON presented a proposal to the 2016 DOE Office of River Protection (ORP) Grand Challenge competition. This proposal presented a novel thermal oxidation system that is intended to combust HLW tank vapors within an internal combustion engine. This proposal was the Grand Challenge winner. As a result, NUCON has developed a prototype of the proposed system and has conducted proof-of-concept tests. Upon successful completion of the NUCON proof-of-concept testing, Washington River Protection Solutions (WRPS) began preparations for more rigorous engineering-scale evaluation of the VAU prototype in FY17 and FY18.

The initial NUCON VAU proof-of-concept testing was based on a propane engine and an 11.4 kVA generator. A safety and operational review of the propane-based option was evaluated and compared to other fuel types (diesel, natural gas). Due to safety and operational issues identified for the propane-based system, a decision was made to terminate further testing with propane and proceed directly to diesel.[2] For the purpose of the engineering-scale performance evaluation, the VAU was modified, replacing the propane generator with a 15 kVA diesel generator. A diesel oxidation catalyst (DOC) and a diesel particulate filter (DPF) were added to the exhaust train to further reduce vapor emissions.

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[1] Rappe KG. 2018. *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs).* Test Plan TP-71248-01, Rev. 0, April 2018, Pacific Northwest National Laboratory, Richland, Washington.

[2] *NUCON Vapor Abatement Unit Propane Prototype Testing Decision Paper*, October 2017, Washington River Protection Solutions, Richland, Washington

1.2 Initial Laboratory Efforts

This work covers an assessment of the performance of the NUCON VAU as operated by WRPS subcontractors. Initial laboratory efforts were aligned with developing and validating the analytical methods to assess the COPC concentrations in the engine exhaust to criteria levels, developing COPC injection and exhaust sampling systems to support VAU testing, and the use of those methods and systems to assess the COPC destruction performance of the VAU.

The core scope of this test is the determination of the performance of the NUCON VAU as an off-gas abatement technology and its feasibility to reach specific COPC removal and purification targets using real-time instrumentation. Also included in this test were methods for collecting off-line samples from the VAU process (e.g., sorbent tubes and SUMMA® canister samples) to provide secondary confirmation of COPC removal in the NUCON VAU and to inform future WRPS design and permitting efforts. These efforts did not modify or optimize performance of the NUCON VAU in an attempt to reach a specific performance target.

1.3 Test Objectives and Target Performance Criteria

The performance targets for the VAU are as follows:

1. COPCs reduced to 10% Hanford tank farm occupational exposure limit (OEL) concentrations($_{\text{HTF}}$OEL) or less, and/or
2. COPCs destroyed and/or removed with 95% or greater efficiency

The performance target of ≤10% $_{\text{HTF}}$OEL was selected since this concentration level is considered safe for any exposure duration and is below a value that qualifies a compound to be a COPC. The performance target of ≥95% destruction and/or removal efficiency (DRE) was selected since it is consistent with both competing technologies (Strobic Air) and the predicted DREs for the VAU technology. The COPC injection concentration of 200% OEL was selected since a ≤10% $_{\text{HTF}}$OEL will be achieved if a DRE of ≥95% is achieved. The high concentration tests were selected based on the highest concentrations observed in SSTs following stabilization. It is not expected (although it is desired) that all COPCs will be destroyed to below 10% $_{\text{HTF}}$OEL in the high concentration tests since the injection concentrations are 1 to 2 orders of magnitude higher than the $_{\text{HTF}}$OEL.

To determine if these success criteria have been meet, the test plan established the test objectives and respective acceptance criteria presented in Table 1.

Table 1. Test Objectives and Target Performance Criteria

	Test Objective	Acceptance Criteria		
1	Validation of detection of selected COPCs in VAU exhaust at or below the following 10% OEL concentration	CAS	Name	10% OEL
		7664-41-7	Ammonia	2.5 ppm
		10024-97-2	Nitrous Oxide	5.0 ppm
		106-99-0	1,3-Butadiene	0.1 ppm
		71-43-2	Benzene	0.050 ppm
		50-00-0	Formaldehyde	0.030 ppm
		75-07-0	Acetaldehyde	2.5 ppm
		110-00-9	Furan	0.00010 ppm
		75-05-8	Acetonitrile	2.0 ppm
		107-12-0	Propanenitrile	0.60 ppm
		62-75-9	N-Nitrosodimethylamine	0.000030 ppm
		108-47-4	2,4-Dimethylpyridine	0.050 ppm
2	Analysis of selected COPCs in the VAU exhaust using the validated method while injecting the "low-level" concentration of that COPC	Complete VAU exhaust analysis of each COPC at low-level injection to calculate destruction efficiency of VAU		
3	Analysis of selected COPCs in the VAU exhaust using the validated method while injecting the "high-level" concentration of that COPC	Complete VAU exhaust analysis of each COPC at high-level injection to calculate destruction efficiency of VAU		
4	Calculation of the DRE for each COPC in (2) and (3) above	Assess abatement feasibility for each COPC in relation to WRPS target of ≥ 95% DRE and < 10% OEL		
5	Acquisition of samples from the VAU process (e.g., sorbent tubes, canister samples, or Tedlar® bag samples) to provide secondary confirmation of COPC removal in the VAU and to inform subsequent WRPS design and permitting activities	Sample acquisition and data compilation		

1.4 Quality Assurance

The WRPS Quality Assurance (QA) requirements (included in requisition 302351, Rev. 2) specified work be completed using a "Basic Research" approach under the PNNL QA program requirements drawn from NQA-1-2000.

This report was developed under the *NUCON Vapor Abatement Unit Testing Quality Assurance Plan*, 71248-QA-001, Rev. 0 (Meier 2018). The PNNL QA Program is based upon the requirements as defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, "Quality Assurance Requirements." PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part I, "Requirements for Quality Assurance Programs for Nuclear Facilities."
- ASME NQA-1-2000, Part II, Subpart 2.7, "Quality Assurance Requirements for Computer Software for Nuclear Facility Applications," including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development."

The PNNL Quality Assurance Program Description / Quality Management M&O Program Description describes the Laboratory-level QA program that applies to all work performed by PNNL. Laboratory-level procedures for implementing the QA requirements described in the standards identified above are deployed through PNNL's web-based "How Do I…?" (HDI) system, a standards-based system for managing and deploying requirements and procedures to PNNL staff. The HDI procedures (called Workflows and Work Controls) provide detailed guidance for performing some types of tasks, such as protecting classified information and procuring items and services, as well as general guidelines for performing research-related tasks, such as preparing and reviewing calculations and calibrating and controlling measuring and testing equipment (M&TE).

The technology maturity of the work is considered scoping in nature, and the NUCON project used PNNL HDI to meet the Basic Research requirements of the *NUCON Vapor Abatement Unit Testing Quality Assurance Plan*. This determination is based on the revised WRPS Quality Assurance Requirements (QAR) form, revision 1a, signed 2/5/2018 by the WRPS Quality and Project Engineers.

Off-line sampling media was sent to the 222-S laboratory, where Wastren Advantage, Inc. (WAI), a DOE contractor performed the required analytical services under their (WAI) QA program. This program supports compliance with the U.S. Environmental Protection Agency (EPA) methods and protocols identified in this report. WAI subcontractors, such as RJLee, also conducted chemical analysis for the 222-S laboratory in compliance with the WAI QA Program.

Off-line samples sent to Aerodyne Reseach for measurements were done under research-level controls as the VOCUS processes and methodologies are still being finalized. The AreoDyne results were used to adjust the furan and N-nitrosodimethylamine (NDMA) measurements made by the performance-calibrated Quadrupole proton transfer reaction mass spectrometer instrument (PTR-MS) as detailed in Section 5.5.

NUCON provided the VAU as a full system for this performance evaluation. The instrumentation, operational controls, and components were not designed or calibrated to the NQA-1 requirements, so information in Section 5.9 is noted as For Information Only. When instrumentation and measurements were required to establish the system's performance related to this testing effort, Category 1[1] or Category 2[2] calibrations were conducted on the M&TE. The team replaced key thermocouples with NQA-1

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[1] Category 1: M&TE that cannot be calibrated by the staff member due to the lack of expertise and/or lack of required standard equipment, processes, or materials needed for the calibration; therefore, equipment is calibrated by a certified supplier. Examples of Category 1 M&TE: flow meter, thermocouple.

[2] Category 2: M&TE that can be calibrated by the staff member based on their expertise, and performed with material/equipment that is traceable to a nationally or internationally recognized standard or physical constant. Examples of Category 2 M&TE: gas chromatograph, mass spectrometer.

calibrated thermocouples (see the M&TE list in Section 4.0) and the performance calibrations using methane tracers to establish exhaust flow rates (see Appendix E).

Data generated during testing was collected following the *Data Management Plan PNNL Assessment of NUCON Vapor Abatement Unit*, DMP-NUCON-001. Additional record documents include the Laboratory Record Book BNW-62516, the Sample Log, and the Test Data Packages.

Testing deviations included the following:

- The Anasorb 747 tubes used were SKC-226-81A type tubes that were not coated with sulfuric acid, which acts as a capture assist agent for ammonia. This was different than the standard Anasorb 747, SK-226-29 tubes specified in the test plan. The different tube caused a quality non-conformance that was documented in Problem Evaluation Request WRPS-PER-2018-1318. The ammonia tubes could not be used for ammonia analysis.

- The PTR-MS was only able to distinguish NDMA at 50% of the OEL and did not reach the 10% of the OEL target. This was after reconfiguring the PTR-MS to obtain improved resolution by using NO+ (see Section 5.5).

- The data files from the AreaRAE were not recoverable, so manually recorded data was used. Additionally, the 1:1 dilution fitting when connected to the pressurized side of the Fourier-transform infrared spectroscopy instrument (FTIR) pump was determined to have a 1 part exhaust to 9.17 part ambient air dilution rate. The manually collected data and the analysis are in Section 5.8.

- The AreaRAE pump was unable to collect gases from the master sample given the pressure differentials between the sample header and the AreaRAE pump (which was designed for just ambient air collection). Data that was suspect during tests 6.2 and 6.3 has been designated in Appendix D as “do not use.” After test 6.3, the suction inlet to the AreaRAE was moved to the pressurized side of the FTIR pump.

2.0 Selected Chemicals of Potential Concern

2.1 COPC Selection Considerations

The 11 COPCs employed in the NUCON VAU tests were chosen to adequately represent the worst-case scenario of DRE for the different classes of compounds in the Hanford tank farm COPC list. The list of Hanford tank farm COPCs includes 61 compounds[1] consisting of inorganic compounds, hydrocarbons (primary olefinic species), alcohols, ketones, aldehydes, furans and substituted furans, phthalates, nitriles, amines, nitrosamines, organophosphates and organophosphonates, halogenated hydrocarbons, pyridines, organonitrites, organonitrates, and isocyanates. The basis for selection of the 11 COPCs was as follows:

- Both ammonia and nitrous oxide were selected as part of the test due to their unique and somewhat unpredictable chemical behavior in combustion and catalytic systems.

- 1,3-butadiene and benzene were chosen to represent two comparatively recalcitrant hydrocarbon species and aromatic species.

- Formaldehyde and acetaldehyde were both selected to represent the most recalcitrant carbonyl groups, and thus adequately represent ketones as well. Additionally, aldehydes will conservatively predict alcohols as an aldehyde represents a more recalcitrant analog of an alcohol.

- Furan was chosen as the most recalcitrant furanic component.

- Benzene was chosen to represent phthalates. Phthalates are comparatively much less stable than benzene. The aromatic ring is the most recalcitrant portion of the phthalate molecule, and thus is adequately represented by benzene.

- Acetonitrile and propanenitrile were both chosen to represent the very unique and recalcitrant nitrile-functionality. The nitrile-functionality adequately represents the amine functionality as it is a comparatively more recalcitrant analog.

- NDMA was chosen to represent the nitrosamine functionality. A nitrosamine was chosen because there is not adequate information available to predict how a nitrosamine will decompose in combustion chemistry. With two methyl-groups, NDMA is comparatively more recalcitrant than one or two ethyl groups or a cyclic species, which are represented by the other nitrosamines on the COPC list.

- Regarding halogenated hydrocarbons, the presence of a halogen within a hydrocarbon molecule almost always destabilizes that structure within combustion chemistry. For this reason, halogenated hydrocarbons were not considered for inclusion in this study.

- A pyridine was chosen to represent the unique pyridine aromatic functionality. Since the behavior of pyridine is expected to be very similar to, yet slightly less recalcitrant than benzene, 2,4-dimethyl pyridine was chosen for comparison.

- Organophosphates and -phosphonates, organonitrites and -nitrates, and organoisocyanates are all molecules containing hydrocarbon cation complexes and inorganic anions. The very strongly dominating electronic nature of the anionic portion of these molecules dominates their behavior in

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[1] Way KJ. Interoffice Memorandum, September 21, 2017. "Tank Operations Contractor – Chemicals of Potential Concern." Rev. 1, WRPS-1604188.1, Washington River Protection Solutions, Richland, Washington.

combustion chemistry and renders them highly reactive and very non-recalcitrant. This knowledge base has been built upon a large amount of experience with vehicle-based combustion chemistry dealing with, for example, phosphate derivatives such as lube oil components and organic sulfates as fuel-derived lubricants.

- Mercury compounds were excluded from the NUCON VAU testing since the understanding of the MERSORB® filter media has already been established in industrial applications.[1]

The full list of Hanford tank farm COPCs and the associated COPC test surrogate is shown in Table G.1 in Appendix G.

Table 2 provides a list of the 11 COPCs selected for testing. Note that the Chemical Abstract Service (CAS) numbers referenced in this test plan are considered definitive. Common chemical names are provided only for convenience and readability.

Table 2. COPCs Selected for NUCON VAU Testing

COPC #	Name	CAS #	Formula	$_{HTF}$OEL (ppm)
20	Ammonia	7664-41-7	NH_3	25
51	Nitrous Oxide	10024-97-2	N_2O	50
2	1,3-Butadiene	106-99-0	C_4H_6	1
21	Benzene	71-43-2	C_6H_6	0.5
30	Formaldehyde	50-00-0	CH_2O	0.3
18	Acetaldehyde	75-07-0	C_2H_4O	25
31	Furan	110-00-9	C_4H_4O	0.001
19	Acetonitrile	75-05-8	C_2H_3N	20
57	Propanenitrile	107-12-0	C_3H_5N	6
6	2,4-Dimethylpyridine	108-47-4	C_7H_9N	0.5
53	N-Nitrosodimethylamine (NDMA)	62-75-9	$C_2H_6N_2O$	0.0003

$_{HTF}$OEL = Hanford tank farm occupational exposure limit concentrations

2.2 Maximum Concentrations

The 2018 tests of the NUCON VAU are intended to ensure that the feed gas for the system test includes concentrations of certain selected Hanford tank COPC vapors that are bounding both for those vapors and for other COPC vapors, those for which the test feed vapors are surrogates. To determine the bounding feed concentrations applicable to planned NUCON VAU operations, several vapor databases were

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[1] The data to complete a preliminary assessment of MERSORB® performance was provided in the MERSORB® Mercury Adsorbents Bulletin 11B28-2012, *MERSORB® Mercury Adsorbents Design and Performance Characteristics,* by NUCON International Columbus, Ohio. MERSORB® has also been evaluated for removal of dimethyl mercury and was selected as the best available control technology for mercury abatement (both elemental mercury and dimethyl mercury) in the AP stack (*Evaluation of Best Available Control Technology for Toxics (tBACT) Double Shell Tank Farms Primary Ventilation Systems Supporting Waste Transfer Operations*. RPP-ENV-46679, Rev. 0, prepared by Washington River Protection Solutions for the U.S. Department of Energy, Office of River Protection, Richland, Washington).

examined to determine the currently relevant maxima for the types of tanks on which the system will be used.

The data sets from which relevant subsets of vapor concentration data were extracted were Tank Waste Information System (TWINS) Headspace (TWINS HS), TWINS Industrial Hygiene (TWINS IH), and SWIHD Headspace (SWIHD HS), as follows:

- TWINS HS concentrations measured in tank headspaces between 1994 and 2005
- TWINS IH concentrations measured between 2005 and July 2017 in stacks, exhausters, breather filters, inlet filters, and a variety of other sources connected to Hanford waste tanks
- SWIHD HS concentrations measured in Hanford waste tank headspaces between 2014 and July 2017

Some of the data were not considered for maxima because they had analytical data quality flags that made them suspect (Hoppe et al. 2016). In cases where there were data for two or more sorbent tubes in series on the same sampled stream of gas, the concentrations for the individual tubes were summed to give the total concentration for the sample.

Two constraints were applied to reduce these data sets by removing measurements that were not applicable to the NUCON VAU system operations.

First, all data that were not from SSTs were removed from consideration because the NUCON VAU system is intended for use only on SST gas/vapor streams from Hanford waste tank headspaces. SST data were also removed in this step if they were not clearly headspace data – for example, if they were drillstring gas or measured at "sources around" a tank or farm.

Second, SST data were removed from consideration if they had been measured before the tank's waste was last modified by remediation or retrieval operations. Pre-stabilization and pre-retrieval data were considered to be out of date and unrepresentative of possible headspace conditions under which the NUCON VAU system would be used. In two cases, C-105 and C-106, the Best Basis Inventory tank activity databases[1] were used to supply latest-activity dates where other sources did not give retrieval end dates. The *Maximum Concentration Values Review for Use in NUCON Vapor Abatement Unit Testing* report (Mahoney et al. 2018) shows the cutoff dates that were used and the online sources of information[2] on which they were based; however, the stabilization report (Swaney 2005) was the preferred basis.

The above-reporting-limit measurements in the reduced data sets were searched for the maximum concentration of each of the COPCs that were within the scope of NUCON VAU testing.[3] As a cross-check, these maxima were compared to the ones that had been reported in PNNL-13366, Rev. 1 (Stock

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[1] These databases can be found at
https://twins.labworks.org/twinsdata/Forms/BuildQuery.aspx?SourceName=txfr.dbo.p_TWINS_Get_Transfer_Events&whatsnew=Tank|Transfers
https://twins.labworks.org/twinsdata/Forms/BuildQuery.aspx?SourceName=tcd.dbo.transfers_denorm&whatsnew=Tank|Transfers

[2] Phoenix Tank Farms Dashboard: https://phoenix.pnnl.gov/apps/tankfarm/index.html
Phoenix Waste Tank Summary Report: https://phoenix.pnnl.gov/apps/tanksummary/summary.html

[3] For reasons discussed in Section 2.0, the COPCs that did not need to be considered were organic nitrates and nitrites, organic nitro compounds, mercury, dimethylmercury, methyl isocyanate, tributyl phosphate, dibutyl butylphosphonate, poly-chlorinated biphenyls, and 2-fluoro-1-propene.

and Huckaby 2004). In many cases, the maxima reported in that July 2004 report were no longer applicable because of remediation or retrieval, or had been superseded by later, higher maxima. Table 3 shows the test-applicable maximum concentrations of the COPCs that are within the scope of NUCON VAU testing.

The subset of COPCs that were used in NUCON VAU test are listed below, together with comments on their maximum concentrations.

- Ammonia: The maximum of 2502 ppm may have been the result of post-stabilization evaporation from liquid left behind in exposed pores of the waste, although stabilization had been completed 4 years before. There are no later measurements from the same tank to confirm this. Headspace ammonia concentrations for other SSTs in SWIHD HS, covering 2014-2017, are less than 500 ppm.
- Nitrous oxide: The maximum was 831 ppm.
- 1,3-butadiene: The maximum was 3.38 ppm.
- Benzene, for itself and as a surrogate for the other aromatic COPCs, which are biphenyl and diethylphthalate (DEP): The maximum benzene was 0.189 ppm, considerably higher than the maximum biphenyl concentration of 0.00142 ppm and also higher than the maximum DEP concentration of 0.064 ppm.
- Formaldehyde and acetaldehyde, for themselves and as surrogates for other oxygenated aliphatic COPCs including alcohols, aldehydes, and ketones: The maxima for these two aldehydes were 0.157 and 2.82 ppm, respectively. While the maxima for other aldehydes and for ketones are in this same range, the alcohols had much higher maxima, 63.5 ppm for 1-butanol (measured in 1994) and 39 ppm for methanol (measured in 2004, 4 years after stabilization). For comparison, the $_{\text{HTF}}$OELs of formaldehyde and acetaldehyde are 0.3 and 25 ppm, respectively. The 1994 maximum of 1-butanol was not used, as it appears to have decreased substantially, based on several later data points in the same tank. In addition, the methanol maximum may have decreased as the time since stabilization has increased, but data to corroborate this assumption are not available.
- Furan, for itself and as a surrogate for other COPCs with furan rings: Two of the furan compounds have higher maxima than any of the others. These higher maxima are 0.547 ppm for furan and 0.721 ppm for 2,5-dihydrofuran.
- Acetonitrile and propanenitrile, for themselves and as surrogates for other nitrile COPCs and for ethylamine: The maxima for these two nitriles are 18.8 and 0.517 ppm, respectively. The propanenitrile maximum is higher than that for any of the longer-chain nitriles, though lower than the ethylamine (ethanamine) maximum of 0.78 ppm. The acetonitrile maximum is much higher. For comparison, the $_{\text{HTF}}$OELs of acetonitrile and propanenitrile are 20 and 6 ppm, respectively.
- NDMA, for itself and as a surrogate for other nitrosamine COPCs: The highest maximum among the nitrosamine COPCs is for NDMA, 0.0621 ppm. The next highest maximum is for N-nitrosomorpholine, 0.00495 ppm.
- 2,4-dimethylpyridine, for itself and as a surrogate for pyridine: Pyridine has the higher of the two maxima, 0.147 ppm versus 0.0338 ppm for 2,4-dimethylpyridine. The $_{\text{HTF}}$OEL for 2,4-dimethylpyridine is 0.5 ppm, higher than either of the maxima.

2.3 COPC Test Conditions

Testing of the NUCON VAU used “high inlet spike” concentrations to represent the maximum measured headspace concentrations for SSTs at Hanford. An evaluation of the maximum COPC values for SSTs in all the historical databases was completed in the *Maximum Concentration Values Review for Use in NUCON Vapor Abatement Unit Tests* (Mahoney et.al. 2018) report and is summarized in Section 2.2. Measurements made prior to interim waste stabilization or waste retrieval were not considered in the verification of maximum measured concentrations as they are not representative of current tank farm conditions. Data for surrogate COPCs were also considered in determining the “high inlet spike” concentrations. Table 3 shows the summary of COPC concentrations used during testing.

Table 3. COPC Concentrations for 200% OEL and High-Concentration Tests (original and revised test concentrations based on reevaluation of SWIHD and TWINS data)

CAS	Name	Maximum Conc. SWIHD/TWINS (COPC or surrogate)	200% OEL Test	High Concentration Test
75-07-0	Acetaldehyde	39 ppm	50 ppm	None
75-05-8	Acetonitrile	18.8 ppm	40 ppm	None
71-43-2	Benzene	0.189 ppm	1 ppm	None
107-12-0	Propanenitrile	0.78 ppm	12 ppm	None
106-99-0	1,3-Butadiene	3.38 ppm	3.4 ppm	None
50-00-0	Formaldehyde	0.157 ppm	0.6 ppm	None
108-47-4	2,4-Dimethylpyridine	0.147 ppm	1 ppm	None
62-75-9	NDMA	0.0621 ppm	0.0006 ppm	0.062 ppm
110-00-9	Furan	0.721 ppm	0.002 ppm	0.017 ppm[a]
7664-41-7	Ammonia	2,502 ppm	50 ppm	630 ppm
10024-97-2	Nitrous Oxide	831 ppm	100 ppm	831 ppm

[a] The maximum for furan was tested in the next phase of testing. The in-tank farm test will be on waste tank BY-108, which at the time of testing was believed to be in cascade with BY-107, where the listed maximum furan sample was collected. Drawings H-2-1308, H-2-1318, H-2-132, and H-2-601in addition to RPP-RPT-50840 showed connected and open cascading overflow lines between BX107, BX108, BX109, BY107, BY108, and BY109. In August 2018 (after testing was complete), a construction implementation drawing H-2-36490 (from 1972) identified the planned isolation of the cascade lines to BY-108, though it is not clear if the isolation effort has completed.

Additional information on the concentration selection process can be found in the *Maximum Concentration Values Review for Use in NUCON Vapor Abatement Unit Tests* report (Mahoney et al. 2018).

3.0 Test Equipment and Methods

While NUCON was procuring and fabricating the additional diesel engine skid to be used for this phase of testing, PNNL was bench testing the analytical equipment to be used during assessment testing. The bench efforts developed the calibration methods and trace analytical methods for detecting COPCs at the identified thresholds, nominally 10% of the OEL in an engine exhaust stream. Additionally, the design and fabrication of the COPC gas injection systems and the sample collection systems were completed.

NUCON VAU performance assessment included three major tests. Test 1 was to confirm the performance of the analytical instrumentation, followed by tests 2 and 3, which evaluated the DRE and resulting exhaust purification for a selection of 11 COPCs that have been measured in Hanford HLW SST passive breather vapor emissions.

The tests were as follows:

- Test 1 – COPC injection into the exhaust stream of the VAU to reach 10% OEL concentration and confirmation of its detection for the 11 COPCs being tested
- Test 2 – COPC injection into the air-intake stream of the VAU to reach 200% OEL concentration for determining VAU DRE for each COPC at that concentration
- Test 3 (where applicable) – COPC injection into the air-intake stream of the VAU to reach a pre-determined high concentration (see Table 3) for determining VAU DRE for the COPC at that concentration.

3.1 Test Equipment

3.1.1 The NUCON VAU Skid

Multiple components on two skids make up the NUCON VAU unit (Figure 1) that was tested by PNNL. The first skid was the original propane VAU unit, consisting of a propane generator and VAU balance-of-plant. The second skid was the diesel engine generator, catalytic converter (diesel oxidation catalyst), particulate filter, and piping for integration to the balance-of-plant on the first skid. During testing on the Q Avenue Pad on the PNNL Richland, Washington Campus, the two skids were referred to as the "NUCON VAU." The propane generator set was disconnected from the VAU piping and was not a component in this testing effort.

Images of the NUCON VAU components are in Appendix A with a general VAU and diesel skid image below.

Figure 1. Photo of the NUCON VAU

The NUCON VAU components are listed below in order of their sequence to the air/exhaust flow stream in the system:

1. Metal particulate screen (60 x 150 mm) connected to the three-way valve (also see Figure A.5). This was the sole path through which ambient air was introduced to the system during steady state testing.
2. Piping on the skid was SA-316/316L stainless steel WLD 2-in. schedule 10S.
3. Referenced as the demister, the first a particulate HEPA filter was left in the 14-in.-diameter x 14-in.-tall (outside housing dimensions) filter/demister housing.
    a. The internal media is an American Air Filter Astrocel®[1] I HEPA Filter part 12A26J6P0A1 (900-895-503) S/N 41621250. The listed test results had a penetration of 0.006%, resistance of 0.8 in. water gauge, at the flow rate of 50 cfm. Size 8” x 8” x 5 7/8”.
4. A Fox Thermal Instruments, Inc. Model FT1-06IDDP1 serial # F00780 Flow Meter set to 0 to 60 standard cubic feet per minute (scfm) per vendor-approved change (FT-101).
5. Yellow K type Thermocouple TT-102 before the flow is warmed in the heat exchanger (K48U-006-4).
6. Ambient air inlet to the heat exchanger that used exhaust air to heat the ambient air before going into the MERSORB®[2] filter. The heat exchanger is to reduce the inlet air relative humidity before entering the filter media (see Figure A.4).
7. Yellow K type Thermocouple TT-103 outlet air temperature after the heat exchanger (McMaster 330-995-5909, SO 1209450-1, S/N CBBC74).
8. A particulate HEPA filter was left in the as-measured 14-in.-diameter x 14-in.-tall (outside housing dimensions) filter housing.
    a. The internal media is an American Air Filter Astrocel® I HEPA Filter part 12A26J6P0A1 (900-895-503). The listed test results for the sister filter (item 3) had a penetration of 0.006%, resistance of 0.8 in. water gauge, at the flow rate of 50 cfm. Size 8” x 8” x 5 7/8”.

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[1] Astrocel is a registered trademark of American Air Filter Company, Inc.

[2] MERSORB is a registered trademark of Selective Absorption Associates Inc.

9. MERSORB® absorbent container made of 24-in.-diameter schedule 10S A-312/SA-312 stainless steel with a length of 64 in. NUCON had not removed the 73 kg of Mersorb® absorbent that had been tested in Ohio for ~45 minutes with mercury. (Inlet air was near the bottom and release air from the column came out near the top.)
10. AMETEK 0.5 HP Sealed Regenerative Blower with XP Motor part EN303AG91L/038026.
    a. The motor is a Baldor-Reliance 854609767 S/N W17011605 (catalog number 515635).
11. Yellow K type Thermocouple TT-109 (label illegible).
12. Omega Model PX419-10WCGI (S/N 472875) Pressure sensor – pressure range +/- 10 output 12-20 12mA zero. Used to control the blower via the programmable logic controller (PLC).
13. Kohler KDI1903ESM Diesel Engine Spec 6D08E1-1 (S/N 4728402750) rated at 28 BHP at1800 rpm with Decision-Maker 3000 controls. Engine power 19-37 KW with 1.861 liters displacement (engine family HKHXL2.49ESM).
    a. Connected to a Kohler 15REOZK 15 kVA Generator (S/N SGM32LMWJ).
14. 4SX-15REOZK Catalytic Purifier muffler emissions control device manufactured by Catalytic Exhaust Products (i.e., DOC).[1]
15. Yellow K type Thermocouple TT-111 (K48U-006-4).
16. Diesel Particulate Filter 758SXS-SC by Catalytic Exhaust Products.[1]
17. Heat exchanger (same as component 6).
18. 2-in. exhaust muffler.
19. Yellow K type Omega Thermocouple TT-112(0226).

Note: A 10-ft-long, 2-in. exhaust pipe was added to the muffler.

20. The circuit breaker box that powers the PLC and the human-machine interface controller and data collection.
21. The Powerhouse Manufacturing (model 11.3-.25-240-1) switch box and 11.25-kVA load bank. This is switched to the full 11.25-kVA load during steady state testing on the diesel engine.

Key interfaces between the other systems and the NUCON VAU include the following:

1. A COPC injection system that delivered measured amounts of COPCs to multiple points on the VAU for CGB and liquid COPC sources.
2. A sampling system that interfaced with the VAU at multiple locations to measure overall and component performance, including provisions for effective particulate (i.e., soot) filtration, required temperature control, and, where necessary, highly accurate exhaust and dilute-inert flow control.
3. A data acquisition and control system that controlled and recorded performance of both systems.

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[1] Parts numbers were from the John Stekar, Catalytic Exhaust Products Limited, November 8, 2017 letter, *Diesel Exhaust Emissions Control Devices for Kohler 15REOZK Diesel Generator Sets*.

The diagram of the intake air and exhaust handling system for the VAU is shown in Figure 2, and the VAU ports are identified in Table 4 along with their respective functions. Note that injection of COPCs for the VAU evaluation occurred downstream from the MERSORB® unit in SP517-519 as noted in Table 4. The rationale behind this approach was to ensure accurate and timely evaluation of the VAU under equilibrium conditions. Comparatively, if a COPC test gas had been introduced upstream of the MERSORB® unit, it would have resulted in a non-equilibrium condition to the volume of the MERSORB® unit combined with a transient affinity of the MERSORB® for each COPC. A non-equilibrium condition for an injected COPC would therefore be transient until the free volume was swept and the MERSORB® achieved equilibrium with the COPC. This could extend over hours, perhaps days, prior to reaching equilibration. For this reason, the injection of COPCs occurred downstream of the MERSORB® unit in SP517-519.

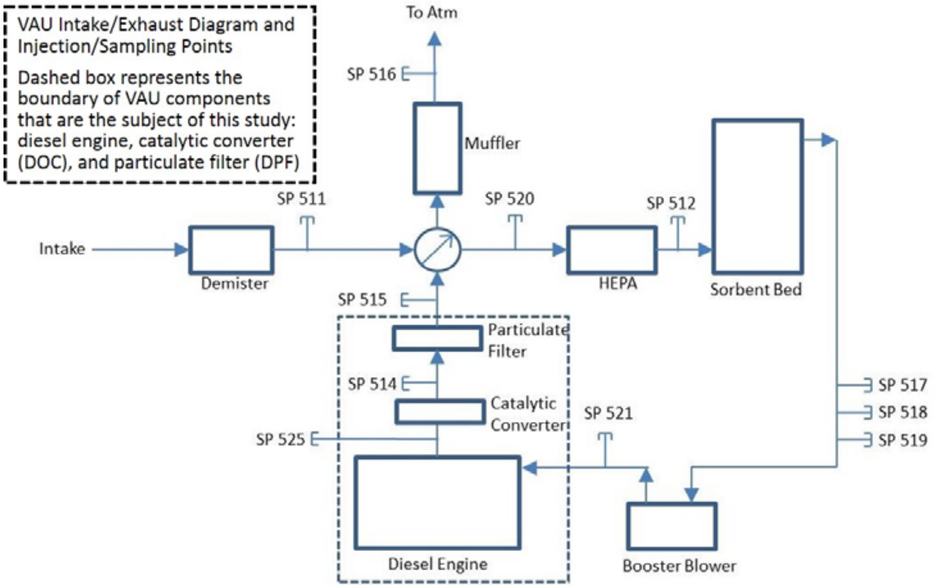

Figure 2. VAU Intake Air and Exhaust Handling System

Table 4. VAU Port Identification and Description of Function

VAU Port	Stream	Precedent	Antecedent	Planned Use
SP511	Intake	Demister	Heat exchanger	Reserved
SP520	Intake	Heat exchanger	HEPA	Reserved
SP512	Intake	HEPA	Sorbent bed	Reserved
SP517	Intake	Sorbent bed	Booster blower	Injection: Tests #2, #3 (DRE)
SP518	Intake	Sorbent bed	Booster blower	Injection: Tests #2, #3 (DRE)
SP519	Intake	Sorbent bed	Booster blower	Injection: Tests #2, #3 (DRE)
SP521	Intake	Booster blower	Engine	Sample: Inlet for Tests #2, #3
SP525	Exhaust	Engine	Catalytic converter	Component DRE sampling
SP514	Exhaust	Catalytic convertor	Particulate filter	Component DRE sampling
SP515	Exhaust	Cat conv/ Particulate filter	Heat exchanger	Injection: Test #1 (detection)
SP516	Exhaust	Muffler	Exhaust outfall	Sample: VAU outlet for all tests

3.1.2 Test Instrumentation

The COPCs were analyzed by appropriate instrumentation, identified in Table 5, that provided the necessary level of detection in the VAU exhaust stream for real-time analysis. The methods used for analysis of each COPC were developed and verified on the bench-scale in PNNL laboratory space.

Table 5. COPC Low Detection Limit Target Instrumentation for Real-Time Analysis

COPC	CAS	Target Instrument	Notes
Ammonia	7664-41-7	FTIR	
Nitrous Oxide	10024-97-2	FTIR	
1,3-Butadiene	106-99-0	PTR-MS	
Benzene	71-43-2	PTR-MS	
Formaldehyde	50-00-0	PTR-MS	
Acetaldehyde	75-07-0	PTR-MS	FTIR for corroboration
Furan	110-00-9	PTR-MS	
Acetonitrile	75-05-8	PTR-MS	
Propanenitrile	107-12-0	PTR-MS	
N-Nitrosodimethylamine	62-75-9	PTR-MS	Preconcentration as required
2,4-Dimethylpyridine	108-47-4	PTR-MS	Preconcentration as required

Details of the instruments used during testing are described below.

1. Ionicon Analytik PTR-MS

   The PTR-MS used in the tests was a PNNL-modified version of an Ionicon Analytik PTR-MS (S/N 44096535).

   This PTR-MS was selected based on previous work at PNNL by Lizabeth Alexander and others (Jobson et al. 2005) using the same PTR-MS being deployed in this project, since significant inferences were not expected at the concentration levels being measured for 1,3-butadiene, acetaldehyde, acetonitrile, benzene, or 2,4-dimethylpyridine. However, there was the potential for interference on propanenitrile, and the potential for interferences increases significantly for the compounds at ~1 ppb or less. However, in the previous cited work, a post-combustion catalytic converter (three-way catalyst) was not employed. The VAU comprises a post-combustion catalytic converter (diesel oxidation catalyst); thus, the potential for inferences is reduced but not eliminated.

   Matrix interferences in the engine exhaust stream and ultra-trace level detection requirements represent the primary challenges to accurate COPC analysis. In addition to the catalytic converter, other mitigation approaches were employed. These include use of different ionization methods using NO+, long averaging cycles, direct injection compared to no injected exhausts, and other operational strategies developed to improve the COPC measurements in the exhaust.

2. Low-level concentration requirements – volatile organic compound (VOC) pre-concentration option

   Although a variety of pre-concentration approaches and methodologies exist, including that described in EPA Method TO-12, this testing was planned and bench tested to deploy an approach similar to that described by Erickson.[1] During instrumentation bench testing, a commercial liquid nitrogen cryogenic trap from Scientific Instrument Services, Inc. was interfaced to the PTR-MS as an approach to pre-concentration of the exhaust effluent prior to the PTR-MS analysis to enhance lower detection limits. Use of the liquid nitrogen cryogenic trap was intended to concentrate the sampled gas stream and effectively enhance the lower detection limits for the PTR-MS.

   Qualification of the preconcentrator (i.e., cryogenic trap) was performed early in project as part of the instrument readiness activity and method development. As there are multiple potential options for equipment and operating strategy; qualification testing is necessary to ensure that the range of potential options can be reduced before the design is finalized. Consequently, the final strategy was based on the ability to concentrate exhaust effluent and its components, as well as the ability of design and operational methodology to manage water during the trapping phase. The qualification of a preconcentrator was assessed in conjunction with the PTR-MS for the ability of these two integrated components to reliably measure the application COPC(s) at the necessary level(s).

   The Agilent 6890N Gas Chromatograph (S/N US10443076) was installed for use as a component of the pre-concentrator operations to rapidly heat the cryogenic trap.

   The use of the preconcentration system was expected to be limited to the testing of the furans and the reliable detection of 0.03 ppb NDMA.

   Given the high diesel backgrounds for NDMA and furan, the use of the preconcentration systems was not implemented during tests 5.1, 5.2, or 5.3. So, while it was developed during the bench phase of instrumentation development, it was not used during the VAU performance testing.

3. FTIR

   The FTIR used in testing was an MKS-2030 MultiGas Analyzer (S/N 01858) specifically designed for exhaust gas temperatures. FTIR spectroscopy was used as the primary detection method for a selection of COPCs and corroboratory (to PTR-MS) detection for additional COPCs as shown in Table 1. FTIR spectroscopy was also used during shakedown as primary analysis for a selection of emission criteria pollutants of specific interest to engine exhaust applications, including moisture, NO, NO_2, and CO. Vendor-supplied methods and certified calibrations were used for COPC identification and quantification. Additionally, FTIR spectroscopy was used to assist with the identification of other components in the exhaust stream.

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[1] Matthew Howard Erickson, *Measuring Diesel Exhaust Gas Phase Organics With A Thermal Desorption Proton Transfer Reaction Mass Spectrometer*. A dissertation submitted for the Doctor of Philosophy, Washington State University, July 2013.

4. Gas chromatography/mass spectrometry (GC/MS)

   The Agilent 6890N Gas Chromatograph (S/N US10411048) with the Agilent 5973 Mass Selective Detector (S/N US40630240) were used to assist with primary component analysis, chemical interference assessment, and sensitivity improvement. Although a variety of GC detectors can be used for NDMA determination, GC/MS with chemical ionization and MS/MS was the process that was utilized.

   Given the high diesel backgrounds for NDMA and furan, the use of the GC/MS was not implemented during tests 5.1, 5.2, or 5.3. So, while it was developed during the bench phase of instrumentation development, it was not used during the VAU performance testing.

5. AreaRAE PGM-5020 Photoionizer detector (PID)

   A PID was provided by WRPS and was used to measure VOCs. The total VOC concentration was measured in the exhaust. DREs for the VOC data available are calculated and reported using PID results. The AreaRAE PGM-5020 Photoionizer detector serial number is 295-00393.

3.1.3 COPC Injection System

The injection system was designed to deliver measured amounts of COPC test gases to different points on the VAU depending on the phase of testing. A process flow diagram (PFD) of the COPC injection systems is shown in Figure 3. The test gas injection points were as follows:

1. Test 1 (demonstration/validation of 10% OEL detection in exhaust) – SP515 downstream of the DPF, but upstream of the heat exchanger
2. Test 2 and test 3 (DRE testing) – SP517-519 downstream of MERSORB® unit, but upstream of intake staging pump

The initial equipment and component considerations included tubing, mass flow controllers, valves, physical support structure, and considerations for control and thermal management. Wetted parts were in the inerted form (using SilcoNert™ tubing[1]) to minimize unwanted chemistry or retention of compounds on the surface of the injection system. Depending on the selected concentration of the COPC test gases, thermal management (e.g., heat trace/insulation) was required to prevent condensation of COPCs.

As shown in Figure 3, the injection system was designed to provide multiple COPC test gases simultaneously manifolded prior to the final injection, with potential consideration for remote switching and purging of the test lines when changing among COPCs or between test phases.

Provisions in the design also provide flow measurement of the inlet air (used For Information Only measurements) to the VAU.

The assembled system was performance tested and QA-affecting mass flow controllers were user-calibrated using DryCal[2] units.

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[1] SilcoNert is a trademark of SilcoTek, which is the world's leading provider of high performance coatings applied by chemical vapor deposition.

[2] A product of Mesa Labs.

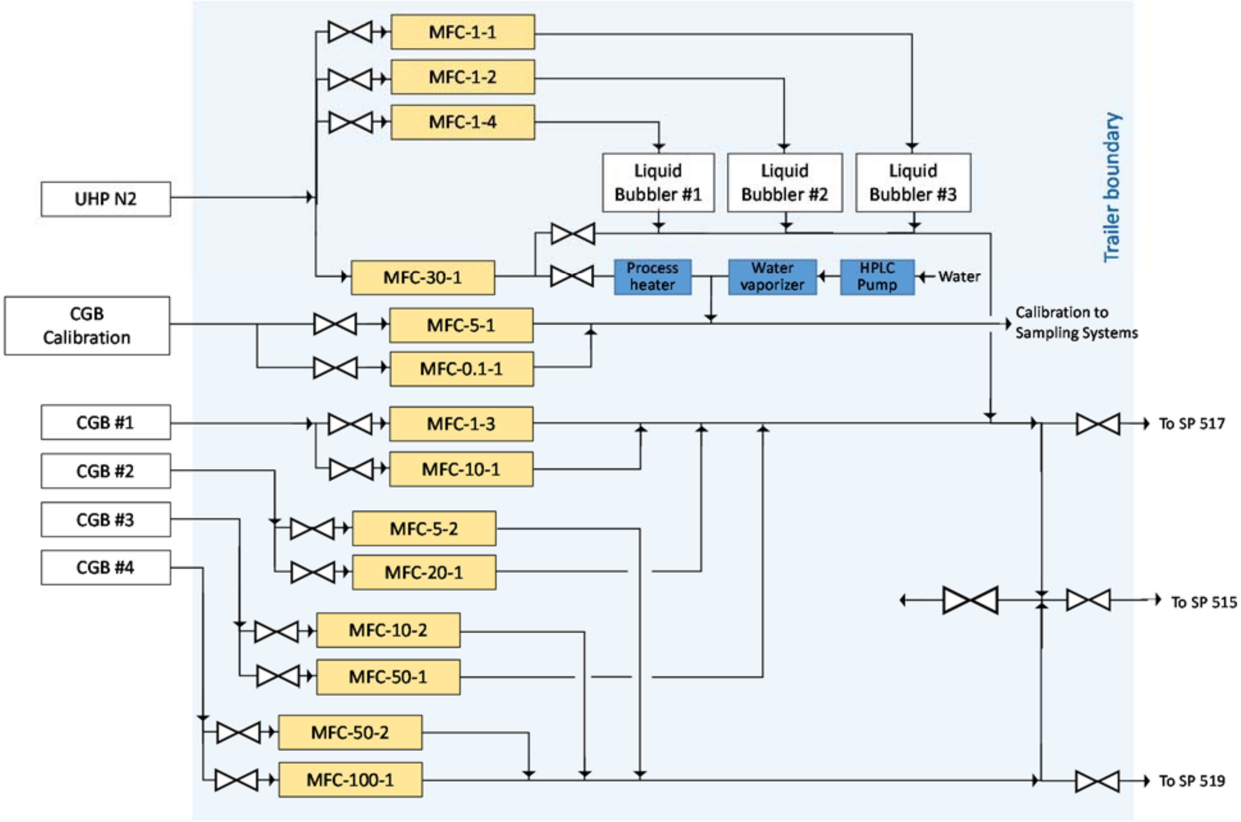

Figure 3. Process Flow Diagram of VAU COPC Injection System

3.1.4 Sampling System

The PFD for the sample acquisition and delivery system is shown in Figure 4, and is designed to deliver a VAU exhaust stream from one of several sampling ports on the VAU skid. The system design provided both filtered and conditioned exhaust to the primary analytical systems, and unfiltered exhaust when needed to the particulate analysis system. The system released the instrumentation exhaust gases through stacks on the trailer roof. Note that the PTR-MS was also used to analyze unconditioned exhaust, while the other instruments required pre-filtration.

The two sampling points required to accurately assess the performance of the VAU are as follows:

1. The sample port downstream of the muffler (SP516), which is the source for all exhaust samples. This port was also used during the 10% OEL detection testing prior to use in all phases of DRE testing.
2. The sample port after the booster blower and immediately before the engine (SP 521), which is the sample location for validating the COPC inlet concentration during DRE testing.

Additionally, some samples at ports after the diesel engine (SP525) and after the catalytic converter (SP514) were collected and analyzed on-line to help understand the contribution of individual system components to the VAU performance.

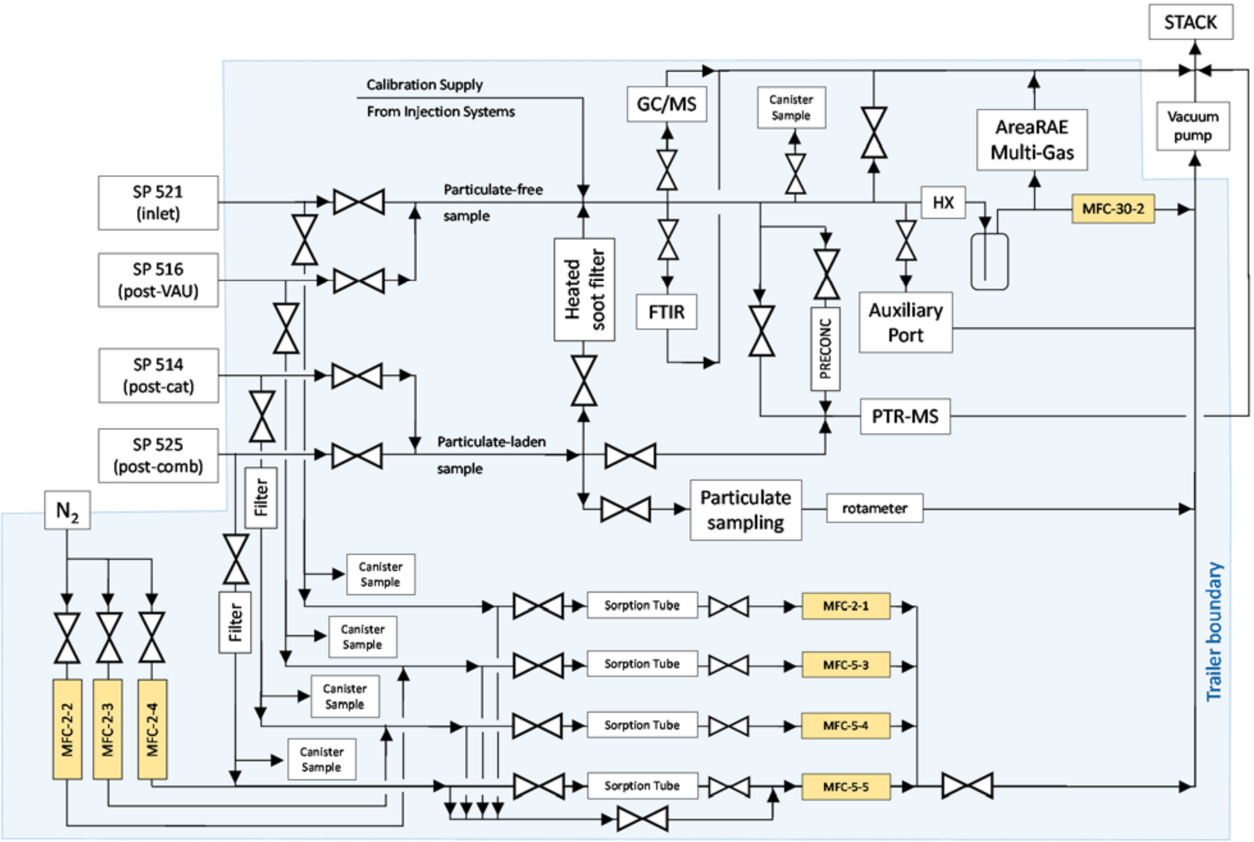

Figure 4. PFD of VAU Exhaust Sampling System and Analytical Systems

The exhaust sampling port considerations included the need for a port that would be most representative of the exhaust outfall (i.e., to atmosphere/environment) and the need for at least one upstream port separated by sufficient mixing to be used for injection of test gases for the 10% OEL detection validation. The post-muffler port, SP516, met both criteria as being the nearest port to the stack outfall and being upstream of port SP515, which was used to inject test gas to achieve the 10% OEL detection validation necessary to demonstrate confidence in sample analysis. SP516 and SP515 are separated by the heat exchanger and the muffler that represent mixing chambers without significant expected changes to or treatment of the compounds represented in the exhaust stream. While the heat exchanger is tube-in-tube, the muffler represents a tortuous path to mix the exhaust stream with test gases injected at SP515 prior to sampling.

The other sample point used for this test was intake sample port SP521, immediately upstream of the engine. This port was used to validate the concentration of test gas that was fed to the engine during the DRE testing phases. The SP521 port is downstream of the booster blower, which is downstream of the main test gas inlet (port SP517). The active operation of the booster blower provides mechanical mixing of the intake stream with the injected test gases in order to provide a representative sample of the intake air to the engine.

A baseline air sample was collected from intake sample port SP521 prior to injection of test gases. This provided an accurate baseline of the air that exits the MERSORB® tank and enters the engine.
The sampling system was designed with particulate management, both to protect the analytical instrumentation from particulates in the VAU exhaust and to determine if the particulate stream contains a

measurable amount of COPCs. The particulate management was configured to allow for switching between filter units as well as recovery of particulates from the filters. The particulate sampling included an alternative system in the event that the conditioning and sampling objectives could be combined efficiently into a single unit operation.

Thermal management was required for the sample streams to ensure that the sample was provided to the analytical instrumentation at an appropriate temperature, nominally ~190°C. Primary considerations for thermal management include temperature compatibility of the analytical instrumentation and minimization of adsorption or condensation of any exhaust species or reaction product. This required design considerations for active heating. The active heating consisted of sections of vendor-supplied heated tubing that was controlled by the data acquisition and control system.

As shown in Figure 4, a primary sample loop was designed into the system using a vacuum pump to provide a continuous loop of VAU exhaust through the sampling lines and out to a safe exhaust point. This provided sufficient amounts of sample to the sampling lines for each instrument to draw upon (actively or passively).

3.1.5 Off-Line Sampling System

The VAU sampling system also included the capability for acquiring samples for off-line analysis from the four sample locations (one inlet and three exhaust). The VAU inlet at SP521 and VAU outlet (i.e., tailpipe) at SP516 would support VAU DRE corroboration; the diesel engine outlet at SP525 (before the catalyst) and catalyst outlet at SP514 (before the DPF) would be for VAU component assessment to support subsequent WRPS design and permitting efforts (herein referred to as “engineering samples”). Sample acquisition for each COPC for off-line analysis can come in the following forms:

1. Sorbent tube sample acquisition and analysis by approved method (as detailed in Table 6) and certified laboratory analysis. This will support analysis of formaldehyde, NDMA, and ammonia.
2. SUMMA® canister sample acquisition and analysis by EPA Method TO-15 and certified laboratory analysis. This will support analysis of nitrous oxide, 1,3-butadiene, benzene, acetaldehyde, furan, acetonitrile, propanenitrile, and 2,4-dimethylpyridine. (The SUMMA® canisters included a 1-hour flow restrictor on the inlet. The restrictor design had an increased suction flow when first opened and would decrease in flow as the vacuum in the SUMMA® canister reduced over time.)

During VAU testing, samples collected for analysis at the inlet and tailpipe of the VAU included at a minimum real-time analysis (by PTR-MS or FTIR) ***AND*** one method of off-line analysis as described above. Also during VAU testing, samples collected for analysis after the engine and after the catalyst included real-time analysis ***OR*** one method of off-line analysis as described above. Thus, only a single analysis (i.e., without corroboration) was required for the latter engineering samples, and included either (i) real-time analysis by PTR-MS or FTIR, (ii) sorbent tube, or (iii) canister sample. However, it is important to note that during testing priority was directed towards ensuring with high confidence the real-time analyses at the VAU inlet and VAU outlet (i.e., tailpipe) at SP521 and SP516, respectively. Typically during most of the testing (with two exceptions), samples at SP525 and SP514 were successfully analyzed on-line to help understand the contribution of individual system components to the VAU performance. In two situations, testing was not able to accommodate with high confidence a real-time measurement after the catalyst and before the DPF (Port C, SP514). However, the DPF was demonstrated during testing to have little to no impact on COPC removal performance, and thus in the two situations where a port C real-time analysis sample was not feasible, the difference between post-engine (port B) and tailpipe (port D) results can be confidently attributed to catalyst performance versus the DPF.

For this report, all the DREs are calculated from the analytical results provided by the real-time instrumentation, as the results of on-line testing are not yet complete.

Solid adsorbents in metal or glass tubes (i.e., sorption tubes) and/or specially-prepared stainless steel SUMMA® canisters designed to collect the relevant COPC samples for most tests were used to collect samples from the engine inlet air, after the engine, after the catalytic converter, and after the particulate filter (i.e., after the VAU). The absorption tubes and/or canisters were used per the detail shown in Table 7 for required capture media (e.g., SUMMA® canister and/or sorbent tube type) and analytical method for that COPC. The sorption tube and canister samples were analyzed by an ORP subcontractor (WAI at 222-S laboratory) with established analytical methods, protocols, and programs. The assignment of field blanks, travel blanks, and duplicate samples was established prior to testing with WRPS. Additionally, the preliminary target collection parameters for sorption tubes (e.g., flow rates) in Table 7 are based on a collection cycle without the addition of nitrogen dilution for moisture control and temperature adjustments.

Table 6. Sorption Tubes for VAU DRE Corroboration and VAU Component Assessment

COPC	Sorption Tube Type	Exhaust Volume (L)	Target Flow Rate (mL/min)	Analytical Method
Ammonia	Anasorb® (a) 747 (sulfuric acid), SKC-226-81 (b)	24.01+/- 0.70	200	OSHA-ID-188 IC
Formaldehyde	DNPH Treated Silica Gel, SKC-226-119	24.63 +/- 6.57	200	EPA TO-11A HPLC
NDMA	Thermosorb® (c)/N	241.48 +/- 9.74	2000	NIOSH-2522 Modified GC-TEA

[a] Anasorb is a registered trademark of SKC, Inc.

[b] While the Test Plan was based on Anasorb® 747 (sulfuric acid), SKC-226-29 tube, actual testing used the SKC-226-81 model that resulted in a non-conformance condition discussed in Section 5.6.

[c] Thermo-Sorb is a registered trademark of the Carboline Company

Table 7. Sorption Tube Collection Times

COPC	Test	Flow Rate (mL/min)	Inlet Conc (ppm)	Inlet Test Time (min)	Exhaust Conc (ppm)	Outlet Test Time (min)
Ammonia	Test #2	200	50	45	2.5	135
Ammonia	Test #3	200	630	45	2.5	135
Formaldehyde	Test #2	200	0.6	20	0.03	80
NDMA	Test #2	2000	0.0006	80	0.00003	320
NDMA	Test #3	2000	0.062	80	0.00003	320

Notes:

62-75-9 NDMA	1) Diluted with 3 parts N2 gas per 1 part exhaust when sucked through the tube. It should also be noted on the NDMA Test #2 a media failure in the inlet tube did not allow the collection of that sample.
50-00-0 Formaldehyde	1) Diluted with 3 parts N_2 gas per 1 part exhaust when sucked through the tube
7664-41-7 Ammonia	1) Diluted with 2 parts N_2 gas per 1 part exhaust when sucked through the tube. Slight in-line moisture was observed after 4 hours of sample collection on the last duplicate tube sample. Additional dilution gas was added to later formaldehyde and NDMA sampling.

For the off-line sampling, sorption tube traveler and blank quality assurance samples were collected for each sampling event. Additionally, random (locations pulled from a hat) duplicate off-line media samples were collected as listed below.

- Duplicate SUMMA® canisters were collected from the 200% OEL tests from the following:
  - The acetaldehyde/acetonitrile test from ports SP521 and SP516
  - The 1,3-butadiene/formaldehyde/2,4-dimethylpyridine test from port SP521
  - The ammonia/nitrous oxide test from port SP516
  - The NDMA/furan test from port SP514
- Duplicate sorption tubes were collected from the 200% OEL tests as follows:
  - A DNPH Treated Silica Gel, SKC-226-119 tube was pulled during the 1,3-butadiene/formaldehyde/2,4-dimethylpyridine test from port SP514.
  - Four Anasorb 747 (sulfuric acid), SKC-226-81[1] tubes were pulled during the ammonia/nitrous oxide testing. One was from port SP521, one from SP225, one from port SP514, and the one from port SP516.

Collection of Condensable Gases in the Exhaust Stream

Engine exhaust contains condensable gases (including a significant amount of water), which can result in condensation formation and unknown collection efficiencies when cooling the exhaust to the required temperature for sorbent tube collection. To mitigate this effect, during sorption tube collection the exhaust gas was *diluted* to a level where supersaturation of water was avoided as dilution is preferred over H_2O separation to avoid the inadvertent removal of COPCs with H_2O separation. Additionally, dilution allowed for the sorption tube samples to be collected at a sample temperature that was within an appropriate range per manufacturer recommendations.

3.2 Test Methods

Test objectives included the following:

- Demonstrate detection of each COPC in the VAU exhaust stream to 10% OEL concentration.
- Measure COPC concentration at the VAU inlet and VAU outlet for VAU DRE assessment, and acquire samples (sorbent tube or canister) for off-line analysis for corroboration.
- Provide means for determining COPC concentration at post-engine and post-catalyst locations by either on-line analysis or sample acquisition (sorbent tube or canister) for off-line analysis.

Testing of the COPC in the NUCON VAU and associated sampling systems was performed in two phases:

1. Post-combustion injection (test 1) using single-component COPC CGB blends

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[1] While the Test Plan was based on Anasorb®[1] 747 (sulfuric acid), SKC-226-29 tube, actual testing used the SKC-226-81 model that resulted in a Non-conformance condition discussed in section 5.6.

2. Pre-combustion injection (tests 2 and 3) using either single-component COPC CGB blends or COPC delivery from a liquid bubbler

Each test injected one to three COPCs simultaneously to facilitate extended duration analysis dwell times for maximizing signal-to-noise ratio. This allowed highly efficient comparison of the signal with and without the COPC injection. This strategy was useful for quantifying ultra-trace level COPCs to a high-confidence level.

3.2.1 Post-combustion COPC Injection for Analytical Sensitivity Validation (Test 1)

Table 8 shows the tests for test 1 – post-combustion COPC injection to ≤10% of the OEL concentraton for validation of COPC detection in the engine exhaust. The results of test 1 for each COPC are documented in Section 5.0. Each test number in Table 8 corresponds to the respective test number in the test matrix (Section 4.1) and the corresponding sample matrix (Section 4.2). These tests were performed to demonstrate the detection efficacy of the real-time sampling and analysis system under operating conditions. For these tests, SP515 was used to inject individual or groups of COPCs into the VAU exhaust immediately after the DPF to ≤10% the OEL of each COPC. Then, SP516 was used to obtain the VAU exhaust sample (including the injected COPC) after the heat exchanger and muffler (see Figure 2). Sample acquisition for off-line analysis was not performed during these tests.

Table 8. Test 1 – 10% of OEL Detection/Validation

10% of OEL concentration in exhaust COPC detection/validation						
Test	CAS	Name	Conc.	Instrument	Inj. Port	Samp. Port
1.1	75-07-0	Acetaldehyde	2.5 ppm	PTR-MS or FTIR	SP515	SP516
1.1	75-05-8	Acetonitrile	2.0 ppm	PTR-MS or FTIR	SP515	SP516
2.1	71-43-2	Benzene	0.050 ppm	PTR-MS	SP515	SP516
2.1	107-12-0	Propanenitrile	0.60 ppm	PTR-MS	SP515	SP516
3.1	106-99-0	1,3-Butadiene	0.10 ppm	PTR-MS	SP515	SP516
3.1	50-00-0	Formaldehyde	0.030 ppm	PTR-MS	SP515	SP516
3.1	108-47-4	2,4-Dimethylpyridine	0.050 ppm	PTR-MS	SP515	SP516
4.1	62-75-9	NDMA	0.000030 ppm	PTR-MS	SP515	SP516
5.1	110-00-9	Furan	0.00010 ppm	PTR-MS	SP515	SP516
6.1	7664-41-7	Ammonia	2.5 ppm	FTIR	SP515	SP516
6.1	10024-97-2	Nitrous Oxide	5.0 ppm	FTIR	SP515	SP516

The concentrations of 10% OEL shown in Table 8 represent the target detection thresholds for each COPC. Experience with the PTR-MS has demonstrated sensitivity to ~0.1 ppb for each COPC in the absence of specific interferences.

Each of the analytical instruments was used to analyze a specific subset of the test COPCs during testing. Test log books and data sheets were used to record time and date of test activities to enable accurate integration of the data from the various test systems and test activities as described in the Laboratory Record Book and data packages.For each of the 10% OEL exhaust detection/validation tests, the following steps were taken:

1. Staff performed pre-job and system readiness check.
2. Analytical equipment was warmed up, calibrated/checked, and a baseline air evaluation was completed as needed. Some of this was concurrent with VAU startup and warmup.
3. The VAU system was started and operated to steady state[1] conditions.
4. The steady state baseline exhaust profile was captured at the stack exhaust sampling port (SP516) prior to COPC injection.
5. Measurements were taken on the exhaust to calculate the amount of COPC test gases required to be injected to achieve the target concentration in the exhaust stream. Refer to the testing matrix in Table 8.
6. The injection system was brought online to provide nominally one to three target COPCs at 10% OEL concentration in the exhaust stream using the post-catalytic converter port (SP515).
7. A series of samples was taken with the target analytical equipment, depending on the target COPCs used. Analysis was performed up to 5 to 10 times (or cycles) per set.
8. The injection of the COPC test gas was stopped.
9. Calibration of the instrument was re-verified and logged if necessary.
10. If needed, upon achieving steady state after stopping the final injection, the baseline exhaust and/or baseline air was checked.
11. In most cases the systems were shut down since calibration and detection testing normally consumed a full day. In cases were the 200% OEL tests could also be completed, testing would proceed to step 6 in the 200% OEL process.

3.2.2 Pre-combustion COPC Injection for DRE Evaluation (Test 2 and Test 3)

Tests 2 and 3 were performed to determine the efficacy of the NUCON VAU for removal of COPCs under the defined operating conditions, and to inform subsequent WRPS design and permitting activities.

For tests 2 and 3, SP517 was used to inject the COPCs into the VAU air inlet before the booster blower. Testing was performed at 200% OEL injected concentration in test 2 for each COPC as shown in Table 9. Each test number in Table 9 corresponds to the respective test number in the test matrix (Section 4.1) and the corresponding sample matrix (Section 4.2). On-line analysis compared the results from the VAU inlet (SP521 after the booster blower) to the VAU outlet (SP516) to determine a DRE for each COPC using the target instrument identified in Table 9.

Testing was performed at a high concentration injected level in test 3 for a selection of the COPCs as detailed in Table 10. Similarly, the test number in Table 10 corresponds to the respective test number in the test matrix (Section 4.1) and the corresponding sample matrix (Section 4.2). On-line analysis similarly compared the results from the VAU inlet to the VAU outlet to determine a DRE for each COPC using the target instrument identified in Table 10.

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[1] Steady state conditions were identified when the VAU exhaust gas temperatures after the catalytic converter and after the muffler were stable and no longer increasing (normally achieved after 1 hour of operation). Then the FTIR and/or the PTR-MS were used to evaluate if the exhaust gases from port D had reached steady emission levels.

As discussed prior, samples were acquired for off-line analysis at the VAU inlet and VAU outlet (i.e., tailpipe) for VAU DRE confirmation (to on-line analysis) in the form of either sorption tube (per the detail in Table 6 and Table 7) or SUMMA® canister samples. Additionally, engineering samples were acquired between the diesel engine and the DOC (SP525) and between the DOC and the DPF (SP514), in the form of on-line instrumentation, sorption tube samples, or canister samples.

Table 9. Test 2 –200% OEL Intake Concentrations for DRE Assessment

200% OEL Intake Concentration COPC Testing						
Test	CAS	Name	Conc.	Target Instrument	Inj. Port	Samp. Port
1.2	75-07-0	Acetaldehyde	50 ppm	PTR-MS	SP517	SP516
1.2	75-05-8	Acetonitrile	40 ppm	PTR-MS	SP517	SP516
2.2	71-43-2	Benzene	1.0 ppm	PTR-MS	SP517	SP516
2.2	107-12-0	Propanenitrile	12 ppm	PTR-MS	SP517	SP516
3.2	106-99-0	1,3-Butadiene	3.4 ppm	PTR-MS	SP517	SP516
3.2	50-00-0	Formaldehyde	0.60 ppm	PTR-MS	SP517	SP516
3.2	108-47-4	2,4-Dimethylpyridine	1.0 ppm	PTR-MS	SP517	SP516
4.2	62-75-9	N-Nitrosodimethylamine	0.00060 ppm	PTR-MS	SP517	SP516
5.2	110-00-9	Furan	0.0020 ppm	PTR-MS	SP517	SP516
6.2	7664-41-7	Ammonia	50 ppm	FTIR	SP517	SP516
6.2	10024-97-2	Nitrous Oxide	100 ppm	FTIR	SP517	SP516

Table 10. Test 3 – High Intake Concentration for DRE Assessment

High Intake Concentration COPC Testing						
Test	CAS	Name	Conc.	Target Instrument	Inj. Port	Samp. Port
-	75-07-0	Acetaldehyde	<test not required>			
-	75-05-8	Acetonitrile	<test not required>			
-	71-43-2	Benzene	<test not required>			
-	107-12-0	Propanenitrile	<test not required>			
-	106-99-0	1,3-Butadiene	<test not required>			
-	50-00-0	Formaldehyde	<test not required>			
3.3	108-47-4	2,4-Dimethylpyridine	<test not required>			
4.3	62-75-9	N-Nitrosodimethylamine	0.062 ppm	PTR-MS	SP517	SP516
5.3	110-00-9	Furan	0.017 ppm	PTR-MS	SP517	SP516
6.3	7664-41-7	Ammonia	630 ppm	FTIR	SP517	SP516
6.3	10024-97-2	Nitrous Oxide	830 ppm	FTIR	SP517	SP516
Test not required since the testing conditions at 200% OEL already bounded the high-concentration test conditions.						

VAU DREs for each COPC were calculated in Section 5 on the actual exhaust profile collected during testing as follows:

$$DRE = 1 - \frac{[Concentration\ of\ COPC\ in\ exhaust]}{[Concentration\ of\ COPC\ in\ intake]} \tag{1}$$

The DRE calculations do not compensate for COPCs produced from the engine (i.e., without injection) nor do they compensate for COPCs present in the baseline air. Thus, this potentially resulted in an apparent lower destruction efficiency if the COPC was formed by engine combustion. In extreme cases, this resulted in negative DRE values. Similarly, this can present a perceived COPC mass imbalance of % DRE and relation to % OEL remaining in the VAU outlet. Thus, for clarity, the results in Appendix F and Section 5.5.2 should be referenced for detailed COPC assessment.

In cases where interfering components were found during testing (i.e., not the COPC) in the PTR-MS data, the DRE required background subtraction of the interference in addition to a larger number of analyses to confidently quantify the remaining target COPC in the exhaust above the signal from the interference.

Each of the analytical instruments was employed to analyze only their specific subset of the full COPC list during the post-combustion testing. For each set of tests for a specific set of COPCs, the following steps were taken:

1. Staff performed pre-job and system readiness check.
2. Analytical equipment was warmed up, calibrated/checked, and baseline air evaluation was completed as needed. Some of this was concurrent with VAU startup and warmup.
3. The VAU system was started and operated to steady state conditions.[1]
4. The steady state baseline exhaust profile was captured at the stack exhaust sampling port prior to COPC injection at SP516.
5. Measurements were taken on the intake to calculate the amount of COPC test gases required to be injected to achieve the target COPC concentrations in the intake stream. Refer to the testing matrices.
6. The injection system was brought on-line to provide nominally one to three target COPCs at the indicated concentrations in an intake injector port downstream (after) the MERSORB® bed, nominally SP517 through SP519.
7. Concentration of the injected COPC mix in the intake was analyzed at SP521.
8. A series of samples was taken with the target analytical equipment, exact configuration depending on the target COPC and the concentration. Analysis was performed up to 5 to 10 times per set.
9. The injection of the COPC test gas was stopped.
10. Calibration of the instrument was re-verified and logged if necessary.
11. If needed, upon achieving steady state after stopping the final injection, the baseline exhaust and/or baseline air was checked.
12. Systems were shut down, as testing always finished at the end of the work day.

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[1] Steady state conditions were identified when the VAU exhaust gas temperatures after the catalytic converter and after the muffler were stable and no longer increasing (normally achieved after 1 hour of operation). Then the FTIR and/or the PTR-MS were used to evaluate if the exhaust gases from port D had reached steady emission levels.

3.2.3 Multi-component DRE Testing

At the conclusion of COPC specific testing, the Test Plan included a multi-component DRE test on a subset of COPCs as shown in Section 4.1, test 7.1. This test was intended to assess the relation of COPC DRE to the presence of different combinations and concentrations of other COPCs. It is a single test using only on-line analytical instrumentation with no sample collection for off-line analysis.

Given the results of the COPC specific testing, the fact that many of the COPCs had been tested with other COPCs in the same injection, and the operational limits for the PTR-MS (needing to operate in either the NO+ or H_3O+ mode), the additional value of this test became very limited. On June 11, WRPS, ORP, and PNNL determined that the multi-component DRE test would not be conducted during this phase of testing. The impact of multiple gas interactions is to be observed during future testing in the tank farms on Hanford waste tank BY-108.

4.0 Test Matrix, Sampling Matrix, and Calibrated Equipment

The details of the testing sequence (or test matrix), the sampling matrix, and the calibrated instrumentation are in this section. This shows the testing that was completed and establishes a framework for understanding the detailed test results in Section 5.0.

4.1 Test Matrix

The test matrix from the test plan and the original planned test execution are show in Table 11.

Table 11. NUCON VAU Master Test Matrix from the Test Plan

Test	COPC name	CAS	Conc [ppm]	Evaluation	CGB Flow [SLPM]	Bubbler Flow [SLPM]	COPC Injection Port
0.1	(multiple)	(multiple)	(n/a)	Shakedown - baseline air	(n/a)	(n/a)	(n/a)
0.2	(multiple)	(multiple)	(n/a)	Shakedown - baseline engine	(n/a)	(n/a)	(n/a)
1.1.a	Acetaldehyde	75-07-0	2.5	Detection	15.0	(n/a)	SP 515
1.1.b	Acetonitrile	75-05-8	2	Detection	9.97	(n/a)	SP 515
1.2.a	Acetaldehyde	75-07-0	50	DRE	(n/a)	0.059	SP 517-9
1.2.b	Acetonitrile	75-05-8	40	DRE	(n/a)	0.506	SP 517-9
1.3.a	Acetaldehyde	75-07-0	(no test)	(no test)	(no test)	(no test)	(no test)
1.3.b	Acetonitrile	75-05-8	(no test)	(no test)	(no test)	(no test)	(no test)
2.1.a	Benzene	71-43-2	0.05	Detection	0.374	(n/a)	SP 515
2.1.b	Propanenitrile	107-12-0	0.6	Detection	5.98	(n/a)	SP 515
2.2.a	Benzene	71-43-2	1	DRE	5.8	(n/a)	SP 517-9
2.2.b	Propanenitrile	107-12-0	12	DRE	93.4	(n/a)	SP 517-9
2.3.a	Benzene	71-43-2	(no test)	(no test)	(no test)	(no test)	(no test)
2.3.b	Propanenitrile	107-12-0	(no test)	(no test)	(no test)	(no test)	(no test)
3.1.a	1,3-Butadiene	106-99-0	0.1	Detection	1.50	(n/a)	SP 515
3.1.b	Formaldehyde	50-00-0	0.03	Detection	1.50	(n/a)	SP 515
3.1.c	2,4-Dimethylpyridine	108-47-4	0.05	Detection	14.96	(n/a)	SP 515
3.2.a	1,3-Butadiene	106-99-0	3.4	DRE	39.8	(n/a)	SP 517-9
3.2.b	Formaldehyde	50-00-0	0.6	DRE	23.4	(n/a)	SP 517-9
3.2.c	2,4-Dimethylpyridine	108-47-4	1	DRE	(n/a)	0.282	SP 517-9
3.3.a	1,3-Butadiene	106-99-0	(no test)	(no test)	(no test)	(no test)	(no test)
3.3.b	Formaldehyde	50-00-0	(no test)	(no test)	(no test)	(no test)	(no test)
3.3.c	2,4-Dimethylpyridine	108-47-4	(no test)	(no test)	(no test)	(no test)	(no test)
4.1.a	N-Nitrosodimethylamine	62-75-9	0.00003	Detection	0.045	(n/a)	SP 515
4.2.a	N-Nitrosodimethylamine	62-75-9	0.0006	DRE	0.700	(n/a)	SP 517-9
4.3.a	N-Nitrosodimethylamine	62-75-9	0.062	DRE	72.3	(n/a)	SP 517-9
5.1.a	Furan	110-00-9	0.0001	Detection	0.150	(n/a)	SP 515
5.2.a	Furan	110-00-9	0.002	DRE	2.34	(n/a)	SP 517-9
5.3.a	Furan	110-00-9	0.017	DRE	19.5	(n/a)	SP 517-9
6.1.a	Ammonia	7664-41-7	2.5	Detection	0.125	(n/a)	SP 515
6.1.b	Nitrous Oxide	10024-97-2	5	Detection	0.249	(n/a)	SP 515
6.2.a	Ammonia	7664-41-7	50	DRE	1.95	(n/a)	SP 517-9
6.2.b	Nitrous Oxide	10024-97-2	100	DRE	3.89	(n/a)	SP 517-9
6.3.a	Ammonia	7664-41-7	630	DRE	24.5	(n/a)	SP 517-9
6.3.b	Nitrous Oxide	10024-97-2	831	DRE	32.4	(n/a)	SP 517-9
7.1.a	Acetonitrile	75-05-8	40	Multi-component DRE	(n/a)	0.506	SP 517-9
7.1.b	2,4-Dimethylpyridine	108-47-4	1	Multi-component DRE	(n/a)	0.282	SP 517-9
7.1.c	Ammonia	7664-41-7	630	Multi-component DRE	24.5	(n/a)	SP 517-9
7.1.d	Nitrous Oxide	10024-97-2	100	Multi-component DRE	3.89	(n/a)	SP 517-9
7.1.e	N-Nitrosodimethylamine	62-75-9	0.062	Multi-component DRE	72.3	(n/a)	SP 517-9
7.1.f	Furan	110-00-9	0.017	Multi-component DRE	19.5	(n/a)	SP 517-9

4.2 Sampling Matrix

The sampling matrix from the test plan is detailed in Table 12 and shows both on-line and off-line analytical samples.

Table 12. NUCON VAU Master Sampling Matrix from the Test Plan

Test	COPC name	CAS	PTR-MS	Precon/ PTR-MS	FT-IR	AreaRAE Multi-Gas	GC/MS	Particulate	Canister Sample (e.g., SUMMA)	DNPH Treated Silica Gel, SKC-226-119	Thermosorb/N	TDU Tenax TA	Anasorb 747 (sulfuric acid) SKC-226-29
0.1	All 11 Test COPCs	(multiple)		SP 521	SP 521	SP 521							
0.2	All 11 Test COPCs	(multiple)	SP 516	SP 516	SP 516	SP 516							
1.1	Acetonitrile Acetaldehyde	75-05-8 75-07-0	SP 516		SP 516								
1.2	Acetonitrile Acetaldehyde	75-05-8 75-07-0	SP 521 SP 516		SP 521 SP 516	SP 521 SP 516		SP 525 SP 514	SP 521 SP 525 SP 514 SP 516				
2.1	Benzene Propanenitrile	71-43-2 107-12-0	SP 516		SP 516								
2.2	Benzene Propanenitrile	71-43-2 107-12-0	SP 521 SP 516		SP 521 SP 516	SP 521 SP 516		SP 525 SP 514	SP 521 SP 525 SP 514 SP 516				
3.1	1,3-Butadiene Formaldehyde 2,4-Dimethylpyridine	106-99-0 50-00-0 108-47-4	SP 516										
3.2	1,3-Butadiene Formaldehyde 2,4-Dimethylpyridine	106-99-0 50-00-0 108-47-4	SP 521 SP 516			SP 521 SP 516		SP 525 SP 514	SP 521 SP 525 SP 514 SP 516	SP 521 SP 525 SP 514 SP 516			
4.1	N-Nitrosodimethylamine	62-75-9		SP 516									
4.2	N-Nitrosodimethylamine	62-75-9	SP 521	SP 516		SP 521 SP 516		SP 525 SP 514			SP 521 SP 525 SP 514 SP 516		
4.3	N-Nitrosodimethylamine	62-75-9	SP 521	SP 516		SP 521 SP 516		SP 525 SP 514			SP 521 SP 525 SP 514 SP 516		
5.1	Furan	110-00-9		SP 516									
5.2	Furan	110-00-9	SP 521	SP 516		SP 521 SP 516		SP 525 SP 514				SP 521 SP 525 SP 514 SP 516	
5.3	Furan	110-00-9	SP 521	SP 516		SP 521 SP 516		SP 525 SP 514				SP 521 SP 525 SP 514 SP 516	
6.1	Ammonia Nitrous Oxide	7664-41-7 10024-97-2			SP 516								
6.2	Ammonia Nitrous Oxide	7664-41-7 10024-97-2			SP 521 SP 516	SP 521 SP 516		SP 525 SP 514	SP 521 SP 525 SP 514 SP 516				SP 521 SP 525 SP 514 SP 516
6.3	Ammonia Nitrous Oxide	7664-41-7 10024-97-2			SP 521 SP 516	SP 521 SP 516		SP 525 SP 514	SP 521 SP 525 SP 514 SP 516				SP 521 SP 525 SP 514 SP 516
7.1	Acetonitrile 2,4-Dimethylpyridine Ammonia Nitrous Oxide N-Nitrosodimethylamine Furan	(multiple)	SP 521 SP 516	SP 516	SP 521 SP 516	SP 521 SP 516							

4.3 Calibrated Equipment

An M&TE list was used to track all calibrated equipment used during testing (see Table 13). The M&TE list identifies the instrument and the calibration type for the instrument. The types of calibrations are as follows:

- Cat 1 M&TE: all M&TE calibrated externally by a qualified calibration laboratory
- Cat 2 M&TE: all M&TE that is user-calibrated
- Cat 3 M&TE: commercial measuring devices that are not adjustable and provide adequate accuracy
- Cat FIO M&TE: “For Information Only”; Cat 1 and 2 M&TE that is not being used for quality-affecting measurement

Table 13. NUCON VAU List of Calibrated Equipment

M&TE Name	Serial #	PNNL Property #	Calibration # / Calibration Sticker ID / Lot #	Calibration Expires	Location/ Comments	Category 1, 2, 3, FIO
6890N Gas Chromatograph, Agilent (GC/MS)	US10411048	WD81253	NA	NA	Q Ave Pad Test Trailer	2
5973 Mass Selective Detector, Agilent (GC/MS)	US90432021	NA	NA	NA	Q Ave Pad Test Trailer	2
6890N Gas Chromatograph, Agilent (Precon)	US10443076	WD47408	NA	NA	Q Ave Pad Test Trailer	2
MKS MultiGas 2030 FTIR Continuous Gas Analyzer	01858	Rented	NA	NA	Q Ave Pad Test Trailer	2
Ionicon Analytik PTR-MS	44096535	Rented	NA	NA	Q Ave Pad Test Trailer	2
AreaRAE PGM-5020 Photoionizer detector (PID)	295-00393	NA	NA	NA	Q Ave Pad Test Trailer	FIO
DryCal FlexCal, Low Flow (5 – 500 sccm)	143298	NA	143298	03/2019	Q Ave Pad On Demand	1
DryCal FlexCal, Medium Flow, (50 – 5,000 sccm)	135623	NA	135623	07/2018	Q Ave Pad On Demand	1
DryCal FlexCal, High Flow (300 – 30,000 sccm)	143371	NA	143371	03/2019	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – 9 component gas mix	Cylinder # CC2017706893	NA	Lot# 18028.1	02/2019	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – 9 component gas mix	Cylinder # CC2017709006	NA	Lot# 18028.2	02/2019	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – 6 component gas mix	Cylinder # CC508261	NA	Lot# 18058.2		Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – 6 component gas mix	Cylinder # CC508266	NA	Lot# 18058.1		Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – NH_3/N_2 gas mix	Cylinder # EB0096054	NA	Lot# 7-352-105	12/2019	Q Ave Pad On Demand	1

M&TE Name	Serial #	PNNL Property #	Calibration # / Calibration Sticker ID / Lot #	Calibration Expires	Location/ Comments	Category 1, 2, 3, FIO
Certified Compressed Gas Bottle – N_2O/N_2 gas mix	Cylinder # CC704001	NA	Lot# 7-352-123	12/2020	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – N_2O/N_2 gas mix	Cylinder # CC704012	NA	Lot# 7-352-122	12/2020	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – CH_4/N_2 gas mix	Cylinder # TW00-279245	NA	Lot#8-085-200	3/2021	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle – CH_4/N_2 gas mix	Cylinder # MLK-000746	NA	Lot#8-085-201	3/2021	Q Ave Pad On Demand	1
MFC-30-1, MKS Mass Flow Controller, Injection/Calibration	021773073	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-5-1, MKS Mass Flow Controller, Calibration	001333065	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-0.1-1, MKS Mass Flow Controller, Calibration	021582322	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-20-1, MKS Mass Flow Controllers, Injection	783570	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-2-2, MKS Mass Flow Controllers, Sampling	021575979	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-2-3, MKS Mass Flow Controllers, Sampling	021575978	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-2-4, MKS Mass Flow Controllers, Sampling	001146981	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-2-1, MKS Mass Flow Controller, Sampling	021575980	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-5-3, MKS Mass Flow Controller, Sampling	788541	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-5-4, MKS Mass Flow Controller, Sampling	021575982	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-5-5, MKS Mass Flow Controllers, Sampling	660821	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-30-2, MKS Mass Flow Controllers, Sampling	017327638	NA	NA	NA	Q Ave Pad Test Trailer	2

M&TE Name	Serial #	PNNL Property #	Calibration # / Calibration Sticker ID / Lot #	Calibration Expires	Location/ Comments	Category 1, 2, 3, FIO
MFC-1-1, MKS Mass Flow Controllers, Injection	001146978	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-1-2, MKS Mass Flow Controllers, Injection	001339187	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-1-3, MKS Mass Flow Controller, Injection	000298914	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-1-4, MKS Mass Flow Controller, Injection	001146983	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-10-1, MKS Mass Flow Controllers, Injection	487551	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-50-1, Brooks Mass Flow Controller, Injection	0199090114644001	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-5-2, MKS Mass Flow Controller, Injection	001218810	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-10-2, MKS Mass Flow Controller, Injection	487550	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-50-2, Brooks Mass Flow Controller, Injection	0109100401006001	NA	NA	NA	Q Ave Pad Test Trailer	2
MFC-100-1, MKS Mass Flow Controller, Injection	000926067	NA	NA	NA	Q Ave Pad Test Trailer	2
Thermocouple- Type K, OMEGA	0226	NA	0226	02/26/2020	Q Ave Pad VAU SP 516, Port TE-112	1
MKS Type 247D, 4 Channel Readout	00160077	NA	NA	NA	Q Ave Pad Test Trailer	2
MKS Type 247D, 4 Channel Readout	001055002	NA	NA	NA	Q Ave Pad Test Trailer	2
MKS Type 247D, 4 Channel Readout	001149018	NA	NA	NA	Q Ave Pad Test Trailer	2
MKS Multi gas Controller, 647C	000818648	WD32984	NA	NA	Q Ave Pad Test Trailer	2

M&TE Name	Serial #	PNNL Property #	Calibration # / Calibration Sticker ID / Lot #	Calibration Expires	Location/ Comments	Category 1, 2, 3, FIO
Brooks Micro Processor Control & Read Out Unit, 0154BEC2A11A	0199120124922001	NA	NA	NA	Q Ave Pad Test Trailer	2
Fox Model FT1Thermal Gas Mass Flow Meter, VAU Air Flow Meter, FT1-061DDP1	F00780	NA	F00780	Calibrated 12/5/2016 Recalibration date not provided	Q Ave Pad VAU SP 521 3rd party property	FIO
Fluke 787 Process meter	6850044	NA	6850044	10/24/2018	Q Ave Pad On Demand	1
Fluke T/C Calibrator	3179173	NA	3179173	10/19/2018	Q Ave Pad On Demand	1
Certified Compressed Gas Bottle –Propionitrile	Cylinder # CC2018713342 Installed 5/14/18	NA	Lot# 18077.4	03/2019	Q Ave Pad On Demand	1
MKS Model 247D	000729217	NA	NA	NA	Q Ave Pad Test Trailer	2
MKS Type 247, 4 Channel Readout	001127162	NA	NA	NA	Q Ave Pad Test Trailer	2

5.0 Test Results

Testing results are shown in the following subsections identified by the test numbers from the test matrix in Table 11 [taken from the test plan, *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)*[1]], including modifications made during the actual testing. This starts with ambient air and diesel engine exhaust baselines (test 0). The dates when each test was conducted are provided in Table 14.

Table 14. List of Tests Conducted

Test Data Package	Description	Test	Date(s)	Notes
Test 0.1	Shakedown Test		4/30/18	
Test 0.2	Shakedown Practice Baseline		5/1/18	
Test 0.2a	Collection of Exhaust and Ambient Baselines	Baselines	5/4/18	
Test 1.1	Acetaldehyde & Acetonitrile	10% Detection	6/1/18	
Test 1.2	Acetaldehyde & Acetonitrile	200% OEL DRE	6/4/18	
Test 2.1	Benzene & Propanenitrile	10% Detection	5/14/18	
Test 2.2	Benzene & Propanenitrile	200% OEL DRE	5/15/18	
Test 3.1-3.2	1,3-Butadiene, Formaldehyde, & 2,4-Dimethylpyridine	10% Detection & 200% OEL DRE	5/17/18-5/18/18	Test and measurement process required a redesign – Test was redone
Test 3.2a	1,3-Butadiene & Formaldehyde	200% OEL DRE	5/30/18	Gases injected individually
Test 3.2b	2,4-Dimethylpyridine	200% OEL DRE	5/31/18	
Test 4.1 & 5.1	Furan & NDMA	10% Detection	6/6/18-6/7/18	
Test 4.2 & 5.2	Furan & NDMA	200% OEL DRE	6/11/18	
Test 4.3 & 5.3	Furan & NDMA	High Concentration DRE	6/13/18	
Test 6.1	Ammonia & Nitrous Oxide	10% Detection	5/7/18	
Test 6.2	Ammonia & Nitrous Oxide	200% OEL DRE	5/9/18	
Test 6.3	Ammonia & Nitrous Oxide	High Concentration DRE	5/10/18	

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[1] Rappe KG. 2018. *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)*. Test Plan TP-71248-01, Rev. 0, April 2018, Pacific Northwest National Laboratory, Richland, Washington.

5.1 Ambient Air and Diesel Engine Exhaust Baselines (Test 0)

Test 0.2a was conducted on May 4, 2018. The test included ambient air measurements from outside of the instrumentation trailer (north of the VAU skid), VAU inlet air baseline measurements from port A, and VAU diesel engine exhaust measurements from port D. Ambient air measurements were made by the PTR-MS in real-time. Additionally, an ambient air SUMMA® canister sample was collected and sent to 222-S for analysis. VAU measurements of inlet air at port A and exhaust at port D were made by the PTR-MS and FTIR in real-time, with the results provided in Table 15. Additionally, SUMMA® canister samples were collected from all four sample ports (A, B, C and D) and sent to 222-S laboratory for analysis.

Table 15. Baseline COPCs Measurements from Test 0.1/0.2

COPC	Test	Ambient Air		VAU Inlet (port A)		VAU Outlet (Port D)	
		PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]
Acetaldehyde	0.1, 0.2	0.036	0.652	0.042	0.632	0.605	1.69
Acetonitrile	0.1, 0.2	0.001	-	0.001	-	0.052	-
Benzene	0.1, 0.2	0.00103	-	0.00115	-	0.07097	-
Propanenitrile	0.1, 0.2	0.0023	-	0.0022	-	0.0123	-
1,3-Butadiene	0.1, 0.2	-[a]	-	-[a]	-	-[a]	-
Formaldehyde	0.1, 0.2	0.0889	< 0	0.094	< 0	0.522	0.430
2,4-Dimethylpyridine	0.1, 0.2	-[a]	-	-[a]	-	-[a]	-
NDMA	0.1, 0.2	-[a]	-	-[a]	-	-[a]	-
Furan	0.1, 0.2	0.0060	-	0.0065	-	0.0907	-
Ammonia	0.1, 0.2	-	< 0	-	0.005	-	< 0
Nitrous Oxide	0.1, 0.2	-	0.20	-	0.19	-	0.78
Other Compounds		**FTIR [ppm]**		**FTIR [ppm]**		**FTIR [ppm]**	
Carbon Monoxide	0.1, 0.2	0.04		0.04		79.0	
Carbon Dioxide	0.1, 0.2	320.5		356		74571	
Water	0.1, 0.2	11861		10854		63428	
Nitric Oxide	0.1, 0.2	0.03		0.04		307.9	
Nitrogen Dioxide	0.1, 0.2	0		0		111.0	
Methane	0.1, 0.2	3.1		3.1		1.9	
other NMHC[b], C_1	0.1, 0.2	2.1		1.3		35.2	

[a] PTR-MS in H_3O+ ionization mode; quantification not feasible due to signal interference.

[b] Non-methane hydrocarbon

All of the test 0.2a measurements with the PTR-MS were made using water in the discharge to create H_3O+ for the PTR-MS chemical ionization process. The fuel for the VAU was 50% ultra-low sulfur on-road winter diesel fuel and 50% ultra-low sulfur off-road summer diesel fuel. Additional inlet and exhaust baseline measurements were collected during each specific COPC test and can be found in Appendix F, with a selection of exhaust baseline measurements key for subsequent analysis shown in Table 16.

Table 16. Baseline COPCs Exhaust Measurements from Other Testing

COPC	Test	Exhaust Background PTR-MS [ppm]	Exhaust Background FTIR [ppm]	Instrument
Acetaldehyde	1.1	0.26	0.082	PTR-MS (H_3O+)
Acetonitrile	1.1	0.011	-	PTR-MS (H_3O+)
Benzene	2.2	0.0025	-	PTR-MS (H_3O+)
Propanitrile	2.2	0.0009	-	PTR-MS (H_3O+)
1,3-Butadiene	3.1	0.0008	-	PTR-MS (NO+)
Formaldehyde	3.2a	0.72	-	PTR-MS (H_3O+)
2,4-Dimethylpyridine	3.2b	0.0053	-	PTR-MS (NO+)
NDMA	4.3	0.0010	-	PTR-MS (NO+)
Furan	5.3	0.00022	-	PTR-MS (NO+)
Ammonia	6.1	-	0.06	FTIR
Nitrous Oxide	6.1	-	0.85	FTIR

5.2 Acetaldehyde and Acetonitrile (Test 1)

Test 1.1 confirmed the ability to detect acetaldehyde and acetonitrile in the exhaust at ~10% of the OEL concentration for each, with the results presented in Table 17 and Appendix E. This was performed with PTR-MS as the primary analysis instrument; additionally, in this and subsequent testing of acetaldehyde and acetonitrile, the PTR-MS employed water in the discharge to create H_3O+ for the chemical ionization process. The FTIR provided corroboration of the PTR-MS acetaldehyde analysis. A calculated 2.44 ppm of acetaldehyde and 2.08 ppm of acetonitrile were injected into the VAU exhaust, with 3.07 ppm and 3.2 ppm subsequently measured, respectively, on top of comparatively small concentrations pre-existing in the exhaust. Both of these measurements were confidently detected above the pre-existing baseline exhaust concentrations for each, which were comparatively small, thus confirming the ability to proceed with subsequent acetaldehyde and acetonitrile testing.

Table 17. Acetaldehyde and Acetonitrile 10% Detection Results

COPC	Test	all in [ppm] 10% OEL Target	Calculated Exhaust Spike	Measured at Port D PTR-MS	Measured at Port D FTIR	Exhaust Baseline
Acetaldehyde[a,b]	1.1	2.5	2.44	4.0	3.07	0.26
Acetonitrile	1.1	2	2.08	3.2	-	0.01

[a] FTIR results are "For Information Only"

[b] CO_2 interference impacted accuracy of measurements in the PTR-MS. Later testing was not impacted.

Test 1.2 evaluated COPC removal performance of the VAU with 200% OEL injection of acetaldehyde and acetonitrile into the inlet of the diesel engine. PTR-MS and FTIR measurements were made from all sample ports, with the results presented in Table 18 and Appendix F. Additionally, SUMMA® canister samples were collected from all sample ports along with duplicate SUMMA® canister samples from ports A and D and sent to 222-S laboratory for analysis.

Table 18. Acetaldehyde and Acetonitrile: 200% OEL DRE Results

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				PTR-MS [ppm]	PTR-MS [ppm]
Acetaldehyde[a]	1.2	50	61.9	75.5	0.28	0.73	99.6%	Yes	Yes	6.2	0.53
Acetonitrile	1.2	40	40.8	-	0.014	-	>99.9%	Yes	Yes	7.1	0.23

[a] FTIR results are For Information Only.

In test 1.2, 61.9 ppm acetaldehyde and 40.8 ppm acetonitrile were measured at the engine inlet with injection, and 0.28 ppm acetaldehyde and 0.014 ppm acetonitrile were measured at the VAU tailpipe. This calculates to a VAU DRE of 99.6% for acetaldehyde and >99.9% for acetonitrile. Thus, the VAU met both the ≤10% OEL purification targets (≤ 2.5 ppm acetaldehyde and ≤ 2.0 ppm acetonitrile) and ≥95% DRE targets for acetaldehyde and acetonitrile removal.

The measurements from ports B and C in test 1.2 were 6.2 ppm and 0.53 ppm for acetaldehyde, respectively, and 7.1 ppm and 0.23 ppm for acetonitrile, respectively. Thus, as shown in Table 38 and Appendix F, the diesel engine contributed 90.0% DRE for acetaldehyde and and 82.6% DRE acetonitrile, and the catalyst (and DPF) provided an additional 9.1% (and 0.4%) DRE for acetaldehyde and 16.9% (and 0.5%) DRE for acetonitrile. These results demonstrate that the VAU engine reduced concentration significantly, though would not have met target performance criteria for acetaldehyde or acetonitrile during the test without the catalyst.

5.3 Benzene and Propanenitrile (Test 2)

Test 2.1 confirmed the ability to detect benzene and propanenitrile in the exhaust at <10% of the OEL concentration for each, with the results presented in Table 19 and Appendix E. In this and subsequent benzene and propanenitrile testing, the PTR-MS provided primary analysis using H_3O+ ionization. A calculated 0.014 ppm of benzene and 0.077 ppm of propanenitrile were injected into the VAU exhaust, with 0.014 ppm and 0.20 ppm subsequently measured at port D, respectively. Both of these measurements were confidently detected above the pre-existing exhaust baseline concentrations for each, which were comparatively small, thus confirming the ability to proceed with subsequent benzene and propanenitrile testing.

Table 19. Benzene and Propanenitrile: 10% Detection Results

COPC	Test	all in [ppm]				Exhaust Baseline
		10% OEL Target	Calculated Exhaust Spike	Measured at Port D		
				PTR-MS	FTIR	
Benzene	2.1	0.05	0.014	0.014	-	0.002
Propanenitrile	2.1	0.6	0.077	0.205	-	0.0009

Test 2.2 evaluated COPC removal performance of the VAU with 200% OEL injection of benzene and propanenitrile into the inlet of the engine. PTR-MS measurements were made from all sample ports, with the results presented in Table 20 and Appendix F. SUMMA® canister samples were collected from all sample ports and sent to 222-S laboratory for analysis. Additionally, an ambient air sample was collected in a SUMMA® canister and sent to RJLee for analysis.

Table 20. Benzene and Propanenitrile: 200% OEL DRE Results

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				PTR-MS [ppm]	PTR-MS [ppm]
Benzene	2.2	1	0.86	-	0.023	-	97.3%	Yes	Yes	0.34	0.034
Propanenitrile	2.2	12	16.4	-	0.010	-	>99.9%	Yes	Yes	2.0	0.062

In test 2.2, 0.86 ppm benzene and 16.4 ppm propanenitrile were measured at the engine inlet with injection, and 0.023 ppm benzene and 0.010 ppm propanenitrile were measured at the VAU tailpipe. This calculates to a VAU DRE of 97.3% for benzene and >99.9% for propanenitrile. Thus, the VAU met both the ≥95% DRE targets and ≤10% OEL targets (≤ 0.05 ppm benzene and ≤ 0.6 ppm propanenitrile) for benzene and propanenitrile removal and purification.

The measurements from ports B and C in test 2.2 were 0.34 ppm and 0.034 ppm benzene, respectively, and 2.0 ppm and 0.062 ppm propanenitrile, respectively. Thus, as shown in Table 38 and Appendix F, the diesel engine contributed DREs of 60.5% for benzene and 87.6% for propanenitrile, and the catalyst (and DPF) provided an additional 35.6% (and 1.2%) DRE for benzene and 12.0% (and 0.3%) DRE for propanenitrile. These results show similarly that the VAU would not have met either target performance criteria for benzene or propanenitrile during the test without the catalyst, and was imperative for high benzene removal.

5.4 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine (Test 3)

Test 3.1 efforts performed on May 18, 2018, confirmed the ability to detect formaldehyde in the exhaust at ~10% of the OEL concentration using the PTR-MS with H_3O+ ionization, with the results presented in Table 21 and Appendix E. A calculated 0.030 ppm of formaldehyde was injected into the VAU exhaust, with 0.558 ppm subsequently measured at port D; this was on top of 0.516 ppm that was pre-existing in the baseline VAU exhaust. Nonetheless, the 0.030 ppm injection was confidently detected above the exhaust baseline and confirmed the ability to proceed with subsequent formaldehyde testing.

During test 3.1 on May 18, 2018, 1,3-butadiene and 2,4-dimethylpyridine were also injected into the exhaust at ~10% OEL each but not confidently measured for reasons that will be discussed later in this section in more detail. One of those reasons included the inadequacy of the PTR-MS to accurately quantify 1,3-butadiene and 2,4-dimethylpyridine in the exhaust under H_3O+ ionization mode. This prompted a modification to the PTR-MS to employ an NO+ ionization strategy for measurement of 1,3-butadiene and 2,4-dimethylpyridine in the VAU.

Subsequently, test 3.1 efforts continued on May 30, 2018, and confirmed the ability to detect 1,3-butadiene in the exhaust at ~10% of the OEL concentration using the PTR-MS with NO+ ionization, with the results also presented in Table 21 and Appendix E. A calculated 0.093 ppm of 1,3-butadiene was injected into the VAU exhaust, with 0.174 ppm subsequently measured at port D. This was confidently detected above the pre-existing exhaust baseline concentration for 1,3-butadiene, which was comparatively small, thus similarly confirming the ability to proceed with subsequent 1,3-butadiene testing.

As previously mentioned, 2,4-dimethylpyridine was not accurately quantified using the PTR-MS in H_3O+ ionization mode, requiring its measurement under NO+ ionization mode. 2,4-Dimethylpyridine testing difficulties were also compounded by extremely long required passivation times to reach steady state during testing. For this reason, analytical validation for 2,4-dimethylpyridine was chosen to be addressed during test 3.2.

Table 21. 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine: 10% Detection Results

COPC	Test	all in [ppm]				Exhaust Baseline
		10% OEL Target	Calculated Exhaust Spike	Measured at Port D		
				PTR-MS	FTIR	
1,3-Butadiene	3.1	0.1	0.093	0.174	-	0.0008
Formaldehyde [a]	3.1	0.03	0.030	0.558	0.0189	0.516
2,4-Dimethylpyridine [b]	3.1	0.05	0.047	*n.d.*	-	*n.d.*

[a] FTIR results are "For Information Only"

[b] The test identified that modified analytical methods would be required for accurate measurement.

n.d. - not detected, i.e., no elevation of the PTR-MS signal observed above background/baseline levels

Test 3.2 efforts were started on May 18, 2018, to attempt to measurement of COPC removal performance of the VAU with 200% OEL VAU inlet injections of 1,3-butadiene, formaldehyde, and 2,4-dimethylpyridine. Shortly into testing, observations were made that questioned the accuracy and reliability of the results, and elucidated the need to modify the PTR-MS ionization mode. These observations included the collection and release of water clusters inside the PTR-MS, and very "sticky" release trends from the 2,4-dimethylpyridine. In subsequent test 3.2 testing discussed below, these analytical and testing challenges were further characterized and understood to allow accurate VAU performance assessment.

In test 3.2 on May 18, 2018, it was determined that off-line media sampling would not be adversely impacted by the challenges in collecting on-line measurements in the PTR-MS, and thus could proceed in confidence. The media samples collected included SUMMA® canisters from ports A, B, C, and D, and DNPH treated silica gel tubes (SKC-226-119, for formaldehyde analysis) from ports A, B, C and D. A duplicate SUMMA® sample was collected from port D and a duplicate DNPH treated silica gel tube was collected from port A.

Evaluations of test 3.2 operations and results on May 18, 2018, led to the following changes in test strategy and in PTR-MS operation for subsequent test 3.2 efforts:

1. *1,3-Butadiene and 2,4-dimethylpyridine quantification* – The PTR-MS was modified to use zero air in the discharge to create NO+ for the chemical ionization process. The change from water to zero air significantly improved analysis stability and reduced the interference of water clusters on the PTR-MS analysis.

2. *Test 3.2 strategy* – Testing strategy was modified to inject a single COPC at a time for VAU assessment in subsequent test 3.2 efforts.
3. *2,4-Dimethylpyridine test strategy* – Longer dwell times were allowed for 2,4-dimethylpyridine breakthrough and stabilization during VAU assessment to accommodate the "stickiness" and passivation requirements for 2,4-dimethylpyridine to reach steady-state.

Test 3.2 continued on May 30 and 31, 2018 (a.k.a. test 3.2a and 3.2b, respectively), with the changes made discussed above. Testing assessed COPC removal performance of the VAU for 1,3-butadiene, formaldehyde, and 2,4-dimethylpyridine when injected at the inlet individually at 200% OEL for each. PTR-MS and FTIR measurements were made from all sample ports, with the results presented in Table 22 and Appendix F.

Table 22. 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine: 200% OEL DRE Results

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				PTR-MS [ppm]	PTR-MS [ppm]
1,3-Butadiene[a]	3.2	3.4	8.05	-	0.026	-	99.7%	Yes	Yes	0.98	*N.M.*
Formaldehyde[a,b]	3.2	0.6	1.34	0.38	0.727	0.031	45.7%	No	No	2.74	0.83
2,4-Dimethylpyridine[a]	3.2	1	0.98	-	0.0071	-	99.3%	Yes	Yes	0.021	*N.M.*

[a] Tested individually for VAU performance assessment.

[b] FTIR results are For Information Only.

N.M. - not measured

During test 3.2a, as shown in Table 22, using the PTR-MS in NO+ ionization mode, 8.05 ppm 1,3-butadiene was measured at port A and 0.026 ppm was measured at port D for a DRE of 99.7%, thus meeting the ≤0.1 ppm 1.3-butadiene purification target and the ≥95% DRE target for 1,3-butadiene removal. A concentration of 0.98 ppm 1,3-butadiene was measured at port B, showing that the engine provided 87.8% DRE and the catalyst (and DPF) provided an additional 11.8% DRE as shown in Table 38 and Appendix F. This demonstrates that the VAU engine removed 1,3-butadiene significantly, though it would not have met either target performance criteria without the catalyst.

Test 3.2a continued with the PTR-MS in H_3O+ ionization mode to test VAU removal performance for formaldehyde. With a calculated ~0.6 ppm formaldehyde injection, 1.34 ppm was measured at the VAU inlet; as shown in Appendix F, this was a combination of 0.88 ppm pre-existing prior to injection and an additional 0.43 ppm with injection. 0.727 ppm of formaldehyde was measured at the VAU tailpipe, resulting in a VAU DRE of only 45.7%. Thus, the VAU did not meet the 10% OEL target of ≤0.03 ppm formaldehyde or the ≥95% DRE target. The formaldehyde measurements from ports B and C were 2.74 ppm (corroborated by the FTIR) and 0.83 ppm, thus demonstrating that the diesel engine produces comparatively large amounts of formaldehyde that are largely removed subsequently by the oxidation catalysts.

Although the VAU did not reduce formaldehyde concentrations to a low enough level to achieve the performance goals for the system, it is worth noting that this is due to the pre-existence of 0.725 ppm formaldehyde in the VAU exhaust at tailpipe. Diesel engines are well known for producing ppm-quantities of small aldehydes, and thus it is not surprising that this diesel engine produced significant quantities of formaldehyde. This was also demonstrated in test 0.2 where 0.522 ppm formaldehyde was measured at the VAU tailpipe (Table 15). At the VAU tailpipe prior to injection in test 3.2a, 0.725 ppm of formaldehyde was shown to persist through the oxidation catalyst and be present at the VAU tailpipe. Thus, of the 1.34 ppm formaldehyde that was measured at the inlet, if one considers the pre-existing formaldehyde separately, then almost all of the injected amount was removed through the VAU. A DRE metric becomes less meaningful for a situation such as this where the formaldehyde concentration persisting through the VAU to the tailpipe is insensitive to formaldehyde injection at the VAU inlet.

During test 3.2b, as shown in Table 22, using the PTR-MS in NO+ ionization mode, 0.98 ppm 2,4-dimethylpyridine was measured at the VAU inlet at port A and 0.0071 ppm was measured at port D for a DRE of 99.3%, thus meeting the 10% OEL target of ≤0.05 ppm and the ≥95% DRE target for VAU performance. Results from this testing provided indication that the analytical system was successful in measuring ≤1.4% OEL for 2,4-dimethylpyridine. As shown in Table 22 and Appendix F, 0.021 ppm 2,4-dimethylpyridine was measured at port B and showed that the engine provided 97.8% DRE and the catalyst and DPF provided an additional 1.4% DRE. In contrast to prior results, this shows that the engine combustion was sufficient for 2,4-dimethylpyridine removal and did not require exhaust aftertreatment.

SUMMA® canister samples were collected from all sample ports and sent to RJLee for analysis of furan and NDMA in support of future testing needs. Duplicate SUMMA® canister samples were collected from all sample ports and were sent to 222-S for analysis of 2,4-dimethylpyridine. To confirm sample collection on port A, an additional duplicate port A sample using a canister without particulate filtration and without flow restriction was collected and sent to 222-S.

5.5 N-Nitrosodimethylamine and Furan (Test 4 and Test 5)

The testing of the NDMA in test 4 was combined with test 5 for furan evaluation in the VAU. By combining the tests, the project was able to reduce costs and schedule.

The following is a description of the test events and results that led to the determination that the injection of the NDMA and furan could be tested at the same time.

> *On May 4, 2018, emission baseline testing in test 0.2a proceeded with the PTR-MS under H_3O+ mode chemical ionization. The measurements made at Port D for furan and NDMA were prohibitively high and problematic (14 ppb furan and 20.5 ppb NDMA) to continue testing in the current configuration and as prescribed in the test plan. This also prohibited the use of pre-concentration, since ultra-trace level analysis was not possible in the prohibitively high background exhaust. Thus, alternatives to preconcentration were evaluated as the test program proceeded through May.*
>
> *Samples of the baseline (i.e., no COPC injection) inlet air at port A and the diesel exhaust at ports B, C, and D were collected on May 31, 2018, during test 3.2b. These samples were sent to RJLee for evaluation on a Time of Flight PTR-MS (Ionicon 4000) using H_3O+ ionization, with the results presented in Table 23. The results gave clear indication that a significant amount of the furan and NDMA signal (56-80%) coming from the test stand PTR-MS in H_3O+ ionization mode are from masking compounds (i.e., attributed to compounds other than the COPCs).*

Table 23. Masking on Furan and NDMA from the TOF PTR-MA Ionicon 4000 Analysis

Sample Port	**m69.335 (furan ppbv)**	**M69.0699 (isoprene ppbv)**	**Combined (ppbv)**	**Furan as a Percent of Combined**
A	0.58	2.32	2.9	20%
B	119.6	311.7	431.3	28%
C	5.41	12.84	18.25	30%
D	4.62	14.82	19.44	24%

Sample Port	m75.0441 (ethyl acetate ppbv)	M75.0558 (NDMA ppbv)	Combined (ppbv)	NDMA as a Percent of Combined
A	2.42	2.13	4.55	47%
B	79.6	69	148.6	46%
C	28.1	23.6	51.7	46%
D	26.71	23.35	50.06	47%

> *In parallel, evaluations for using the test stand's quadrupole PTR-MS in NO+ ionization mode were conducted on May 30, 2018, during test 3.2a. These results demonstrated the ability to detect furan at 2 ppb in the exhaust and NDMA at 1.3ppb in the exhaust and confirmed improved COPC identification from background compounds in the exhaust.*

Thus, the use of NO+ with long averaging times and targeted calibration without pre-concentration was proposed for use on test 5.1. Differentials between injection runs in the exhaust and non-injection exhaust runs were also included in testing. On June 5, 2018, WRPS, PNNL, and NUCON agreed to the following testing path:

- Test 5 will combine furan and NDMA testing and will operate the PTR-MS in NO+ ionization mode.
- Test 5.1 furan and NDMA 10% OEL detection test
  - Furan (0.0001 ppm) and NDMA (0.00003 ppm)
  - No SUMMA® canisters or tubes (as normal)
- Test 5.2 furan and NDMA 200% OEL DRE test
  - Furan (0.002 ppm) and NDMA (0.0006 ppm)
  - SUMMA® canisters port A, B, C, D (duplicate on port C)
  - Thermosorb/N tube samples will be collected from ports A, B, C, D for 320 minutes to obtain 3:1 dilution and the total vacuum should be set to 2000 mL/min. No duplicate samples should be collected on the tubes.
  - Additional SUMMA® canisters (with no filters or flow restrictors) will be collected and then sent for analysis on the new TOF WERK VOCUS PTR-MS
- Test 5.3 furan and NDMA high concentration DRE test
  - Furan (0.017 ppm) and NDMA (0.062 ppm)
  - SUMMA® canisters port A, B, C, D
  - Thermosorb/N tube samples will be collected from ports A, B, C, D for 320 minutes to obtain 3:1 dilution and the total vacuum should be set to 2000 mL/min. No duplicate samples should be collected on the tubes.

Test 4.1 confirmed the ability to detect NDMA in the VAU exhaust at ~50% of the OEL. The divergence from 10% OEL is elaborated on below. Test 5.1 confirmed the ability to detect furan in the VAU exhaust at <10% OEL. The results are presented in Table 24 and Appendix E. In this and subsequent NDMA and furan testing, the PTR-MS provided primary analysis using NO+ ionization as described prior. A calculated 0.000149 ppm of NDMA was injected into the VAU exhaust, with 0.000781 ppm confidently measured by the PTR-MS at port D on top of a pre-existing 0.000686 ppm NDMA baseline in the VAU exhaust. Similarly, a calculated 0.000049 ppm of furan was injected into the VAU exhaust, with 0.000148 ppm confidently measured by the PTR-MS at port D on top of a pre-existing 0.000104 ppm furan baseline. These results confirmed the ability to proceed with subsequent furan testing.

Analytical validation for NDMA (i.e., test 4.1) started with establishing the PTR-MS detection sensitivities for measuring NDMA. The first step was to measure the pre-existing exhaust baseline for NDMA, this was 0.000686 ppm NDMA. 10% OEL exhaust injection was then started for NDMA (~30 ppt), but that amount of NDMA was not confidently discernable from the comparatively large pre-existing exhaust baseline signal. The rate of NDMA injection was then raised to 100% OEL (~300 ppt) and detection was confidently established. NDMA injection was then sequentially lowered to the minimum value that could be confidently detected above the pre-existing baseline signal, which was 0.000149 ppm (i.e., 149 ppt, ~50% OEL), establishing the sensitivity for NDMA in the VAU exhaust with the PTR-MS. WRPS was present at the test site and confirmed testing could proceed with 50% OEL sensitivity for NDMA.

Table 24. NDMA and Furan: 10% Detection Results

COPC	Test	all in [ppm]				Exhaust Baseline
		10% OEL Target	Calculated Exhaust Spike	Measured at Port D		
				PTR-MS	FTIR	
NDMA	4.1	0.000030	0.000149	0.000781	-	0.000686
Furan	5.1	0.000100	0.000049	0.000148	-	0.000104

Test 4.2 evaluated COPC removal performance of the VAU with 200% OEL injection of NDMA into the inlet of the engine, and simultaneously test 5.2 evaluated analogous VAU performance for furan. PTR-MS measurements were made from all sample ports, with the results presented in Appendix F. SUMMA® canister samples were collected from all sample ports and sent to 222-S laboratory for analysis, along with duplicate SUMMA® canister samples collected from port C. NDMA was sampled onto ThermoSorb/N tubes from ports B, C, and D, which were sent to 222-S laboratory for analysis. A ThermoSorb/N tube was placed on the tube port A sampling system, though early in the testing the media from the tube was expelled and damaged the mass flow control to the collection vacuum on-line A. Thus, a tube sample for port A was not collected at that time.

Also during tests 4.2 and 5.2, five special SUMMA® canisters without particulate filters and without flow restrictors were used to collect two baseline samples (i.e., no COPC injection) from ports A and D and three samples during testing (i.e., with NDMA and furan injection) from ports A, B, and D. These samples were subsequently analyzed by Aerodyne Research, Inc. using the TOFWERK ultra-high-resolution VOCUS-PTR. The purpose of this testing was to quantitatively identify interfering compounds at the furan and NMDA masses measured by the quadrupole to determine the fraction of the test stand

PTR-MS signal that is attributed to the COPC. The VOCUS-PTR results and accompanying summary are provided in Sections 5.5.1 and 5.5.2 and Table 28.

The combined results of the PTR-MS analysis and the TOFWERK ultra-high-resolution VOCUS-PTR measurements are shown in Table 25. As mentioned above, the PTR-MS results alone (i.e., without combination with the results of the TOFWERK ultra-high-resolution VOCUS-PTR) can be found in Appendix F.

Table 25. NDMA and Furan: 200% OEL DRE Results

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				PTR-MS [ppm]	PTR-MS [ppm]
NDMA[a]	4.2	0.0006	0.00034	-	0.000151	-	55.6%	No	No	0.00025	0.00018
Furan[a]	5.2	0.002	0.00234	-	0.000017	-	99.3%	Yes	Yes	0.0578	0.00011

[a] PTR-MS reflects combined results from PNNL PTR-MS and TOFWERK ultra-high resolution VOCUS-PTR

During test 4.2, as shown in Table 25, 0.000340 ppm NDMA was measured at port A and 0.000151 ppm (151 ppt) was measured at port D. This did not meet the ≤10% OEL target of 0.000030 ppm (30 ppt) NDMA in the VAU exhaust, and yielded an NDMA DRE of 55.6%. Thus, neither criteria for VAU performance were met for NDMA at 200% OEL injection. It should be noted that the estimated error associated with the NDMA concentration measurements at this low ultra-trace level (~10-50% OEL) is of similar order of magnitude to the concentration values reported. Thus, this error may be a significant factor in the results presented in Table 25 for NDMA, and may have dictated the perceived performance of the VAU.

Althought the PTR-MS signal without VOCUS PTR-TOF combination reflected a value close to the expected injected NDMA amount, the combined result of the PTR-MS and the VOCUS PTR-TOF was lower than the NDMA injected amount. Reasons for this may include 1) an impact from the blower between the injection port and the sampling port or 2) the lower moisture level in the inlet sample adversely impacting the recovery of the NDMA from the SUMMA canister.

In test 5.2, as shown in Table 25, 0.00234 ppm furan was measured at port A and 0.000017 ppm was measured at port D, yielding a 99.3% VAU DRE value. This met buth the ≤10% OEL target of 0.00010 ppm furan and the ≥95% DRE target for VAU removal performance. The furan measurements from ports B and C were 0.0578 ppm and 0.00011 ppm, respectively. Thus, as shown in Table 38 and Appendix F, the diesel engine produced comparatively large amounts of furan that required the catalyst to remove, which it did so with very high efficiency.

Tests 4.3 and 5.3 evaluated COPC removal performance of the VAU with simultaneous high concentration injection of NDMA and furan into the inlet of the engine. PTR-MS measurements and SUMMA® canister samples were taken from all sample ports, with the latter sent to 222-S laboratory for analysis. A duplicate SUMMA® canister sample was collected from port C and accompanied the other samples. NDMA was sampled onto ThermoSorb/N tubes from all sample ports, which were also sent to 222-S laboratory for analysis. The results for tests 4.3 and 5.3 shown in Table 26 are a product of the PTR-MS measurements in this test and the TOFWERK ultra-high-resolution VOCUS-PTR measurements made in the prior test. This is accomplished by subtracting the concentrations of interfering species identified from the prior analysis from the PTR-MS results measured in this test. Additional detail is presented in Section 5.5.2 and Table 29.

Table 26. NDMA and Furan: High Concentration Results

COPC	Test	High Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				PTR-MS [ppm]	PTR-MS [ppm]
NDMA	4.3	0.062	0.060	-	0.000042	-	>99.9%	Yes	No	0.00205	-[b]
Furan	5.3	0.017	0.021	-	0.000035	-	99.8%	Yes	Yes	0.087	-[b]

[a] PTR-MS reflects combined results from PTR-MS and VOCUS PTR-TOF; see Section 5.5.2.

[b] VOCUS PTR-TOF results not available.

During test 4.3, as shown in Table 26, 0.060 ppm NDMA was measured at port A and 0.000042 ppm was measured at port D. This calculates to a DRE of >99.9%, thus far exceeding the VAU performance target for NDMA removal and almost achieving the ≤10% OEL target of 0.000030 ppm NDMA for exhaust purification. Again, it is worth noting that the estimated error associated with NDMA concentration measurement at this level in the exhaust is of similar order of magnitude as this reported value, and thus may be a factor in the result. At port B, 0.00205 ppm of NDMA was measured, demonstrating that the engine alone removed >95% of the incoming NDMA during high injection.

NDMA DRE performance was observed to improve from 55.6% at 200% OEL inlet injection to >99.9% at high concentration injection. This is the opposite of what is expected when governed solely by homogeneous combustion chemistry where a DRE would remain constant across a wide concentration of inlet COPC concentration. It should be emphasized that ultra-trace level COPC measurement and behavior in lean heterogeneous combustion (i.e., diesel) and catalytic systems is highly complex. A large number of factors could be influencing the results, the vast majority of which are outside of the scope of this test effort. However, the NDMA result that carrys the highest level of confidence is the high concentration DRE measurement of >99.9% that reflects no greater than ~2% error.

During test 5.3 (also shown in Table 26), 0.021 ppm furan was measured at port A and 0.000035 ppm was measured at port D. This calculates to a DRE of 99.8% and meets VAU performance target criteria of >95% removal and purification to below 0.0001 ppm. At port B, 0.087 ppm furan was measured. This showed again that the diesel engine produced comparatively large amounts of furan that required the catalyst to remove, which it did so with high efficiency.

5.5.1 High-Resolution Mass Spectra of Nominal Masses for Furan and NDMA using NO+ Ionization

Supplemental SUMMA® canister analysis was provided by Aerodyne Research, Inc. using the TOFWERK ultra-high-resolution VOCUS-PTR. This was to help identify competing compounds at the furan and NMDA masses measured by the quadrupole. The canisters sent to AeroDyne Research had port A and port D gases before injections and port A, port B, and port D gases collected during NDMA and furan injection.

Normal operation of the PTR-MS using proton transfer from H_3O^+ to a target analyte was successful for many of the organic COPCs. However, it was not feasible for 1,3-butadiene and NDMA because both were observed to have a baseline signal that was highly dependent on the moisture content of the sample. This was prohibitive to confident calibration and measurement in the exhaust stream. In the case of 1,3-butadiene, this is due to an interference at the protonated m/Z of 55 from the second water cluster $H_3O^+(H_2O)_2$, which is present as a byproduct of the formation process for H_3O^+ itself. Under normal conditions, this cluster can be minimized by increasing the electric field in the PTR-MS drift tube. However, the high water levels in the exhaust produced levels of $H_3O^+(H_2O)_2$ that could not be reduced sufficiently in this manner. NDMA, which has a protonated m/Z of 75, also displayed a high dependence on humidity. This resulted in the decision to operate the PTR-MS in an alternate mode using NO^+ as the chemical ionization (CI) agent instead of H_3O^+ as described previously in this report. Use of NO^+ in the PTR-MS was first reported by Knighton et al. (WB Knighton, EC Fortner, SC Herndon, EC Wood, and RC Miake-Lye; Rapid Commun. Mass Spectrom 2009; 23: 3301-3308) as a method for detecting trace levels of 1,3-butadiene in ambient air at levels in the low ppt range. In addition to using NO^+ as a CI agent for 1,3-butadiene in this work, it was discovered that calibration and detection of NDMA was insensitive to variations in water concentration and could be calibrated down to 30 ppt. Detection levels of furan and 2,4-dimethylpyridine were also found to be lower with NO^+ ionization. Thus, furan and 2,4-dimethylpyridine measurements were also performed in the NO^+ mode.

Despite the high sensitivity observed in calibration with furan and NDMA standards, there were background interferences in the exhaust at the masses m/Z 68 for furan and m/Z 74 for NDMA at the very low OEL levels for these compounds. The unit mass resolution of the quadrupole PTR-MS used for measurements in this study was insufficient to resolve this issue. In order to determine the ratio of COPC to interferences for the nominal masses 68 and 74, the project team employed a recently developed high-resolution VOCUS PTR-TOF (Tofwerk AG) mass spectrometer operating with NO^+ as the CI agent, operated by Aerodyne Research, Inc. To accomplish this, SUMMA® canisters were used to sample the VAU inlet at sample port A and the VAU exhaust at sample ports B and D while furan and NDMA were injected into the inlet during the 200% OEL test (test 4.2/5.2). These canisters were then sent to Aerodyne Research Inc. for analysis. Port A was also sampled without injection and sent. Compounds that would be interferences for the quadrupole PTR-MS were cleanly resolved with the VOCUS. Although capable of a resolution of 15,000, the resolution for these measurements was 11,000 due to the instrument tuned for other work at Aerodyne. It is important to note that resources such as calibration standards were not available for the VOCUS measurements, and only a limited amount of time was available on the VOCUS. As a result, although the ratios of species measured from a given summa canister are accurate, absolute values between canisters are only semi-quantitative.

Figure 5 shows the high-resolution spectrum at nominal mass 68 for furan from the sample pulled from the VAU outlet (port D) during 200% OEL injection (test 5.2). In this and subsequent results, the VOCUS background has been subtracted. As can be seen, furan as $C_4H_4O^+$ is cleanly resolved from interfering peaks, which have a number of isomeric possibilities. Identification is not in the scope of this work nor is it necessary. The fraction of the nominal mass due to furan is determined by integrating the peak area for furan and dividing by the total integrated signal at nominal m/Z 68, including the unidentified shoulder around 68.08. The result is 6.4% as the contribution from furan that was observed with the quadrupole PTR-MS in the real-time engine measurements.

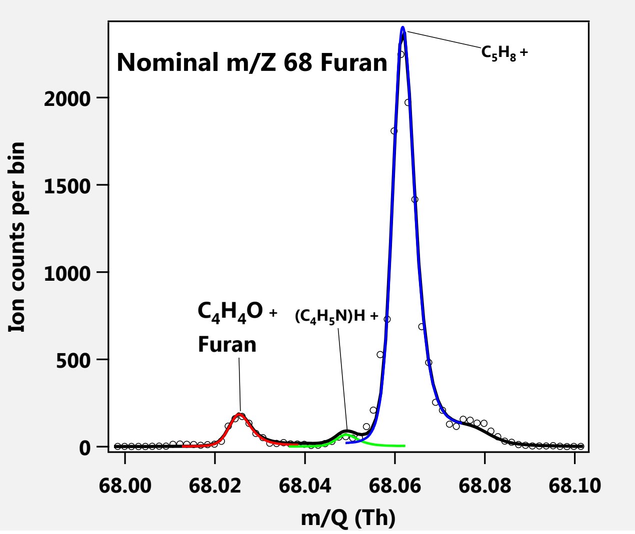

Figure 5. High-Resolution VOCUS Spectrum of m/Z 68 from VAU Outlet (port D) during Injection

Figure 6 shows the high-resolution spectrum at nominal mass 74 for NDMA from the sample pulled from the VAU outlet (port D) during 200% OEL injection (test 4.2). As can be seen, NDMA as $C_2H_6N_2O^+$ is sufficiently resolved from interfering peaks to allow a high confidence fit of the peak. There are more interferences than for furan, and these have a number of isomeric possibilities. Again, identification is not in the scope of this work, nor is it necessary to determine the fraction of the nominal mass due to NDMA. However, it is noted that the presence of peaks such as $(NO)C_3H_8^+$ are adducts of NO^+ rather than products of charge transfer reaction. The peak to the right of $(NO)C_3H_8^+$ that is not fit is due to an isotopic peak from m/Z 73. Integrating the peak area for NDMA and dividing by the total integrated signal at nominal m/Z 74 gives 13.4% as the contribution from NDMA that was observed with the quadrupole PTR-MS in the real-time engine measurements.

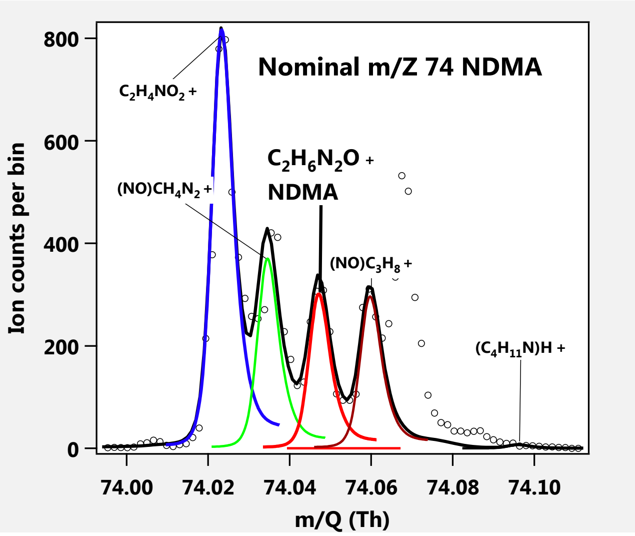

Figure 6. High-Resolution VOCUS Spectrum of m/Z 74 from VAU Outlet (port D) during Injection

High-resolution measurements using the VOCUS were also made of the samples acquired from the VAU inlet at port A with and without furan injection during test 5.2. Figure 7 shows the results of these measurements, with the left figure labeled as a) showing without injection and the right figure labeled as b) showing with injection.

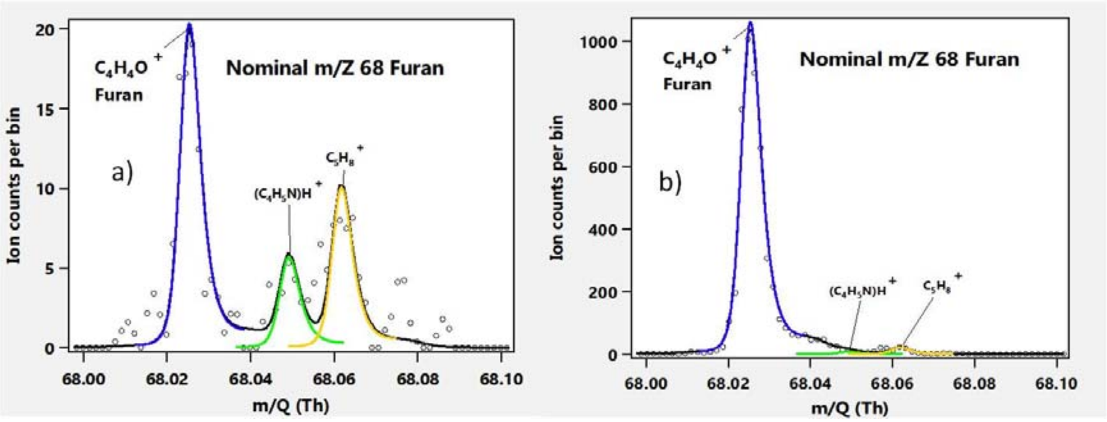

Figure 7. High-Resolution VOCUS Spectrum of m/Z 68 for a) Port A without Injection and b) Port A with Injection

Figure 7a shows that there were trace levels of furan and other species at the nominal mass 68 pre-existing at the inlet prior to injection, and peak integration yields 55.8% contribution from furan as the fraction of the unit mass signal detected by the quadrupole PTR-MS. Figure 7b shows that the vast majority (94.3%) of the quadrupole signal at m/Z 68 is due to the furan with injection. Assignment of the signals from (C_4H_5N)H$^+$ and $C_5H_8^+$ is outside the scope of this work. However, we do note that the same masses were present in the samples from the VAU exhaust exhaust sample.

Figure 8 gives the same results for NDMA sampled from the VAU inlet during test 4.2 a) without injection, and b) with injection. Figure 8a shows the same interfering compounds that were observed in the VAU exhaust sample. These levels are somewhat higher than the background for furan (i.e., at m/Z

68) but are still at a near-trace level with NDMA comprising 26.3% of the signal. Figure 8b shows the levels during injection of NDMA. The NDMA peak increases by a factor of ~5 during injection while background peaks stay the same, resulting in net fraction of 56.7% for NDMA at port A during injection. As before, the peak to the right of $(NO)C_3H_8^+$ that is not fit is due to an isotopic peak from m/Z 73 and was accounted for in peak integration and calculation of the percent NDMA.

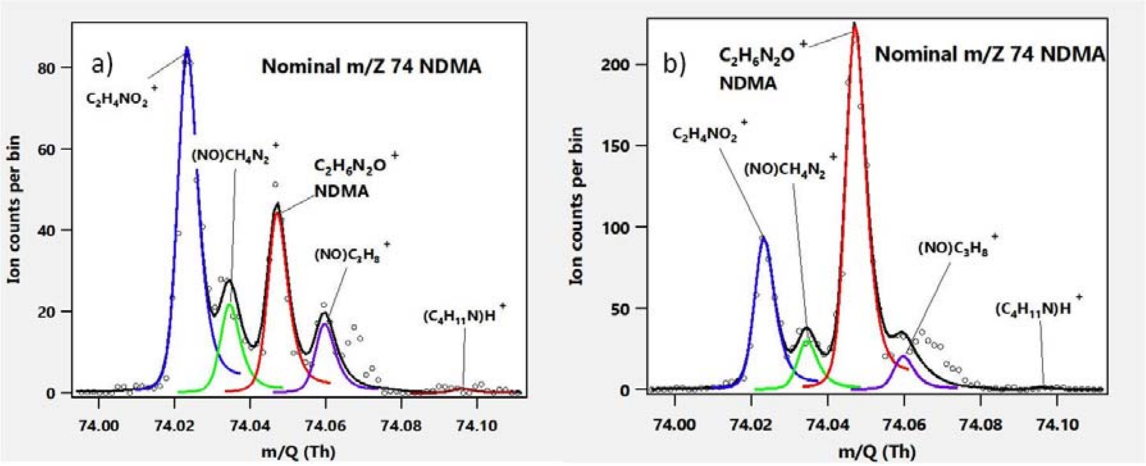

Figure 8. High-Resolution VOCUS Spectrum of m/Z 74 for a) Port A without Injection and b) Port A with Injection

Figure 9 shows the VOCUS spectrum of the VAU exhaust sample from port B after the diesel engine during injection in test 4.2/5.2. In this analysis, NDMA contributed 6.0% of the unit mass signal detected by the quadrupole PTR-MS at m/Z 74, and furan contributed 78.9% of the unit mass signal detected by the quadrupole PTR-MS at m/Z 68.

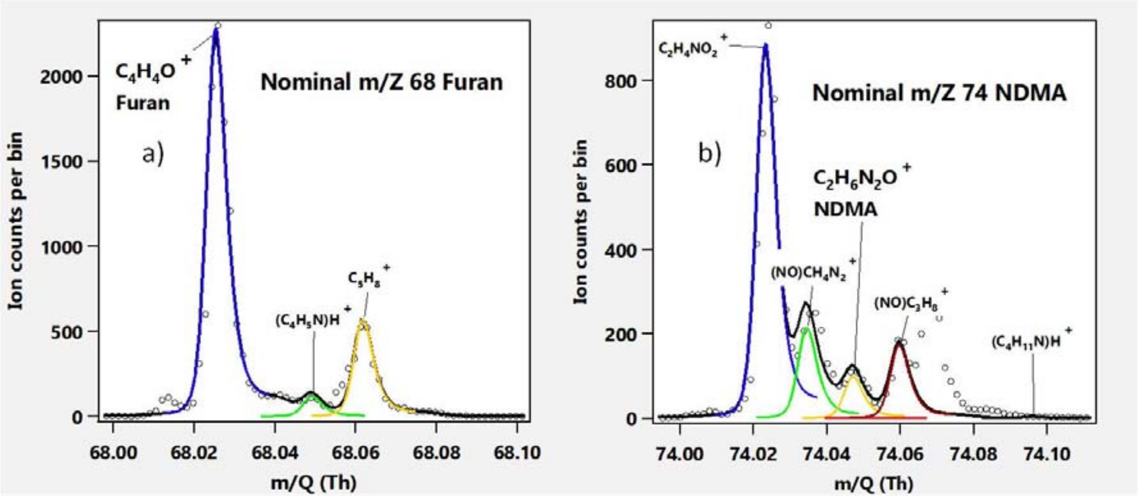

Figure 9. High-Resolution VOCUS Spectrum during Injection for Sampling at Port B for a) m/Z and b) m/Z 74.

5.5.2 Summary of High-Resolution VOCUS PTR-TOF Measurements and Impact on NDMA and Furan Concentrations

The results of the VOCUS PTR-TOF measurements for tests 4.2 and 5.2 are summarized in Table 27; these reflect the discussion from above in this section. Those measurements combined with the PTR-MS measurements from tests 4.2 and 5.2 provide the results in Table 28, which reflect the total, COPC, and interference concentrations measured at m/Z 74 and m/Z 68 for NDMA and furan, respectively. The COPC concentrations in Table 28 are calculated by multiplying the VOCUS PTR-TOF measurements in Table 27 with the PTR-MS response (i.e., m/Z total) from tests 4.2/5.2 in Table 28. Then, the interference concentrations at m/Z 74 and 68 in Table 28 are calculated as the difference between the total and COPC concentrations. The interference concentrations at m/Z 74 and 68 in Table 28 from tests 4.2/5.2 are then used to calculate the respective COPC concentrations in Table 29 by subtracting the interference concentrations from the PTR-MS response (i.e., m/Z total) from tests 4.3/5.3.

In summary, the use of the high-resolution VOCUS PTR-TOF operating on NO^+ provided a measurement that can be accurately used to determine the contribution of furan to m/Z 68 and NDMA to m/Z 74 as measured by the PTR-MS. The results for COPC concentrations in Table 28 and Table 29 are used to determine the results shown for tests 4.2/5.2 in Table 25 and tests 4.3/5.3 in Table 26.

Table 27. TOFWORKS High-Resolution VOCUS PTR-TOF Results

COPC	VOCUS PTR-TOF Measured Contribution of COPC to PTR-MS Signal in Tests 4.2 & 5.2					
	Without COPC Injection		With COPC Injection			
	VAU Inlet	VAU Outlet	VAU Inlet	Port B	Port C	VAU Outlet
Furan	55.8%	*n.m.*	94.3%	78.9%	*n.m.*	6.4%
NDMA	26.3%	*n.m.*	56.7%	6.0%	*n.m.*	13.4%

n.m. - not measured

Table 28. Total, COPC, and Interference Concentrations Measured at m/Z 74 and 68 in Tests 4.2/5.2

COPC	m/Z Total Measured Concentration, & COPC and m/Z Interference Calculated Concentrations in Tests 4.2 & 5.2			
	With COPC Injection			
	VAU Inlet	Port B	Port C [a]	VAU Outlet
	all in [ppm]			
Total m/Z 68	0.00249	0.0733	0.00178	0.00026
Furan	0.00234	0.0578	-	0.000017
Interference m/Z 68	0.00014	0.0155	-	0.00024
Total m/Z 74	0.00060	0.00421	0.00135	0.00113
NDMA	0.00034	0.00025	-	0.000151
Interference m/Z 74	0.00026	0.00396	-	0.00098

[a] PTR-MS signal provided for reference only; VOCUS PTR-TOF not measured for this sample

Table 29. Total and COPC Concentrations at m/Z 74 and 68 in Tests 4.3/5.3

COPC	m/Z Total Measured Concentration, and COPC Calculated Concentration in Tests 4.3 & 5.3			
	With COPC Injection			
	VAU Inlet	Port B	Port C[a]	VAU Outlet
	all in [ppm]			
Total m/Z 68	0.0213	0.102	0.00006	0.00028
Furan	0.0212	0.087	-	0.000035
Total m/Z 74	0.0606	0.00601	*n.d.*	0.00102
NDMA	0.0603	0.00205	-	0.000042

[a] PTR-MS signal provided for reference only; VOCUS PTR-TOF not measured for this sample

n.d. - not detected, i.e., PTR-MS signal less than pre-determined instrument baseline

5.6 Ammonia and Nitrous Oxide (Test 6)

Test 6.1 confirmed the ability to detect ammonia and nitrous oxide in the exhaust at nominally 10% or less of the OEL, with the results presented in Table 30 and Appendix E. This was performed with FTIR as primary analysis. A targeted 2.5 ppm of ammonia and 5.0 ppm of nitrous oxide were injected into the VAU exhaust after the DPF, with 1.36 ppm and 3.57 ppm measured at the VAU tailpipe, respectively. Both of these measurements were confidently detected above the pre-existing baseline exhaust concentrations for each, which were comparatively small, thus confirming the ability to proceed with subsequent ammonia and nitrous oxide testing.

Table 30. Ammonia and Nitrous Oxide: 10% Detection Results

COPC	Test	all in [ppm]				Exhaust Baseline
		10% OEL Target	Calculated Exhaust Spike	Measured at Port D		
				PTR-MS	FTIR	
Ammonia	6.1	2.5	1.97	-	1.36	0.07
Nitrous Oxide	6.1	5	2.92	-	3.57	0.80

Test 6.2 evaluated COPC removal performance of the VAU with 200% OEL of ammonia and nitrous oxide injected into the inlet of the engine. FTIR measurements were made from all sample ports, with the results presented in Table 31 and Appendix F. SUMMA® canister samples were collected from all sample ports and sent to 222-S laboratory for analysis. A duplicate SUMMA® canister sample was collected from the VAU exhaust (port D). Additionally, ammonia was sampled onto Anasorb 747 tubes with duplicates (on all ports) from all sample ports and sent to 222-S laboratory for analysis.

The Anasorb 747 tubes used were SKC-226-81A type tubes that were not coated with sulfuric acid, which acts as a capture assist agent for ammonia. This was different than the standard Anasorb 747, SK-226-29 tubes specified in the test plan. The different tube caused a quality non-conformance that was documented in Problem Evaluation Request WRPS-PER-2018-1318. The ammonia tubes could not be used for ammonia analysis.

Table 31. Ammonia and Nitrous Oxide: 200% OEL DRE Results (Test 6.2)

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				FTIR [ppm]	FTIR [ppm]
Ammonia	6.2	50	-	54.9	-	0.70	98.7%	Yes	Yes	3.2	0.11
Nitrous Oxide	6.2	100	-	105.9	-	28.9	72.7%	No	No	27.9	29.3

During test 6.2, as shown in Table 31, 54.9 ppm ammonia and 105.9 ppm nitrous oxide were measured at the engine inlet (port A), with 0.70 ppm ammonia and 28.9 ppm nitrous oxide measured at the VAU tailpipe. This resulted in a VAU DRE of 98.7% for ammonia, thus meeting both the 10% OEL target of 2.5 ppm and the 95% DRE target for ammonia. Neither the 10% OEL target of 5 ppm nor the 95% DRE target were met for nitrous oxide. This is expected, as nitrous oxide is well-known to the transportation industry to be a problematic and persistent greenhouse gas exhaust effluent. The measurements from ports B and C for ammonia were 3.2 ppm and 0.11 ppm, respectively. The diesel engine provided most of the ammonia removal performance at 94.2% DRE as shown in Table 38 and Appendix F. Thus, the VAU would have just barely not met target performance criteria for ammonia during the test without the catalyst.

Test 6.3 evaluated COPC removal performance of the VAU with high concentration injection of ammonia and nitrous oxide into the inlet of the engine. FTIR measurements were made from ports A, B, C, and D, with the results presented in Table 32 and Appendix F. SUMMA® canister samples were collected from ports A, B, C, and D and sent to 222-S laboratory for analysis. Finally, ammonia was sampled onto Anasorb 747 tubes with duplicates (on all ports) from ports A, B, C, and D, which were sent to 222-S laboratory for analysis.

The Anasorb 747 tubes used were SKC-226-81A type tubes that were not coated with sulfuric acid, which acts as a capture assist agent for ammonia. This was different that the standard Anasorb 747, SK-226-29 tubes specified in the test plan. The different tube caused a quality non-conformance that was documented in Problem Evaluation Request WRPS-PER-2018-1318. The ammonia tubes were not able to be used for ammonia analysis.

Table 32. Ammonia and Nitrous Oxide: High Concentration DRE Results (Test 6.3)

COPC	Test	High Inlet Target	Measured at Inlet (port A)		Measured at Outlet (port D)		VAU DRE	95% DRE Target met?	10% OEL Target met?	Port B	Port C
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]				FTIR [ppm]	FTIR [ppm]
Ammonia	6.3	630	-	665	-	0.3	>99.9%	Yes	Yes	76.3	0.9
Nitrous Oxide	6.3	831	-	853	-	261	69.5%	No	No	236	259

During test 6.3, as shown in Table 32, 853 ppm nitrous oxide and 665 ppm ammonia were measured at the engine inlet (port A), with 261 ppm nitrous oxide and 0.30 ppm ammonia measured at the VAU tailpipe. This resulted in a VAU DRE of >99.9% for ammonia, thus meeting both the 10% OEL target of 2.5 ppm and the 95% DRE target for ammonia. Again, neither the 10% OEL target of 5 ppm nor the 95% DRE target were met for nitrous oxide. The measurements from ports B and C for ammonia were 76.3 ppm and 0.9 ppm, respectively. Thus, as shown in Table 38 and Appendix F, the diesel engine contributed 88.5% DRE with an additional 11.3% from the catalyst. This shows that oxidation catalyst was critical for enabling the VAU to meet performance criteria for ammonia removal with high concentration ammonia injection.

5.7 Multi-component Performance Sensitivity Testing (Test 7)

The multi-gas test in the test plan combined six of the COPC gases at high concentrations to evaluate the performance of the VAU under high stress conditions. The six gases considered for this testing were as follows:

1.	Acetonitrile (75-05-8)	at 40 ppm
2.	2,4- Dimethylpyridine (108-47-4)	at 1 ppm
3.	Ammonia (7664-41-7)	at 630 ppm
4.	Nitrous Oxide (10024-97-2)	at 100 ppm
5.	N-Nitroso-dimethylamine (62-75-9)	at 0.062 ppm
6.	Furan (110-00-9)	at 0.017 ppm

On June 6, WRPS provided the following discussion related to the multi-gas test:

> *These gasses have already been run and DRE's have been calculated. The tests were typically done with two gasses run simultaneously. Based on previous testing, we don't expect changes of DRE based on interaction between compounds. Further, the next step in the technology maturation process is a pilot-scale demonstration on BY-108. The full mixture of vapors in BY-108 will be tested in this phase of testing. The BY-108 vapor mixture will be much more challenging than the proposed engineering-scale multi-gas test. The multi-gas test is a duplication and should be deleted.*

Given the results of the COPC-specific testing, the fact that many of the COPCs had been tested with other COPCs in the same injection, and the operational limits for the PTR-MS (needing to operate in either the NO+ or H_3O+ mode), the additional value of this test became very limited. On June 11, WRPS, ORP, and PNNL determined that the multi-component DRE test would not be conducted during this phase of tests. The impact of multiple gas interactions is to be observed during future testing in the tank farms on Hanford waste tank BY-108.

5.8 Total Volatile Organic Compounds

The VOCs were measured during testing using the AreaRAE PGM-5020 Photoionizer detector, with key results shown in Table 33 and resulting DREs shown in Table 34. The PID was added to the analytical instrumentation setup as a result of comments to the test plan. A special set of DREs for this test are calculated and reported using PID results, but are much less accurate and sensitive than results from the other analytical methods. The PID results are appropriately used to report total VOC concentrations in the exhaust.

Since the AreaRAE requires ≥15% O_2 to function properly and diesel engine exhaust is expected to contain 8–12% O_2, a 1:1 manufacturer dilution fitting was added to the sampling line. An evaluation of the average O_2 levels (18.05%) measured by the AreaRAE during the nitrogen sweep cycles indicates that the dilution was actually greater that this, and that the ratio of exhaust to ambient dilution air (20.95% O_2)

was 1:6.15. This difference was not pursued, but could have been caused by being used on the down-stream side of the FTIR pump which may have been slight pressureized versus ambient pressure that the dilution fitting is designed for.

Table 33. Maximum Exhaust VOC Measurements recorded by PID

Test	Sample Port	VOC as Measured (ppm)	VOC Adjusted for Dilution (1:6.15)
2.1 Benzene & Propanenitrile	D	4.3	26.4
5.1 Furan & NDMA	D	3.7	22.8
5.2 Furan & NDMA	D	4.9	30.13
5.2 Furan & NDMA	D	2.6	16.
5.3 Furan & NDMA	D	3.1	19.1
6.3 Ammonia & Nitrous Oxide	D	35.5	218.3
6.3 Duplicate Ammonia & Nitrous Oxide	D	34.8	214.

Additional AreaRAE readings are in Appendix D.

Table 34. DREs derived from AreaRAE VOC Measurements are Not Meaningful

		VOC in PPM (as recorded, i.e., not adjusted for dilution)			
Test #	Description	Port A Recorded Value	Port A Valued at the Resolution Limit (0.1 ppm)	Port D Recorded Value	VAU System DRE From AreaRAE VOC
2.2	Benzene & Propanenitrile	<DL	0.1	4.3	-4200% Not Meaningful
3.2b	Formaldehyde	4.8		2.7	44%
5.2	Furan & NDMA	<DL	0.1	2.6	-2500% Not Meaningful
5.2	Furan & NDMA	<DL	0.1	2.8	-2700% Not Meaningful
5.2	Furan & NDMA	<DL	0.1	2.7	-2600% Not Meaningful
5.2	Furan & NDMA	<DL	0.1	3.4	-3300% Not Meaningful
5.2	Furan & NDMA	<DL	0.1	2.6	-2500% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	2.3	-2200% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	1.9	-1899% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	3.1	-3000% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	2.2	-2100% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	2.3	-2200% Not Meaningful
5.3	Furan & NDMA	<DL	0.1	2.2	-2100% Not Meaningful

6.3	Ammonia & Nitrous Oxide	0.5		8.4	-1580%
	VOC = volatile organic compound				

The analysis of the DREs from the AeraRAE Model 200-GM-AE-502G data was conducted. The AreaRAE Wireless Multi-Gas Monitor (which includes AreaRAE Steel) Operational & Maintenance Manual[1] (Document 029-4034-000, Revision B, May 2008) provides the following from Tables 1.2 and 1.4 of the manual:

- The VOC range is from 0 to 200 ppm (in the mode it was operated for testing).
- The VOC resolution (and estimated detection limit) is 0.1 ppm (in the mode it was operated).
- Confirmed the oxygen sensor should read 0% with a sweep of nitrogen gas (pages 4-12).

The DRE results are shown in Table 34. The minimum resolution values (or nondetects) were assigned the minimum VOC resolution of 0.01 ppm for perposes of the DRE calculations.

The highest recorded VOC measurement from the AreaRAE at the NUCON VAU tailpipe (SP 516, port D) was 218.3 ppm.

In general, the hand-recorded measurements indicate that the NUCON VAU increases the VOCs. While the increases look large on a percentage basis, the maximum measured VOC during testing was 218.3 ppm. The high percentages of VOC increase are driven by the very low injection levels. (Note: The AreaRAE does not include ammonia in the VOC measurement.)

Prior to testing, it was expected that DRE calculation from VOC measurements made with PID would be problematic due to a number of reasons, including (1) the comparatively large background VOC concentration in the exhaust generated by the diesel engine as shown in Table 15, (2) the comparatively low COPC injection concentrations, (3) the relatively high detection limit (DL) of the PID used in this test, and (4) the fact that different compounds exhibit different responses in a PID. For the latter, this is significant, and response factors can vary up to 2.5 orders of magnitude (≤0.47 to ≥100 when normalized against isobutylene). This requires prior knowledge of hydrocarbon composition in the gas stream for accurate quantification, and thus is not suitable for accurate analysis of a gas stream of unknown composition. The results from this test demonstrated the problems in using a PID to measure DREs in the VAU. First, injection levels were nearly all below detection with the PID. Theoretical injection levels could not be determined because PID correction factors are not known for many of the test COPCs. Second, since the vast majority of VOCs in the exhaust are from the pre-existing background diesel emissions, the noise to signal ratio is very high. Third, as alluded to above, the PID does not speciate; thus, the generation of any byproducts of injection could skew the number significantly. Therefore, it is recommended that PIDs not be used for estimating DRE values in future testing of the VAU.

Total VOCs generated by the VAU with and without injection can be used to compare against generic criteria for diesel engine exhaust using a PID. PID should not be used to compare to VOCs calculated from a different analytical technique (e.g., FTIR), since the PID compares a composite response of all VOCs normalized to a single response factor (usually isobutylene). Since diesel exhaust is a complex mixture of VOCs, PID measurements should only be compared to PID criteria.

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[1] From RAE Systems by Honeywell

5.9 Vapor Abatement Unit Operations

Fuel employed in the VAU during testing was as follows:

- Tests 1.1 and 1.2 – 13% ultra-low sulfur on-road winter diesel fuel and 87% ultra-low sulfur off-road summer diesel fuel.
- Tests 2.1 and 2.2 – 50% ultra-low sulfur on-road winter diesel fuel and 50% ultra-low sulfur off-road summer diesel fuel.
- Tests 3.1 and 3.2 – 13% ultra-low sulfur on-road winter diesel and 87% ultra-low sulfur off-road summer diesel.
- Tests 5.1, 5.2, and 5.3 – 2.5% ultra-low sulfur on-road winter diesel and 97.5% ultra-low sulfur off-road summer diesel.
- Tests 6.1, 6.2, and 6.3 – 50% ultra-low sulfur on-road winter diesel and 50% ultra-low sulfur off-road summer diesel

During VAU break-in and testing operations, numerous items were documented, the most important being flow, temperatures, temperature stabilization, operating pressure, pressure change across the DPF, when power was engaged with the corresponding amount of power applied, operating hours on the unit, and oil level within the generator. All proceeding measurements are “For Information Only” (FIO) since the instrumentation on the VAU was not calibrated to the NQA-1 requirements.

Initial VAU operations began in March of 2018. These operations included the shakedown period and extended into the break-in period for the generator. Testing began after the shakedown period had been completed with ~32 hours of runtime on the engine. This time frame was determined by several factors, which included fixing leaks within the system and allowing the DPF to de-green (i.e., complete a break-in period). After 20 hours of operation, the break-in period for the generator had been completed. At the start of test 0.2, the engine was at 32.9 total operating hours. At 62.4 hours of total runtime on the engine, the oil and the oil filter in the diesel engine were changed. Testing then continued through June 13, 2018. During that time frame, 146.5 hours of runtime had been logged on the diesel engine and the generator.

The typical steady-state inlet air flow to the VAU engine ranged from 49 to 47 scfm. The normal flow to the VAU engine was nominally 52 scfm[1] when power was initially engaged, which then decreased to between 49 to 47.5 scfm after the VAU had warmed up (~1 hour). On one occasion, it was documented that the flow rate had reached a minimum of 42.5 scfm following a benzene injection during steady state operations. These inlet air flow rates were not substantially affected by the ambient weather, but were dependent on the power load applied.

Exhaust flows were measured by using a methane tracer (see Appendix E). Methane was used for its highly recalcitrant nature and resistance to thermal decomposition in the VAU exhaust system, and accurate quantification by the FTIR. A calibrated flow rate of methane of known concentration was injected into the VAU exhaust just after the DPF. The subsequent well-mixed concentration of methane was measured at the VAU tailpipe by the FTIR. The ratio of source methane concentration to measured

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[1] The Fox Thermal Instruments, Inc. Model FT1-06IDDP1 serial # F00780 Flow Meter was set to display standard cubic feet per minute (adjusted for pressure and temperature) over the range of 0 to 60 scfm.

methane concentration at the tailpipe multiplied by the methane tracer flow rate allows for the accurate calculation of total exhaust flow rate. The calculated exhaust flow rates ranged from 52.1 to 57.5 scfm.

Temperatures were monitored in various locations throughout the unit during all operations. These locations included the following: TT-102 was prior to the heat exchange on inlet side, TT-103 was after the heat exchanger on the inlet side, TT-109 was before entering the generator, TT-111 was after the generator and catalytic converter but prior to the DPF and heat exchanger, and last was TT-112, which monitored the exhaust stack temperature. Due to the VAU internal temperatures being very susceptible to changes in ambient weather, it was normal to see steady state temperatures declared at roughly 735°F (TT-111) on cooler days and 770°F (TT-111) on warmer days. All temperatures were closely monitored to ensure TT-109 did not exceed 125°F. Once steady state operation was declared, it was typical to see a jump of 15°F to 30°F from TT-102 to TT-103, while the TT-111 and TT-112 temperatures differed by ~180°F to 200°F. Minor fluctuations from these values were noted during testing, with maximum temperatures at TT-111 exceeding 800°F on select occasions.

As mentioned before, leaks had occurred in the VAU's exhaust systems that were present around the DPF, catalytic converter, and expansion joints. These leaks were mitigated with a high-temperature RTV sealant that was applied to the leaking joints while the unit was non-operational. After the leaks had been fixed, the pressure drop from the inlet side of the DPF to the exit side changed substantially from roughly 2 inches of water column (in. w.c.) during the shakedown period to roughly 4 in. w.c. during testing at normal steady state operations. It was typical for the operating pressure measured at PT-108 located after the blower to range from -2 in. w.c. at startup and level out at -1.5 to -0.1 in. w.c.

Additional notes include the following:

- Oil levels dropped from high to a medium-high level prior to the first oil change. Upon changing the oil, the level remained consistently around the high level mark on the generator oil dipstick.
- The load bank was always operated at full capacity (11.25 kVA) during testing, which resulted in the 15-kVA diesel/generator set having a 75% load with respect to the generator.
- Fuel usage is shown in Table 35.
- Maintenance and operations of the VAU were conducted by TerraGraphics.

Table 35. VAU Diesel Fuel Usage During Testing

Fill-Up Date	Gallons Added	Fuel Type	Notes
2/18/18			Unit was empty
2/19/18	73	Ultralow Sulfur #2 Winter On-Road Diesel	Gauge read slightly higher than full
5/2/18	24.6	Ultralow Sulfur #2 Summer Dyed Diesel	
5/16/18	43.6	Ultralow Sulfur #2 Summer Dyed Diesel	
6/5/18	50	Ultralow Sulfur #2 Summer Dyed Diesel	
6/13/18	~26 left in tank		35% on the fuel gauge at the end of testing
Fuel Used in Testing	165		Engine operating hours at the end of testing 146.5 hours
Fuel usage was ~ 1.13 gallons per hour with a 75% load on the generator			

6.0 Conclusions

PNNL evaluated the performance of the NUCON VAU prototype for the removal of 11 COPCs. The 11 COPCs tested were chosen out of the 61 COPCs[1] measured in Hanford HLW SST vapor emissions either (i) due to the importance of that COPC, (ii) as a surrogate to represent of a class of COPC compounds, or (iii) both. The tests were performed to compare the NUCON VAU performance to the COPC removal target of ≥95% DRE and the COPC purification target of ≤10% Hanford tank farm OEL.

The results from the tests can be summarized by the following three key objectives:

- Validation of detection of the COPCs in the VAU exhaust at or below the target performance criteria concentration, defined as ≤10% of the Hanford tank farm OELs, or higher concentration if necessary due to background interference.
- Determination of the DRE and exhaust purification achieved by the VAU for each COPC supplied at 200% the Hanford tank farm OEL.
- Determination of the DRE and exhaust purification achieved by the VAU for a selection of the COPCs supplied at the maximum concentration observed in Hanford single-shell tanks (including the entire class of compounds that the COPC represents for the types of tanks on which the system will be used). For additional detail see Section 2.2.

PNNL demonstrated the ability to detect 10 of the 11 test COPCs at ≤10% OEL concentration in the NUCON VAU exhaust at tailpipe, with the results summarized in Table 36. The ability to detect 2,4-dimethylpyridine at <2% OEL in the exhaust was demonstrated in test 3.2 with modified analytical methods and extended testing dwell times. The ability to detect NDMA in the NUCON VAU exhaust in PNNL testing was limited to ~50% OEL concentration due to the prohibitively high background interference associated with NDMA detection on the PNNL PTR-MS in the NUCON VAU diesel engine exhaust. For additional detail see Section 5.5.

As summarized in Table 37, the NUCON VAU successfully met target performance criteria for 8 of the 11 COPCs, including acetaldehyde, acetonitrile, benzene, proprionitrile, 1,3-butadiene, 2,4-dimethylpyridine, furan, and ammonia. This included both COPC removal of ≥95% of the COPC amount at the engine inlet, and exhaust purification to ≤10% the OEL.VAU performance criteria were not met for nitrous oxide in either test. This is not surprising since nitrous oxide is well-known as a problematic and persistent greenhouse effluent in the exhaust of combustion systems. The VAU achieved >99.9% removal efficiency for NDMA in the high concentration test. However, VAU target performance metrics failed in the NDMA 200% OEL test, reaching only 50% OEL in the VAU exhaust. The estimated error associated with NDMA concentration measurement at 10-50% OEL is of similar order of magnitude as the calibrated concentration. And thus, NDMA results considering this ultra-trace level are less certain. Formaldehyde removal and purification results were affected by a pre-existing exhaust background concentration that was not impacted by formaldehyde injection. The VAU successfully reduced injected formaldehyde back down to this pre-exising exhaust level.

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[1] Rappe KG. 2018. *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs).* Test Plan TP-71248-01, Rev. 0, April 2018, Pacific Northwest National Laboratory, Richland, Washington.

Table 36. Summary of COPC Detection at 10% OEL in the NUCON VAU Exhaust

COPC	Test	all in [ppm]				Exhaust Baseline
		10% OEL Target	Calculated Exhaust Spike	Measured at Port D		
				PTR-MS	FTIR	
Acetaldehyde[a]	1.1	2.5	2.44	4.0	3.07	0.26
Acetonitrile	1.1	2	2.08	3.2	-	0.01
Benzene	2.1	0.05	0.014	0.014	-	0.002
Propanenitrile	2.1	0.6	0.077	0.205	-	0.0009
1,3-Butadiene	3.1	0.1	0.093	0.174	-	0.0008
Formaldehyde[a]	3.1	0.03	0.030	0.558	0.0189	0.516
2,4-Dimethylpyridine[b]	3.1	0.05	0.047	*n.d.*	-	*n.d.*
NDMA[c]	4.1	0.000030	0.000149	0.000781	-	0.000686
Furan[c]	5.1	0.000100	0.000049	0.000148	-	0.000104
Ammonia	6.1	2.5	1.97	-	1.36	0.07
Nitrous Oxide	6.1	5	2.92	-	3.57	0.80

[a] FTIR results are "For Information Only".

[b] The test identified that modified analytical methods would be required for accurate measurement.

[c] PTR-MS results only for detection; VOCUS PTR-TOF results only used for accurate COPC

n.d. - not detected, i.e., no elevation of the PTR-MS signal observed above background/baseline levels

Table 37. Summary of DRE Values Determined from PNNL Testing of the NUCON VAU

COPC	Test	VAU DRE	95% DRE Target met?	Measured at Outlet (port D)		10% OEL Target met?
				PTR-MS [ppm]	FTIR [ppm]	
Acetaldehyde[a]	1.2	99.6%	Yes	0.28	0.7	Yes
Acetonitrile	1.2	>99.9%	Yes	0.014	-	Yes
Benzene	2.2	97.3%	Yes	0.023	-	Yes
Propanenitrile	2.2	>99.9%	Yes	0.010	-	Yes
1,3-Butadiene	3.2	99.7%	Yes	0.026	-	Yes
Formaldehyde[a]	3.2	45.7%	No	0.73	0.03	No
2,4-Dimethylpyridine	3.2	99.3%	Yes	0.0071	-	Yes
NDMA[b]	4.2	55.6%	No	0.00015	-	No
	4.3	>99.9%	Yes	0.000042	-	No
Furan[b]	5.2	99.3%	Yes	0.000017	-	Yes
	5.3	99.8%	Yes	0.000035	-	Yes
Ammonia	6.2	98.7%	Yes	-	0.7	Yes
	6.3	>99.9%	Yes	-	0.3	Yes
Nitrous Oxide	6.2	72.7%	No	-	29	No
	6.3	69.5%	No	-	261	No

[a] FTIR results are For Information Only.

[b] Reflects combined results from the PTR-MS and the TOFWERK VOCUS-PTR

The component information was measured at the following ports:

- Port A – The inlet port before the diesel engine, a.k.a. SP521.
- Port B – After the engine and before the DOC, a.k.a. SP525; combined with port A, allowed for measuring the contribution of the diesel engine to overall VAU performance.
- Port C – After the DOC and before the DPF, a.k.a. SP514; combined with port B, allowed for measuring the contribution of the oxidation catalyst (DOC) to overall VAU performance.
- Port D – Tailpipe location after the muffler and DPF and before release of exhaust to the environment, a.k.a. SP516; combined with port A, allowed for measuring overall VAU performance, and combined with port C, allowed for measuring the contribution of the diesel particulate filter (DPF) to overall VAU performance (assuming no impact of the muffler or heat exchanger).

Table 38 shows the contribution of the individual VAU components to the overall VAU removal performance.

Table 38. VAU Component Contribution to the Overall VAU Removal Efficiency

COPC	Test	DRE Contribution by Component			Overall VAU DRE
		Engine	Oxidation Catalyst	Diesel Particulate Filter	
Acetaldehyde	1.2	90.0%	9.1%	0.4%	99.6%
Acetonitrile	1.2	82.6%	16.9%	0.5%	>99.9%
Benzene	2.2	60.5%	35.6%	1.2%	97.3%
Propanenitrile	2.2	87.6%	12.0%	0.3%	>99.9%
1,3-Butadiene	3.2	87.8%	11.8%		99.7%
Formaldehyde	3.2	-105%	143%	7.8%	45.7%
2,4-Dimethylpyridine	3.2	97.8%	1.4%		99.3%
NDMA	4.2	25.7%	29.9%		55.6%
	4.3	96.6%	3.3%		>99.9%
Furan	5.2	-2367%	2466%		99.3%
	5.3	-311%	411%		99.8%
Ammonia	6.2	94.2%	5.6%	-1%	98.7%
	6.3	88.5%	11.3%	0.1%	>99.9%
Nitrous Oxide	6.2	73.7%	-1%	0.4%	72.7%
	6.3	72.3%	-3%	-0.2%	69.5%

Both the NUCON VAU diesel engine and catalytic converter contributed significantly to performance for COPC removal and exhaust purification. Nine of the eleven COPCs were reduced significantly by the diesel engine, excluding only formaldehyde and furan. The diesel engine alone provided >95% removal efficiency for 2,4-dimethylpyridine and NDMA (at high concentration), and was the only VAU treatment step to significantly reduce nitrous oxide (>72%).

The oxidation catalyst was extremely important to overall VAU performance, and was critical at enabling the VAU to reach removal and purification criteria for 7 of the 11 COPCs, including acetaldehyde, acetonitrile, benzene, propanenitrile, 1,3-butadiene, furan, and ammonia. Both formaldehyde and furan were produced in comparatively large amounts in the diesel engine but removed with high efficiency by the oxidation catalyst. NDMA was also removed efficiently by the oxidation catalyst in the high-concentration test, but that was not required to reach the VAU removal performance metric. Nitrous oxide was minimally impacted by the oxidation catalyst or the diesel particulate filter.

The highest recorded VOC measured by the AreaRAE at the NUCON VAU tailpipe was 218.3 ppm.

Testing and working with the NUCON VAU has highlighted the following considerations related to the future design of a VAU to be used in the Hanford SST farms:

1. Consider redesigning the MERSORB® media containment to allow for easier media removal when operating in a radioactive environment.
2. Enhancing the load cell for higher resistance levels (over 11.25 kVA) and ensuring that the wiring meets code requirements for the final application in the tank farm.
3. Heating all sampling lines > 150°C.

6.1 Recommendations for Additional Testing

Although the VAU failed to meet all removal and purification criteria for formaldehyde, NDMA and nitrous oxide, it was shown to significantly reduce concentrations of all of the test compounds. Further, 8 of the 11 test compounds met all test acceptance criteria. Of the three COPCs that failed:

- Nitrous oxide is known to persist through engine exhaust aftertreatment (including oxidation catalysts) but nonetheless was shown to be reduced by >72% in the engine. If further reduction of nitrous oxide is required, there are additional methods that could be incorporated in the VAU for treatment; this may include selective catalytic reduction, target-specific activated carbon filtering (i.e., a MERSORB® additive), or other methods.
- Formaldehyde is known as a by-product of diesel combustion and a persistent emission species. Thus, the fact that the VAU demonstrated a consistent low level of formaldehyde in the exhaust is not surprising. However, the test demonstrated that test injections in the VAU inlet did not add to normal emission levels.
- Regarding NDMA, removal criteria were met at high concentration of NDMA. At ultra-trace concentration levels, the variability of the data makes if difficult to determine whether either of the NDMA tests met the purification critera. In any case, further testing is warranted.

This test program was predicated on continuing test efforts on a Hanford SST. WRPS has selected tank BY-108 to be the site for such a demonstration based on its worst case concentration of COPCs, specifically being in cascade with BY-107, which is the highest in furan, among SSTs and its availability of utilities and real estate. Initiation of detailed design and permitting is planned for FY 2019.

When doing the pilot-scale tests, it is advised to consider reactions on the MERSORB® bed that will improve removal efficiency for several compounds. The expected reductions of nitrous oxide, ammonia, and formaldehyde on the carbon (due to cross-reactions) can be further investigated during this phase of system demonstration and operation.

6.2 Impact of Off-Line Media Sampling for Future Testing

Currently, the off-line sampling media (SUMMA® canisters and sorbent tubes) are still at the laboratories for chemical analysis. The 222-S laboratory has notified PNNL of analytical challenges related to the analysis of ammonia tubes and on the NDMA ThermoSorb N tubes for nitrosamines. Additionally, the formaldehyde port A inlet results are significantly different than the levels of gas injected during the time of testing. Repeating the ammonia testing, NDMA testing, or the formaldehyde testing using the current tubes and collection process is not expected to provide information that would change the results or findings of this report. This is because the combination of (i) rigorous COPC calibration procedures of the on-line analytical instrumentation with (ii) the 10% OEL analytical validation efforts were successful at providing confidence in the on-line COPC concentration measurements made during testing.

7.0 References

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Appendix A

NUCON Vapor Abatement Unit Components

Appendix A

NUCON Vapor Abatement Unit Components

Figure A.1. The NUCON Vapor Abatement Unit (looking north) next to the Test Instrumentation Trailer. Includes the southern placed diesel skid assembly and the original northern placed propane skid.

Figure A.2. (Looking south) The metal particulate screen (60 mm x 150 mm) connected to the three-way valve. This was the sole path through which ambient air was introduced to the system during steady state testing. The piping on the skid was 316/316L Stainless Steel WLD 2–in. schedule 10S. Also visible is the first particulate HEPA which is also called the demister (14-in.-diameter x 14-in.-tall outside housing dimensions) filter housing. Both HEPA filter housings have an installed Astrocel® I High Efficiency Particulate Air (HEPA) Filter flow tested for 50 cfm (size 8” x 8” x 5 7/8” part number 12A26J6P0A1, 900-895-503) with nominally 0.8 inches of water resistance. The filters are made by American Air Filter (see image of the west HEPA filter below). Note that one filter is in the HEPA filter housing on the east side of the skid and the second filter in inside the HEPA housing on the west side of the skid.

Figure A.3. (Looking west) Inlet air pipe wrap around the skid. A Fox Thermal Instruments, Inc. Model FT1-06IDDP1 serial # F00780 Flow Meter set to 0 to 60 scfm per vendor-approved change. (FT-101). Then the Yellow K type Thermocouple TT-102 before the flow is warmed in the heat exchanger. The tan box houses the propane engine and generator that were disconnected for the testing.

Figure A.4. (Looking northeast) Under the white and tan insulation fiberglass wrap is the ambient air inlet to the heat exchanger that used exhaust air to heat the ambient air before going into the MERSOB® filter. This is followed by the Yellow K type Thermocouple TT-103 outlet air temperature after the heat exchanger and the second particulate HEPA filter housing.

Figure A.5. (Looking southwest) MERSOB® Absorbant container made of 24-in.-diameter schedule 10S A-312/SA-312 stainless steel with a length of 64 in. NUCON had not removed the 73 kg of Mersorb® Absorbent that had been tested in Ohio for a ~45 minute test with mercury. (Inlet air was near the bottom and release air from the column came out near the top.

Figure A.6. The Kohler KDI1903ESM Diesel Engine Spec 6D08E1-1 (S/N 4728402750) rated at 28 BHP at 1800 rpm with Decision-Maker 3000 controls. Engine power 19-37KW with 1.861 liters displacement. (Engine family HKHXL2.49ESM.) On the lower right image is the connected Kohler 15REOZK 15 kVA Generator (S/N SGM32LMWJ).

Figure A.7. Directly behind the label is the 4SX-15REOZK Catalytic Purifier muffler emissions control device (i.e., diesel oxidation catalyst) manufactured by Catalytic Exhaust Products with the second photo being the diesel particulate filter 758SXS-SC by Catalytic Exhaust Products.

Figure A.8. Exhaust gases then exit the 2-in. exhaust muffler and then out the extended a 10-ft-long 2-in. exhaust pipe that was added to the muffler

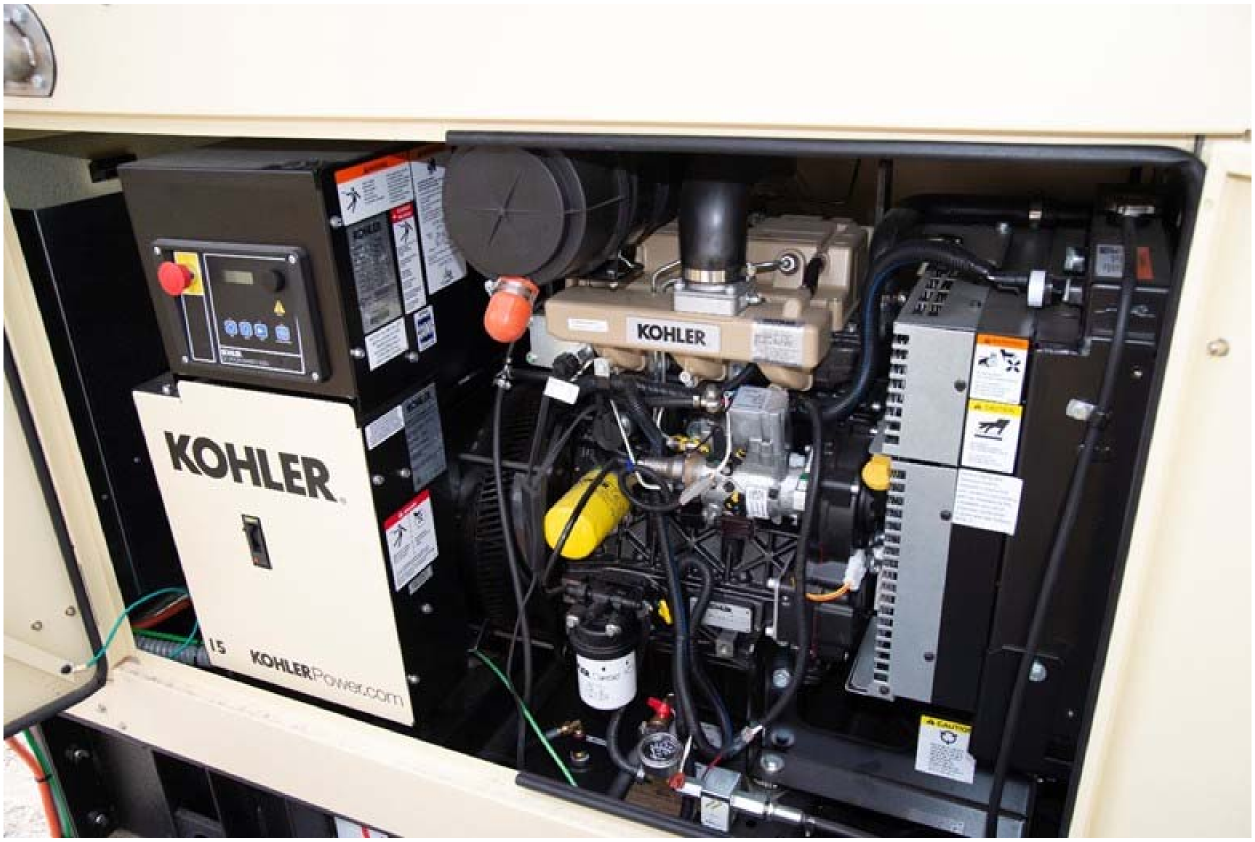

Figure A.9. The engine and generator controls.

Figure A.10. Connected to the electrical output from the generator are the circuit breaker box that powers the PLC controller and the Human Machine Interface (HMI) controller and data collection.

Figure A.11. The Powerhouse Manufacturing (model 11.3-.25-240-1) switch box and 11.25 kVA load bank. This is switched to the full 11.25 kVA load during steady state testing on the diesel engine.

Figure A.12. The repair of the diesel particulate filter soot leak with the high-temperature seal. The insulation was removed during this pretesting repair.

Figure A.13. The top connection to the 4SX-15REOZK Catalytic Purifier muffler emissions control device (i.e., diesel oxidation catalyst) with the insulation pulled back.

Figure A.14. The instrument trailer and the support electrical rack on the Q Avenue Pad.

Figure A.15. Electrical supply rack used for the testing

Appendix B

Instrumentation Trailer

Appendix B

Instrumentation Trailer

Figure B.1. Most of the instrumentation was along the east wall of the trailer. (Left to right) MKS FTIR, PTR-MS, the GC for pre-concentration (not used), the GC-MS (not used), the spare pumps and Mass Spectrometer (under the table and not used), heat tape controllers for the primary analytical sample loop lines (top of the cart), the chiller for sample temperature control (used only in the early testing), the injection system (top of the rack), and the sample collection controls (bottom of the rack).

Figure B.2. The MKS-2030 Multi-Gas Fourier-transform Infrared Analyzer

Figure B.3. The Ionicon Analytik Proton Transfer Reaction Mass Spectrometer (PTR-MS)

Figure B.4. The Agilent 6890N Gas Chromatograph set up as a pre-concentrator (left) for the PTR-MS. The second unit is the Agilent 6890N Gas Chromatograph with an Agilent 5973 Mass Selective Detector (right). Neither device was needed to support final testing.

Figure B.5. The NESLAB RTE-211 was used to cool key sample lines as part of potential temperature controls along the exhaust sampling lines. It was used during shakedown and it was determined not to be necessary in later testing. The heat tape controllers on the top of the cart are part of the seven to ten tapes (depending on the test) that were operated at 120^{o}C to 200^{o}C during testing. They were on the primary analytical sample loop tubes and lines (as well as the intake sample lines) to limit moisture condensation as the exhaust cooled coming from the NUCON VAU. The orange insulation over the heat tape on the sampling header can be seen on the back wall.

Note: The controllers for the exhaust sample lines were in the box under the table along the south wall of the trailer.

Figure B.6. Orange insulation over the heat tape on sample lines B and C can be seen going past the Magnehelic® delta pressure gauge that was added to the Diesel Particulate filter. Exhaust sample line D was also heat taped (shown below).

Figure B.7. The AreaRAE steel PGM-5020 Photoionizer detector (part PGM 5520 s/n 295-003913 WTP# 200-6M-AE-502G) was initially connected to the sample header during the ammonia testing. A post-test review identified that that the vacuum in the VAU in-let caused ambient air to be sucked into the AreaRAE. In later testing, the AreaRAE was connected to the pressurized outlet of the MKS FTIR and readings were manually collected.

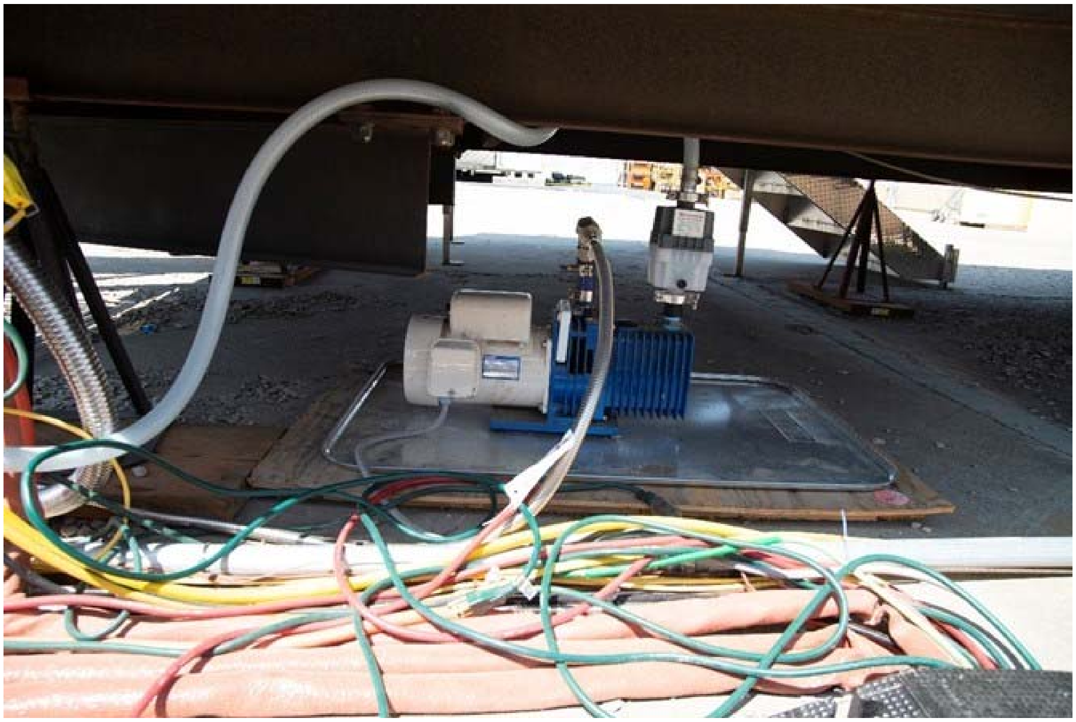

Figure B.8. In addition to the FTIR vacuum pump, a second vacuum pump was located under the trailer to supply mass flow controlled suction to the header, the media tubes, and for general cleaning gas sweeps.

The injection system process flow diagram is in Section 3.1.3. Some of the components of the injection system are shown here.

Figure B.9. Left Image - Outside bottle rack and controls (COPC # 3 & COPC #4, Ultra-Pure Nitrogen, Zero Air, Helium and other support gases). Right Image – Inside Northeast bottle rack and manifold for (COPC #1 through 4, calibration gases A and B). Below is the manifold detail.

Figure B.10. Inside the trailer north end East end valve manifold (COPC#1, 3 &4).

Figure B.11. Inside the trailer north end bottle rack and valves (COPC#1, 3 &4).

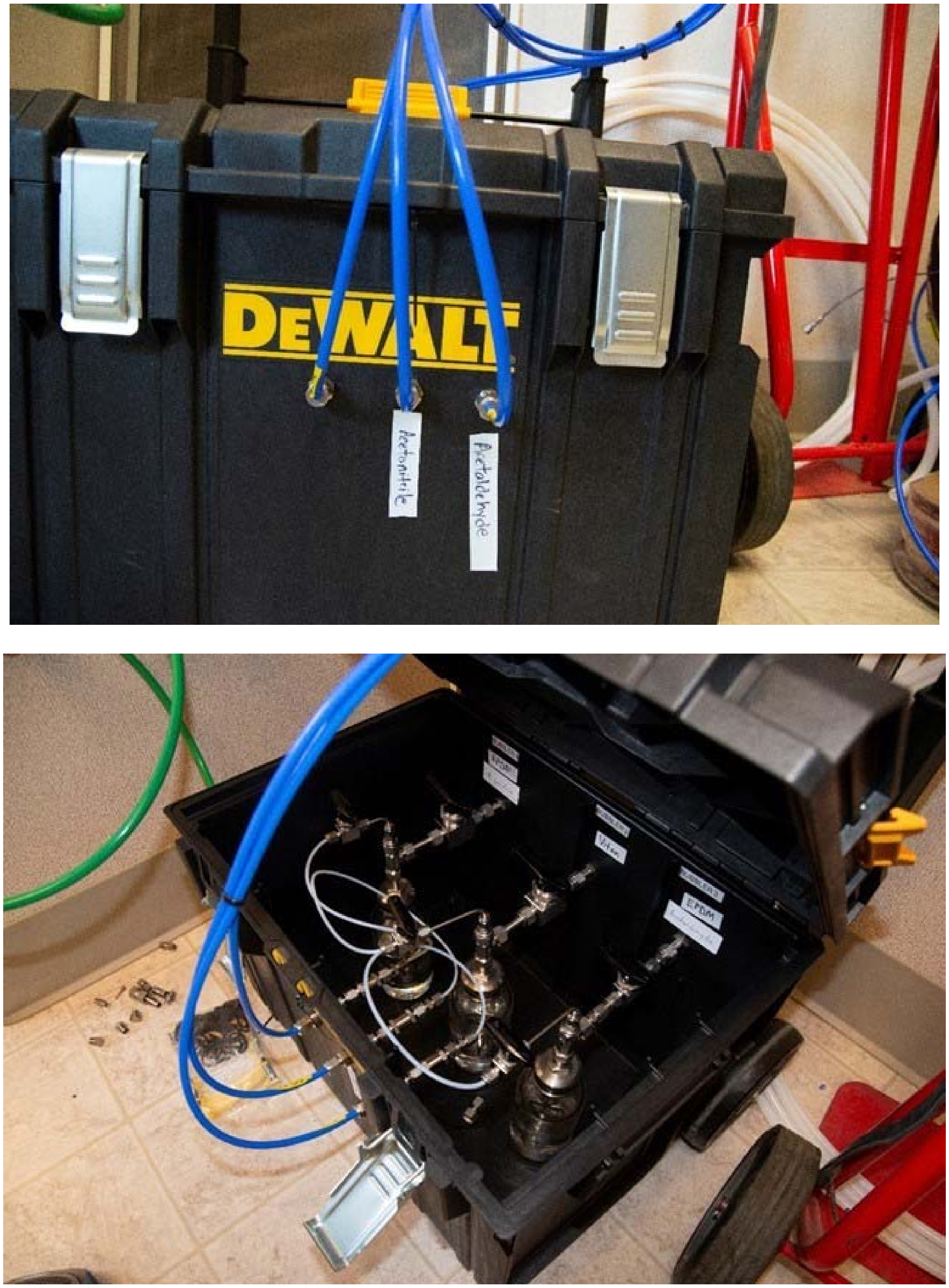

Figure B.12. The liquid bubbler system (on the Northwest wall inside the trailer).

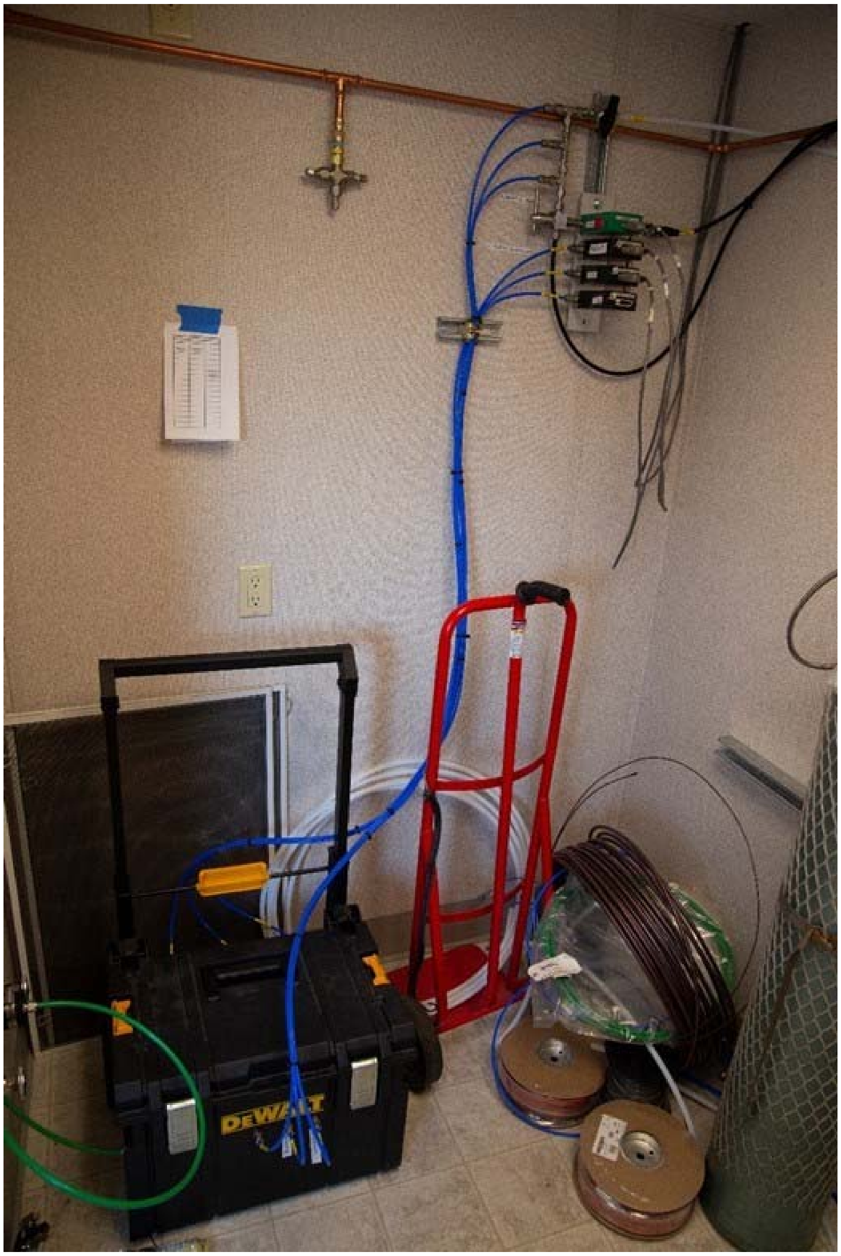

Figure B.13. The mass flow controllers for the bubblers are mounted in the upper right corner.

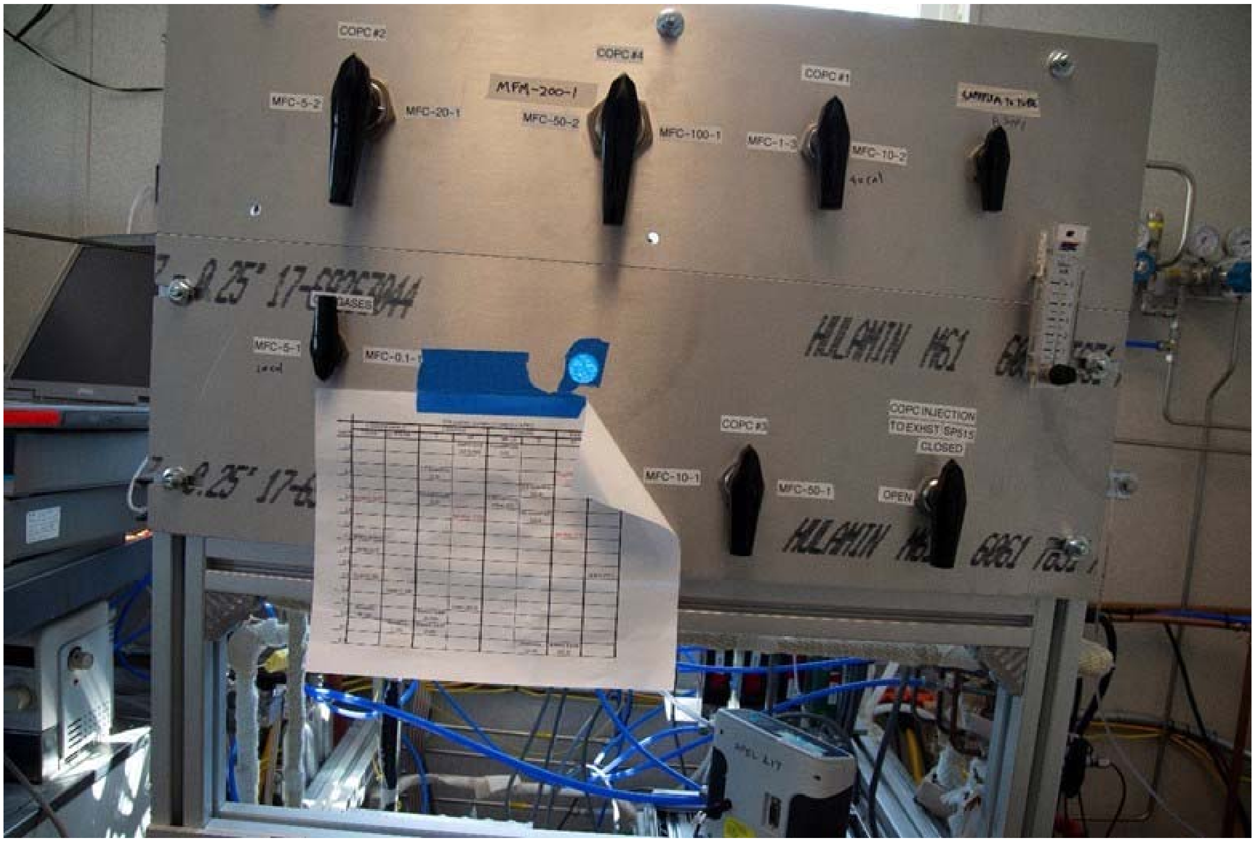

Figure B.14. The upper portion of the gas control rack. The combined top and bottom portions of the rack provide the valving for calibration gases, injection gases, and sampling gas pathways.

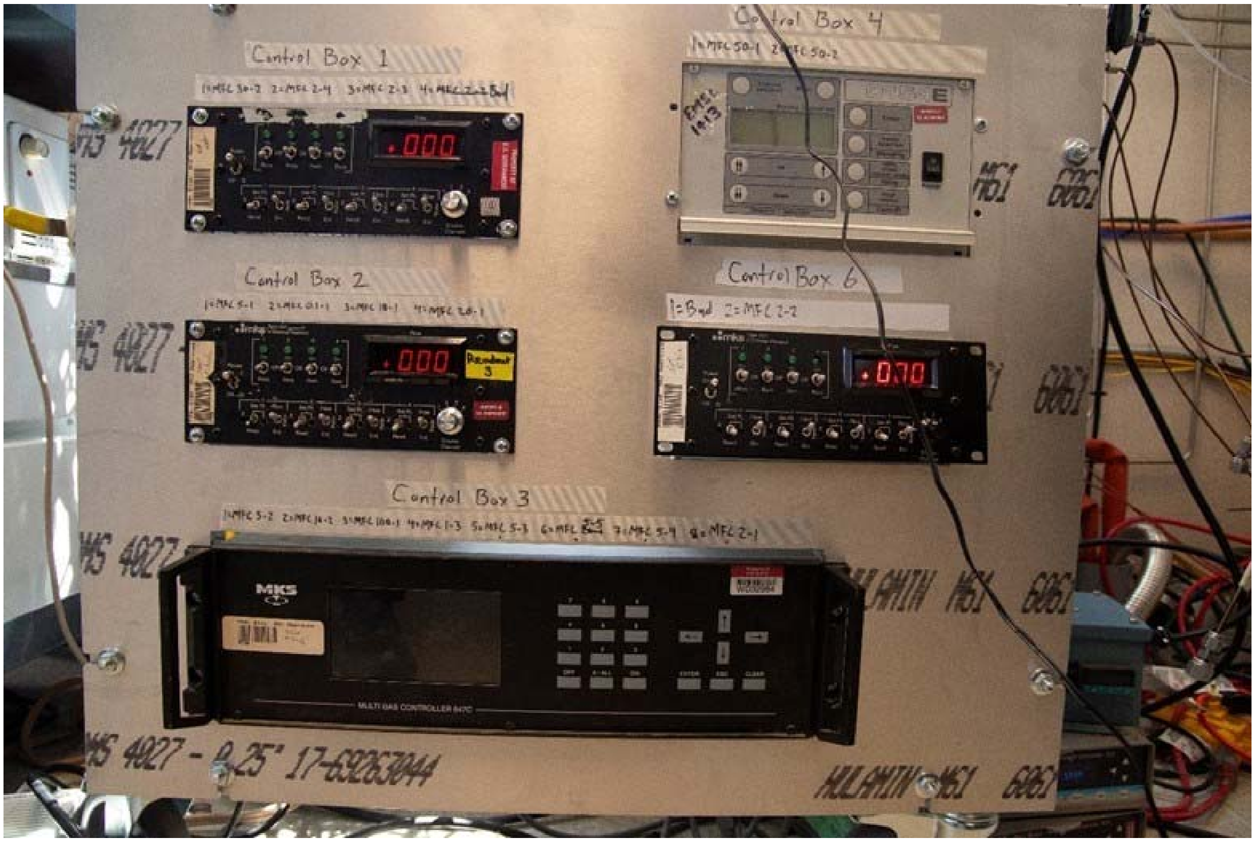

Figure B.15. The lower portion of the gas control rack. The combined top and bottom portions of the rack provide the control (via control boxes) of the many mass flow controls (detailed in Sections 3.1.3 and 3.1.4) for the injection gases, calibration gases, support gases, dilution gases, and for vent/sweep functions. Additional control boxes for the bubblers and the nitrogen are below.

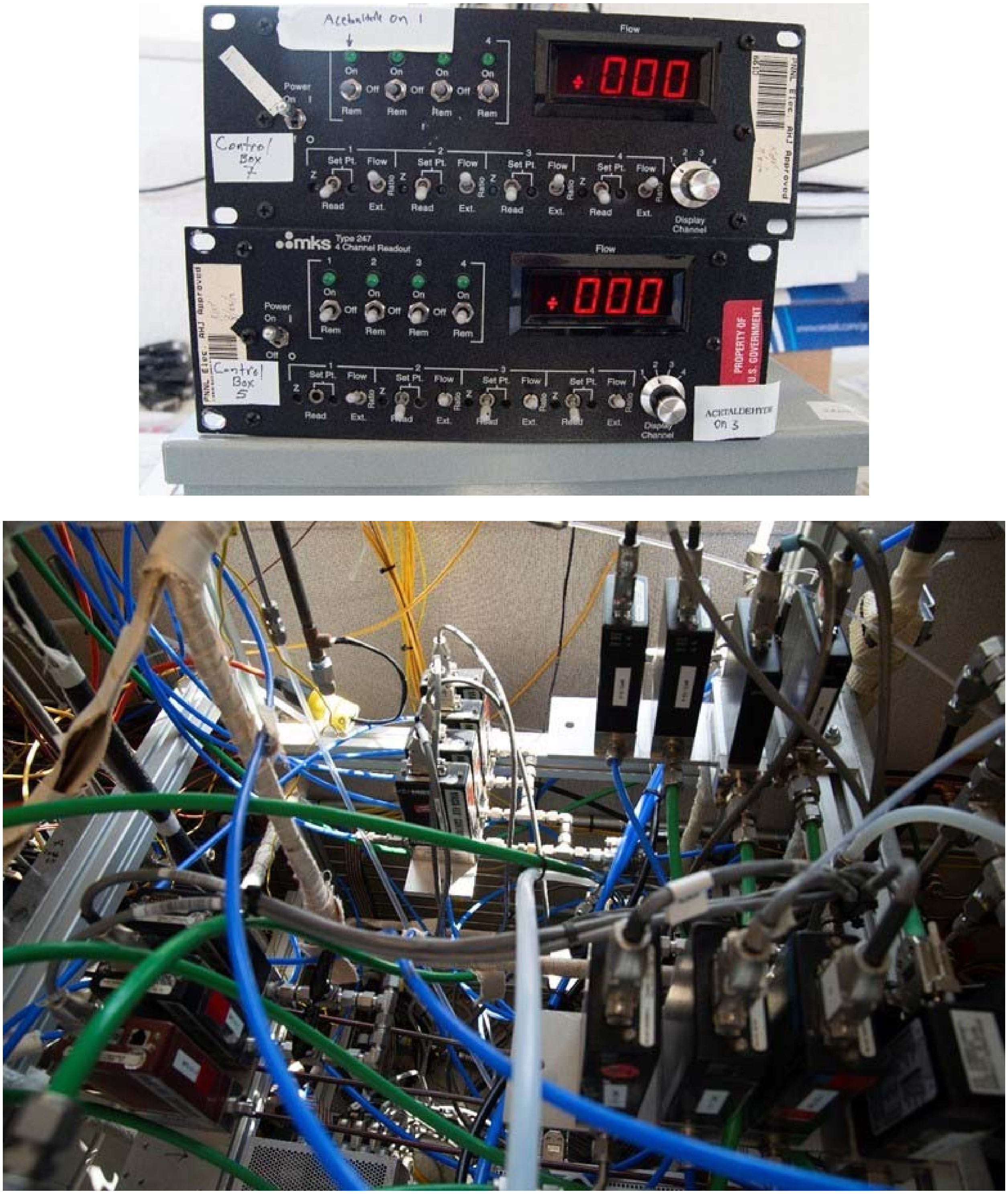

Figure B.16. Inside the gas control rack are mounted the mass flow controllers and many tube pathways to meter/direct the injection and sampling flows.

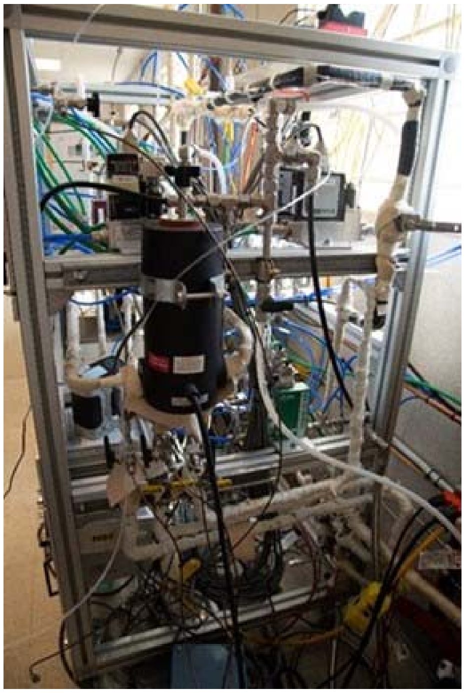

Figure B.17. Valves for the SUMMA® Canister sample collections are on the south side of the rack. Below the Standard 6 liter SUMMA® Canister sent to 222-S with the particulate filter and the 1 hour flow restrictor attached. On the right is the special condition 6 liter SUMMA® Canister that does not have a particulate filter or a flow restrictor. The special canisters were analyzed at either RJLee (with an Ionicon TOF[1]-4000), 222-S, AeroDyne Research Inc. (with a TOFWERK Vocus™ PTR-TOF[1]-12000), or at PNNL.

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[1] The TOF units are time-of-flight Proton transfer reaction mass spectrometer devices. VOCUS is a trademark of TOFWERK AG (Thun, Germany)

Figure B.18. A Kent Scientific "Gene" syringe pump (s/n 207032) was mounted to the top of the rack to supply moisture as needed to the PTR-MS calibration gas runs. The syringe pump was only used initially and was replaced with the HPTLC pump (bottom) when the syringe pump was found to be unreliable (kept stalling under large backpressure). The HPTLC moisture pump (see below) that was used later in testing was the RoHS (part number 310SFT01 s/n 20046277).

Figure B.19. The north side of the gas control rack included the sorption tube sample collection system.

Some of the things not shown were the heat tape controllers for the FTIR, PTRMS, heated soot filter, nitrogen preheater, water vaporizer, and exhaust lines from the VAU.

Appendix C

Mass Flow Controller Calibrations

Appendix C

Mass Flow Controller Calibrations

MFC Label	MFC-0.1-2	Control box	2
Function	COPC calibration	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	0.1080
LRB ref	BNW-62516-72,-73	Intercept	-0.00202
Dry Cal	Low range	RSQ	1.0000
Date	6/6/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SCCM]**	**Flow #2 [SCCM]**	**Flow #3 [SCCM]**	**AVG Flow [SLPM]**
850	85.0%	85.0%	89.92	89.64		0.090
180	18.0%	18.0%	17.42			0.017
66	6.6%	6.6%	4.913	5.050		0.005
300	30.0%	30.0%	30.64			0.031
500	50.0%	50.0%	51.93			0.052

MFC Label	MFC-1-1	Control box	7
Function	Bubbler carrier	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	0.9566
LRB ref	BNW-62516-46, -47, -48	Intercept	0.01782
Dry Cal	L (M for 600, 950)	RSQ	0.9976
Date	5/16/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
20	2.0%	1.9%	0.020137			0.020
200	20.0%	19.8%	0.21521			0.215
400	40.0%	39.9%	0.427			0.427
600	60.0%	59.8%	0.582			0.582
950	95.0%	94.8%	0.921			0.921

MFC Label	MFC-1-2	Control box	7
Function	Bubbler carrier	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	0.9615
LRB ref	BNW-62516-46, -47, -48	Intercept	0.01400
Dry Cal	L (M for 600, 950)	RSQ	0.9985
Date	5/16/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
20	2%	1.7%	0.017101			0.017
200	20%	19.7%	0.2135			0.214
400	40%	39.3%	0.422			0.422
600	60%	58.8%	0.582			0.582
950	95%	93.4%	0.927			0.927
900	90%	88.4%	0.874			0.874

MFC Label	MFC-1-3	Control box	3
Function	COPC injection	Channel	4
MFC Mfg	MKS Instruments, Inc.	Slope	0.9645
LRB ref	BNW-62516-46, -47, -48	Intercept	0.01450
Dry Cal	L (M for 60, 95)	RSQ	0.9983
Date	5/16/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2%	2.0%	0.019436			0.019
20	20%	20.0%	0.2123			0.212
40	40%	40.0%	0.42267			0.423
60	60%	60.0%	0.58563			0.586
95	95%	94.9%	0.92537			0.925

MFC Label	MFC-1-4	Control box	5
Function	Bubbler carrier	Channel	3
MFC Mfg	MKS Instruments, Inc.	Slope	0.9655
LRB ref	BNW-62516-46, -47, -48	Intercept	0.01979
Dry Cal	L (M for 600, 950)	RSQ	0.9977
Date	5/16/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
20	2%	1.9%	0.022532			0.023
200	20%	19.9%	0.21893			0.219
400	40%	39.9%	0.43208			0.432
600	60%	59.8%	0.58912			0.589
950	95%	94.8%	0.93135			0.931

MFC Label	MFC-2-1	Control box	3
Function	Port A tube sample	Channel	8
MFC Mfg	MKS Instruments, Inc.	Slope	2.001
LRB ref	BNW-62516-46, -47, -48	Intercept	0.00475
Dry Cal	L (M for 60, 90)	RSQ	0.9999
Date	5/8/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2.0%	2.0%	0.040			0.040
10	10.0%	10.0%	0.215			0.215
40	40.0%	40.0%	0.803			0.803
60	60.0%	60.0%	1.196			1.196
90	90.0%	90.0%	1.812			1.812

MFC Label	MFC-2-2	Control box	6
Function	Port B tube dilution	Channel	2
MFC Mfg	MKS Instruments, Inc.	Slope	1.958
LRB ref	BNW-62516-46, -47, -48	Intercept	0.000221
Dry Cal	M	RSQ	1.0000
Date	5/11/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
20	2%	1.8%	0.035153			0.035
100	10%	9.9%	0.19855			0.199
400	40%	39.7%	0.78597			0.786
600	60%	59.8%	1.1762			1.176
900	90%	89.7%	1.7601			1.760

MFC Label	MFC-2-3	Control box	1
Function	Port C tube dilution	Channel	3
MFC Mfg	MKS Instruments, Inc.	Slope	2.029
LRB ref	BNW-62516-46, -47, -48	Intercept	0.00553
Dry Cal	M	RSQ	0.9999
Date	5/8/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
20	2%	1.7%	0.037403			0.037
100	10%	9.6%	0.21588			0.216
400	40%	39.7%	0.81953			0.820
600	60%	59.7%	1.2254			1.225
900	90%	89.6%	1.829			1.829

MFC Label	MFC-2-4	Control box	1
Function	Port D tube dilution	Channel	2
MFC Mfg	MKS Instruments, Inc.	Slope	2.110
LRB ref	BNW-62516-46, -47, -48	Intercept	0.01692
Dry Cal	M	RSQ	0.9999
Date	5/8/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
20	2%	1.9%	0.048149			0.048
100	10%	10.0%	0.23825			0.238
400	40%	40.2%	0.86449			0.864
600	60%	60.2%	1.2812			1.281
900	90%	90.6%	1.9142			1.914

MFC Label	MFC-5-1	Control box	2
Function	COPC calibration	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	5.546
LRD ref	BNW-62516-7	Intercept	-0.00531
Dry Cal	L	RSQ	0.9997
Date	4/24/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SCCM]**	**Flow #2 [SCCM]**	**Flow #3 [SCCM]**	**AVG Flow [SLPM]**
20	2.0%		106.220	106.420	106.810	0.106
10	1.0%		49.312	50.009	49.052	0.049
30	3.0%		160.870	159.720	160.710	0.160
19	1.9%		100.440	100.470	100.750	0.101

MFC Label	MFC-5-1	Control box	2
Function	COPC calibration	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	4.964
LRB ref	BNW-62516-46, -47, -48	Intercept	0.00686
Dry Cal	M	RSQ	0.9999
Date	5/2/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
10	1.0%	0.9%	0.040			0.040
100	10.0%	9.9%	0.511			0.511
400	40.0%	39.8%	2.010			2.010
600	60.0%	59.9%	2.988			2.988
800	80.0%	79.8%	3.967			3.967

MFC Label	MFC-5-2	Control box	3
Function	COPC injection	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	4.940
LRB ref	BNW-62516-46, -47, -48	Intercept	-0.00191
Dry Cal	M	RSQ	0.9999
Date	5/8/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2.0%	2.0%	0.074			0.074
20	20.0%	20.0%	0.998			0.998
40	40.0%	40.0%	1.993			1.993
60	60.0%	60.0%	2.968			2.968
90	90.0%	90.0%	4.429			4.429

MFC Label	MFC-5-3	Control box	3
Function	Port B tube sample	Channel	5
MFC Mfg	MKS Instruments, Inc.	Slope	4.935
LRB ref	BNW-62516-33, -46, -47, -48	Intercept	0.08028
Dry Cal	M	RSQ	0.9999
Date	5/9/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2.0%	2.0%	0.162			0.162
20	20.0%	20	1.079			1.079
40	40.0%	40	2.0711			2.071
60	60.0%	60	3.037			3.037
90	90.0%	90	4.5155			4.516

MFC Label	MFC-5-4	Control box	3
Function	Port C tube sample	Channel	7
MFC Mfg	MKS Instruments, Inc.	Slope	4.949
LRB ref	BNW-62516-46, -47, -48	Intercept	0.02204
Dry Cal	M	RSQ	1.0000
Date	5/8/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2.0%	2.0%	0.117			0.117
10	10.0%	10.0%	0.521			0.521
40	40.0%	40.0%	2.006			2.006
60	60.0%	60.0%	2.986			2.986
90	90.0%	90.0%	4.478			4.478

MFC Label	MFC-5-5	Control box	3
Function	Port D tube sample	Channel	6
MFC Mfg	MKS Instruments, Inc.	Slope	5.035
LRB ref	BNW-62516-33, -46, -47, -48	Intercept	0.06687
Dry Cal	M	RSQ	1.0000
Date	5/9/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
2	2.0%	2.0%	0.154			0.154
20	20.0%	20.0%	1.0879			1.088
40	40.0%	40.0%	2.0864			2.086
60	60.0%	60.0%	3.086			3.086
90	90.0%	90.0%	4.5938			4.594

MFC Label	MFC-10-1	Control box	2
Function	COPC injection	Channel	3
MFC Mfg	MKS Instruments, Inc.	Slope	10.69
LRB ref	BNW-62516-46, -47, -48	Intercept	-0.0747
Dry Cal	M (H for 600, 900)	RSQ	0.9989
Date	5/14/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
20	2%	1.9%	0.20			0.2047
100	10%	9.9%	1.0			1.0305
400	40%	39.9%	4.0			3.9807
600	60%	59.9%	6.4			6.4236
900	90%	89.9%	9.59			9.5879

MFC Label	MFC-10-2	Control box	3
Function	CH4 tracer injection	Channel	2
MFC Mfg	MKS Instruments, Inc.	Slope	10.22
LRD ref	BNW-62516-26	Intercept	-0.0499
Dry Cal	H	RSQ	0.9999
Date	5/7/2018		

set point (0 - 100)	set point %	reading %	Flow #1 [SCCM]	Flow #2 [SCCM]	Flow #3 [SCCM]	AVG Flow [SLPM]
10	10%	10.0%	972.92	973.42	974.11	0.9735
30	30%	30.0%	3063.4	3068.4	3066.9	3.066
50	50%	50.0%	5082.3	5084.6	5082.2	5.083
85	85%	85.0%	8609.3	8600.0	8600.0	8.603
2	2%	2.0%	110.22	107.47	108.93	0.1089

MFC Label	MFC-20-1	Control box	2
Function	COPC injection	Channel	4
MFC Mfg	MKS Instruments, Inc.	Slope	20.69
LRD ref	BNW-62516-46, -47, -48	Intercept	-0.0404
Dry Cal	M (H for 600, 950)	RSQ	0.9996
Date	5/8/2018		

set point (0 - 100)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
20	2%	1.8%	0.38			0.379
200	20%	19.8%	3.9			3.911
400	40%	39.8%	8.4			8.411
600	60%	59.9%	12.5			12.477
950	95%	94.9%	19.51			19.510

MFC Label	MFC-30-1	Control box	5
Function	Dilution, carrier	Channel	2
MFC Mfg	MKS Instruments, Inc.	Slope	33.98
LRD ref	BNW-62516-6	Intercept	0.2382
Dry Cal	H	RSQ	0.9998
Date	4/24/2018		

set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
50	5%		1.842	1.872	1.892	1.869
100	10%		3.889	3.900	3.907	3.899
200	20%		7.061	7.067	7.049	7.059
300	30%		10.384	10.340	10.272	10.332
400	40%		13.718	13.727	13.725	13.723
500	50%		17.075	17.169	17.105	17.116
600	60%		20.511	20.589	20.560	20.553
700	70%		23.972	24.023	24.016	24.004
800	80%		27.616	27.631	27.653	27.633

MFC Label	MFC-30-1	Control box	5
Function	Dilution, carrier	Channel	2
MFC Mfg	MKS Instruments, Inc.	Slope	34.17
LRB ref	BNW-62516-46, -47, -48	Intercept	0.1185
Dry Cal	H	RSQ	0.9998
Date	5/3/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
50	5%	4.80%	1.783			1.783
200	20%	19.80%	7.107			7.107
400	40%	39.80%	13.736			13.736
600	60%	59.80%	20.429			20.429
800	80%	79.90%	27.592			27.592

MFC Label	MFC-30-2	Control box	1
Function	Primary sample loop flow	Channel	1
MFC Mfg	MKS Instruments, Inc.	Slope	32.89
LRD ref	BNW-62516-8	Intercept	0.4049
Dry Cal	H	RSQ	0.9997
Date	4/26/2018		

set point (0 - 1000)	set point %	reading %	Flow #1 [SLPM]	Flow #2 [SLPM]	Flow #3 [SLPM]	AVG Flow [SLPM]
50	5%	4.8%	1.819	1.821	1.822	1.821
100	10%	9.8%	3.604	3.612	3.651	3.622
200	20%	19.9%	7.057	7.067	7.070	7.065
300	30%	29.8%	10.438	10.442	10.442	10.441
400	40%	39.8%	13.721	13.733	13.733	13.729
500	50%	49.9%	16.913	16.914	16.912	16.913
600	60%	59.9%	20.132	20.129	20.136	20.132
700	70%	69.9%	23.479	23.439	23.449	23.456
800	80%	79.9%	26.518	26.512	26.505	26.512

MFC Label	MFC-30-2				Control box	1
Function	Primary sample loop flow				Channel	1
MFC Mfg	MKS Instruments, Inc.				Slope	32.84
LRB ref	BNW-62516-46, -47, -48				Intercept	0.3872
Dry Cal	H				RSQ	0.9997
Date	5/11/2018					
set point (0 - 1000)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
50	5%	4.8%	1.821			1.821
200	20%	19.8%	7.065			7.065
400	40%	39.8%	13.729			13.729
600	60%	59.8%	20.132			20.132
800	80%	79.8%	26.512			26.512

MFC Label	MFC-100-1				Control box	3
Function	COPC injection				Channel	3
MFC Mfg	MKS Instruments, Inc.				Slope	106.6
LRB ref	BNW-62516-46, -47, -48				Intercept	-4.5955
Dry Cal	H				RSQ	1.000
Date	5/8/2018					
set point (0 - 100)	**set point %**	**reading %**	**Flow #1 [SLPM]**	**Flow #2 [SLPM]**	**Flow #3 [SLPM]**	**AVG Flow [SLPM]**
5	5%	5.0%	0.65			0.6516
10	10%	10.0%	6.0947			6.0947
15	15%	15.0%	11.49			11.4900
25	25%	24.9%	22.071			22.0710
30	30%	30.0%	27.331			27.3310

Appendix D

AreaRAE Data

Appendix D

AREARAE Data

The direct instrument readings recorded in the table have not been adjusted for the effects of the 1:1 dilution fitting. This fitting allowed 1 part of the sample to be blended with 1 part atmospheric air. The dilution was required for the exhaust gases since they had less than the required 15% O_2 required to accurately run the AreaRAE. The dilution fitting was used for all AreaRAE measurements during testing.

An evaluation of the average O_2 levels (18.05%) measured by the AreaRAE during the nitrogen sweep cycles indicates that the ratio of exhaust to ambient air (20.95% O_2) may be closer to 1: 6.15. This difference may be caused by being used on the pressurized side of the Fourier-transform infrared spectroscopy instrument (FTIR) pump, which is different than the ambient pressure that the dilution fitting is designed for.

The “N” port designation means the header line was closed to the Vapor Abatement Unit (VAU) and being sweeped by the nitrogen purge gas to clear the header and instrument lines.

The AreaRAE was a model 200-GM-AE-502G Multi-Gas Multi-Detector AreaRAE PGM5520 with the serial number 295-003913.

Table D.1. Manually Recorded AreaRAE Measurements

Time	Date	Test	Port	NH$_3$ ppm	VOC ppm	CO ppm	LEL gas %	O$_2$ %	Notes
13:53	4/30/18	0.1	D	DNR	2.32	DNR	DNR	DNR	no injection LRB 62516-11
14:45	4/30/18	0.1	D	DNR	0.2	DNR	DNR	DNR	no injection LRB 62516-11
16:08	4/30/18	0.1	A	DNR	0	DNR	DNR	DNR	no injection LRB 62516-11
19:25	5/9/2018	6.2	N/A	DNR	DNR	DNR	DNR	DNR	Area RAE date and time: 09/09/2017 23:36
8:32	5/10/2018	6.3	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer
12:29	5/10/2018	6.3	B	5	0	DNR	DNR	20.5	MFC-100-1 = 45.6 to achieve 44 SLPM (619 - 623 ppm nitrous oxide). Vacuum pump pulling outside air into area RAE
12:38	5/10/2018	6.3	B	0	34.8	141	3	12.3	vacuum off
15:01	5/10/2018	6.3	D	1	8.4	0	2	18.5	MFC-100-1 = 34.8; MFC-5-5 = 2.6; MFC-2-4 = 056; MFC-5-4 = 3.6; MFC-2-3 = 064. Just turned vacuum pump off, MFC-30-2 was set to ~248 previously. Acts like it is reading ambient air from under trailer.
16:14	5/10/2018	6.3	A	~~2~~	~~0~~	~~0~~	~~DNR~~	~~20.9~~	MFC-100-1 = 34.8; MFC-5-5 = 2.6; MFC-2-4 = 056; MFC-5-4 = 3.6; MFC-2-3 = 064. Possible suction of atmosphere through area RAE given low pressure in inlet line at port A. This data should not be used
16:27	5/10/2018	6.3	C	0	35.4	1	3	14.7	connected to summa port
16:39	5/10/2018	6.3	C	0	35.7	1	3	14.8	connected to summa port
16:42	5/10/2018	6.3	A	~~1~~	~~0.5~~	~~0~~	~~2~~	~~20.5~~	connected to summa port This data should not be used

Time	Date	Test	Port	NH_3 ppm	VOC ppm	CO ppm	LEL gas %	O_2 %	Notes
17:40	5/10/2018	6.3	D	DNR	DNR	DNR	DNR	DNR	Area RAE not reading correctly when moved to summa D
18:06	5/10/2018	6.3	A	DNR	DNR	DNR	DNR	DNR	17:40 - 18:06 not collecting a sample when connected to port A This data should not be used
18:43	5/10/2018	6.3	N/A	DNR	DNR	DNR	DNR	DNR	Disconnected from port D summa. Determined to move area RAE to a pressurized tube off the FTIR pump outlet
Prior to testing on May 14 the sample array was moved to the pressurized side of the FTIR pump									
15:27	5/14/2018	2.1	D	DNR	4.3	1	DNR	DNR	N2 set to 25.95 SLPM (MFC-30-1 = 726)
16:13	5/14/2018	2.1	N	0	DNR	1	DNR	18.9	
8:45	5/15/2018	2.2	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer; as found times matched
12:23	5/15/2018	2.2	A	1	0	0	0	20.9	
10:55	5/17/2018	3.1	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer; as found times matched
13:54	5/18/2018	3.1	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer; as found times matched
10:06	5/30/2018	3.2A	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer
12:43	5/31/2018	3.2B	N/A	DNR	DNR	DNR	DNR	DNR	sync Area RAE clock to computer; as found Area RAE clock = 12:42
13:59	5/31/2018	3.2B	D	0	2.7	0	0	19.6	Area Rae was changing through the morning
14:26	5/31/2018	3.2B	D	0	3	0	0	19.5	
15:16	5/31/2018	3.2B	A/B	~~0~~	4.8	19	0	19.4	Transition from Port B to Port A at 15:15 computer clock time
15:47	5/31/2018	3.2B	A	0	0	0	0	20.9	

Time	Date	Test	Port	NH_3 ppm	VOC ppm	CO ppm	LEL gas %	O_2 %	Notes
16:25	5/31/2018	3.2B	A	0	0	0	0	20.9	
17:02	5/31/2018	3.2B	A	0	0	0	0	20.9	
17:18	5/31/2018	3.2B		1	0	0	0	20.9	N_2 sweep (suspect)
9:15	6/6/2018	5.1	N	1	0	0	0	18	
9:40	6/6/2018	5.1	N	1	0	0	0	18	
10:05	6/6/2018	5.1	N	1	0	0	0	17.4	
10:57	6/6/2018	5.1	N	1	0	0	0	18.1	
11:37	6/6/2018	5.1	N	1	0	0	0	18.1	
12:25	6/6/2018	5.1	N	1	0	0	0	18.2	
13:02	6/6/2018	5.1	N	1	0	0	0	17.6	
13:45	6/6/2018	5.1	N	1	0	0	0	17.9	
14:17	6/6/2018	5.1	D	0	2.6	0	0	19.6	
15:00	6/6/2018	5.1	D	0	3.2	0	0	19.6	
15:40	6/6/2018	5.1	D	0	3.5	0	0	19.6	
16:21	6/6/2018	5.1	D	0	3.7	0	0	19.5	
8:55	6/7/2018	5.1	A	1	0.4	0	0	20.5	
9:23	6/7/2018	5.1	N	2	0.4	0	0	17.8	
10:00	6/7/2018	5.1	N	2	0	0	0	18	
11:54	6/7/2018	5.1	D	0	3.4	1	0	19.7	
12:50	6/7/2018	5.1	D	0	3.2	0	0	19.8	
13:43	6/7/2018	5.1	N	0	0	0	0	18.3	
8:54	6/12/2018	5.2	N	1	0	0	0	18.1	
10:15	6/12/2018	5.2	B	0	3.8	9	0	17	
11:01	6/12/2018	5.2	D	0	2.6	0	0	19.9	
12:16	6/12/2018	5.2	D	0	2.8	0	0	19.6	
13:04	6/12/2018	5.2	C	0	3.2	0	0	19.6	
14:04	6/12/2018	5.2	B	0	4.7	19	0	19.5	
15:15	6/12/2018	5.2	D	0	2.7	0	0	19.6	
16:02	6/12/2018	5.2	D	0	3.4	0	0	19.6	

Time	Date	Test	Port	NH_3 ppm	VOC ppm	CO ppm	LEL gas %	O_2 %	Notes
17:45	6/12/2018	5.2	D	0	2.6	0	0	19.7	
8:29	6/13/2018	5.3	N	1	0.4	0	0	18.1	
8:57	6/13/2018	5.3	N	2	0.5	0	0	18.2	
10:03	6/13/2018	5.3	A	1	0	0	0	20.9	
11:05	6/13/2018	5.3	D	0	2.3	0	0	19.8	
11:53	6/13/2018	5.3	C	0	2.4	0	0	19.7	
12:58	6/13/2018	5.3	D	0	1.9	0	0	19	
14:14	6/13/2018	5.3	D	0	3.1	0	0	19.4	
15:00	6/13/2018	5.3	D	0	2.2	0	0	19.8	
15:52	6/13/2018	5.3	D	0	2.3	0	0	19.8	
16:23	6/13/2018	5.3	D	0	2.2	0	0	19.9	

The AreaRAE data file was not recoverable at the end of testing.

DNR = Did Not Record

Appendix E

COPC Calibrations, Methane Tracer Measurements for Exhaust Flow Determination, and Test Data

Appendix E

COPC Calibrations, Methane Tracer Measurements for Exhaust Flow Determination, and Test Data

Table E.1. FTIR Calibration – Ammonia and Nitrous Oxide

Date	Time Start	COPC	Source [ppm]	MFC-30-1		MFC-5-1		% H_2O (FTIR)	[COPC] Delivered [ppm]	FTIR response		Notes
				Set	Flow [SLPM]	Set	Flow [SLPM]			[ppm]	$STD_{[ppm]}$	
7-May-18	12:24	Ammonia	1260	40.0%	12.8	1.0%	0.047	0%	4.6	4.5	0.026	• Source: single-component mix • PTR-MS not used
7-May-18	12:16	Ammonia	1260	80.0%	25.5	1.0%	0.047	0%	2.3	2.2	0.013	
9-May-18	9:59	Ammonia	1260	28.9%	9.3	9.8%	0.500	0%	64.0	64.9	0.187	
9-May-18	10:14	Ammonia	1260	18.1%	5.9	1.8%	0.088	0%	18.4	18.5	0.030	
9-May-18	10:27	Ammonia	1260	80.0%	25.5	1.0%	0.047	0%	2.3	2.6	0.020	
10-May-18	10:52	Ammonia	1260	28.9%	9.3	9.8%	0.500	0%	64.0	66.6	0.098	
10-May-18	11:20	Ammonia	1260	10.6%	3.6	79.8%	4.104	0%	674	662.5	0.923	
7-May-18		Nitrous oxide	1260			0%	0	0%				• Source: single-component mix • PTR-MS not used
7-May-18	11:16	Nitrous oxide	1260	61.1%	19.5	1.0%	0.047	0%	3.0	3.4	0.076	
7-May-18	11:36	Nitrous oxide	1260	36.5%	11.7	1.8%	0.088	0%	9.4	9.9	0.103	
7-May-18	16:36	Nitrous oxide	1260	61.1%	19.5	1.0%	0.047	0%	3.00	3.5	0.046	
9-May-18	8:52	Nitrous oxide	1260	61.1%	19.5	1.0%	0.047	0%	3.0	3.0	0.048	
9-May-18	9:14	Nitrous oxide	1260	36.5%	11.7	1.8%	0.088	0%	9.4	9.7	0.030	
9-May-18	9:31	Nitrous oxide	1260	28.9%	9.3	19.8%	1.015	0%	123.5	131.8	0.187	
10-May-18	8:40	Nitrous oxide	1260	0%	0	80.0%	4.114	0%	1260	747.8	2.057	
10-May-18	8:52	Nitrous oxide	1260	11.3%	3.8	80.0%	4.114	0%	656	516.0	0.706	
10-May-18	9:00	Nitrous oxide	1260	11.3%	3.8	39.8%	2.044	0%	442	395.3	0.317	
10-May-18	9:15	Nitrous oxide	1260	5.5%	2.0	79.8%	4.104	0%	853	617.7	1.512	
10-May-18	9:26	Nitrous oxide	1260	15.2%	5.0	19.8%	1.015	0%	212	200.1	0.332	
10-May-18	10:24	Nitrous oxide	1260	28.9%	9.3	19.8%	1.015	0%	123	131.0	0.145	
10-May-18	10:36	Nitrous oxide	1260	28.9%	9.3	9.8%	0.500	0%	64.0	69.0	0.087	

Table E.2. PTR-MS Calibration – Benzene and Propanenitrile

Date	Time Start	COPC	Source [ppm]	MFC-30-1		MFC-5-1		MFC-0.1-1		% H_2O (FTIR)	[COPC] Delivered [ppm]	PTR-MS discharge	PTR-MS response		Notes
				Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]				[cts]	$STD_{[cts]}$	
14-May-18	11:09	Benzene	2.5	28.7%	9.3	0.8%	0.036	0%	0	0%	0.0097	H_3O+	390	39	• Source: 6-component mix
14-May-18	12:26	Benzene	2.5	13.5%	4.5	6.8%	0.344	0%	0	0%	0.178		4647	118	
14-May-18	12:45	Benzene	2.5	14.0%	4.6	1.8%	0.088	0%	0	0%	0.046		1774	62	
14-May-18	13:05	Benzene	2.5	14.1%	4.7	0.8%	0.036	0%	0	0%	0.019		776	44	
14-May-18	13:18	Benzene	2.5	2.6%	1.0	79.8%	3.969	0%	0	0%	1.98		87627	364	
14-May-18	13:24	Benzene	2.5	11.3%	3.8	19.8%	0.990	0%	0	0%	0.52		19928	215	
14-May-18	13:39	Benzene	2.5	11.3%	3.8	0%	0	0%	0	0%	0		0	13	
14-May-18	13:53	Propionitrile	150	11.3%	3.8	0%	0	0%	0	0%	0	H_3O+	0	37	• Source: single-component mix
14-May-18	13:57	Propionitrile	150	72.6%	23.1	0.8%	0.036	0%	0	0%	0.23		14241	199	
14-May-18	14:07	Propionitrile	150	72.5%	23.1	1.8%	0.088	0%	0	0%	0.57		32392	324	
14-May-18	14:12	Propionitrile	150	72.2%	23.0	3.8%	0.191	0%	0	0%	1.23		68420	546	
14-May-18	14:18	Propionitrile	150	69.8%	22.2	19.8%	1.015	0%	0	0%	6.5		321922	1968	
14-May-18	14:30	Propionitrile	150	66.9%	21.3	39.8%	2.044	0%	0	0%	13.1		557448	2330	

Table E.3. PTR-MS Calibration (and FTIR Corroboration) – 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine

Date	Time Start	COPC	Source [ppm]	MFC-30-1		MFC-5-1		% H_2O (FTIR)	[COPC] Delivered [ppm]	PTR-MS discharge	PTR-MS response		FTIR response		Notes
				Set	Flow [SLPM]	Set	Flow [SLPM]				[cts]	$STD_{[cts]}$	[ppm]	$STD_{[ppm]}$	
30-May-18	11:00	1,3-Butadiene	5.2	10.9%	3.7	79.8%	4.104	2.2%	2.69	NO+	29126	0	-	-	• Source: 6-component mix
30-May-18	11:19	1,3-Butadiene	5.2	21.7%	7.1	5.9%	0.299	2.7%	0.21		2395	123	-	-	
30-May-18	11:25	1,3-Butadiene	5.2	16.7%	5.5	39.8%	2.044	3.2%	1.37		15999	310	-	-	
30-May-18	11:30	1,3-Butadiene	5.2	22.4%	7.3	1.0%	0.047	2.6%	0.032		366.4	19	-	-	
30-May-18	11:35	1,3-Butadiene	5.2	22.6%	7.4	0%	0	2.3%	0		2.2	12	-	-	
30-May-18	13:12	Formaldehyde	1.2	10.9%	3.7	79.8%	4.104	2.1%	0.62	H_3O+	3326	109.4	0.467	0.079	• Source: 6-component mix • FTIR data F.I.O.
30-May-18	13:20	Formaldehyde	1.2	16.7%	5.5	39.8%	2.044	1.9%	0.32		1823	55.3	0.207	0.062	
30-May-18	13:26	Formaldehyde	1.2	19.7%	6.4	19.8%	1.015	2.2%	0.16		931.6	48.6	0.137	0.065	
30-May-18	13:34	Formaldehyde	1.2	22.3%	7.3	1.8%	0.088	2.2%	0.014		148.6	27.7	0.002	0.070	
30-May-18	13:47	Formaldehyde	1.2	22.3%	7.3	0.0%	0	2.2%	0		74.5	23.0	-	-	
31-May-18	10:03	2,4-Dimethylpyridine	5	28.9%	9.3	1.8%	0.088	4.9%	0.044	NO+	1749.0	80.0	-	-	• Source: 6-component mix

Table E.4. PTR-MS Calibration (and FTIR Corroboration) – Acetaldehyde and Acetonitrile

Date	Time Start	COPC	Source	MFC-30-1		MFC-5-1		% H_2O (FTIR)	[COPC] Delivered	PTR-MS discharge	PTR-MS response		FTIR response		Notes
			[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]		[ppm]		[cts]	$STD_{[cts]}$	[ppm]	$STD_{[ppm]}$	
1-Jun-18	9:44	Acetaldehyde	100	18.6%	6.1	0%	0	2.1%	0	H_3O+	0	0			• Source: 9-component mix • FTIR data F.I.O.
1-Jun-18	10:31	Acetaldehyde	100	18.6%	6.1	1.0%	0.047	2.1%	0.74		24917	322	0.94	0.17	
1-Jun-18	10:59	Acetaldehyde	100	18.5%	6.1	1.8%	0.088	2.2%	1.40		48247	408	1.6	0.10	
1-Jun-18	11:30	Acetaldehyde	100	18.2%	6.0	3.8%	0.191	2.2%	3.03		97373	591	2.9	0.18	
1-Jun-18	11:35	Acetaldehyde	100	17.9%	5.9	5.8%	0.294	2.2%	4.7		148995	1207	4.2	0.13	
1-Jun-18	11:51	Acetaldehyde	100	15.9%	5.2	19.8%	1.015	2.1%	15.9		407808	2795	13.0	0.14	
1-Jun-18	12:04	Acetaldehyde	100	8.0%	2.7	73.2%	3.764	2.1%	56.6		823586	3982	48.0	0.18	
1-Jun-18	9:44	Acetonitrile	80	18.6%	6.1	0%	0.000	2.1%	0	H_3O+	0	0	-	-	• Source: 9-component mix
1-Jun-18	10:31	Acetonitrile	80	18.6%	6.1	1.0%	0.047	2.1%	0.59		25053	333	-	-	
1-Jun-18	10:59	Acetonitrile	80	18.5%	6.1	1.8%	0.088	2.2%	1.12		48571	870	-	-	
1-Jun-18	11:30	Acetonitrile	80	18.2%	6.0	3.8%	0.191	2.2%	2.43		94982	784	-	-	
1-Jun-18	11:35	Acetonitrile	80	17.9%	5.9	5.8%	0.294	2.2%	3.73		154116	2434	-	-	
1-Jun-18	11:51	Acetonitrile	80	15.9%	5.2	19.8%	1.015	2.1%	12.7		447869	2320	-	-	
1-Jun-18	12:04	Acetonitrile	80	8.0%	2.7	73.2%	3.764	2.1%	45.3		991208	6913	-	-	

Table E.5. PTR-MS Calibration – NDMA and Furan

Date	Time Start	COPC	Source	MFC-30-1		MFC-5-1		MFC-0.1-1		% H_2O (FTIR)	[COPC] Delivered	PTR-MS discharge	PTR-MS response		Notes
			[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]		[ppm]		[cts]	$STD_{[cts]}$	
6-Jun-18	10:35	NDMA	0.1	5.5%	2.0	79.8%	4.104	0%	0	0	0.068	NO+	4325.8	42.7	• Source: 6-component mix
6-Jun-18	12:08	NDMA	0.1	11.3%	3.8	79.8%	4.104	0%	0	0	0.052		3210.1	58.6	
6-Jun-18	12:15	NDMA	0.1	14.3%	4.7	9.8%	0.500	0%	0	0	0.0095		674.3	38.0	
6-Jun-18	12:25	NDMA	0.1	27.4%	8.9	9.8%	0.500	0%	0	0	0.0053		390.6	15.2	
6-Jun-18	12:32	NDMA	0.1	28.6%	9.2	1.8%	0.088	0%	0	0	0.00094		108.0	10.2	
6-Jun-18	12:40	NDMA	0.1	52.0%	16.6	0%	0	85.0%	0.084	0	0.00050		34.9	6.5	
6-Jun-18	12:52	NDMA	0.1	52.0%	16.6	0%	0	18.0%	0.017	0	0.000102		12.9	4.8	
6-Jun-18	13:02	NDMA	0.1	52.0%	16.6	0%	0	6.6%	0.006	0	0.000033		5.1	4.9	
6-Jun-18	13:02	NDMA	0.1	52.0%	16.6	0%	0	0%	0	0	0		0.0	4.3	
6-Jun-18	10:35	Furan	0.1	5.5%	2.0	79.8%	4.104	0%	0	0	0.068	NO+	8664.6	60.5	• Source: 6-component mix
6-Jun-18	12:08	Furan	0.1	11.3%	3.8	79.8%	4.104	0%	0	0	0.052		6428.3	69.2	
6-Jun-18	12:15	Furan	0.1	14.3%	4.7	9.8%	0.500	0%	0	0	0.0095		1126.3	26.1	
6-Jun-18	12:25	Furan	0.1	27.4%	8.9	9.8%	0.500	0%	0	0	0.0053		701.4	16.9	
6-Jun-18	12:32	Furan	0.1	28.6%	9.2	1.8%	0.088	0%	0	0	0.00094		121.8	8.5	
6-Jun-18	12:40	Furan	0.1	52.0%	16.6	0%	0	85.0%	0.084	0	0.00050		69.0	6.7	
6-Jun-18	12:52	Furan	0.1	52.0%	16.6	0%	0	18.0%	0.017	0	0.000102		13.8	4.4	
6-Jun-18	13:02	Furan	0.1	52.0%	16.6	0%	0	6.6%	0.006	0	0.000033		3.0	3.9	
6-Jun-18	13:15	Furan	0.1	52.0%	16.6	0%	0	0%	0	0	0		0.0	4.0	

Table E.6. Methane Tracer Measurements for Exhaust Flow Determination

Date	Time	Test	Tracer	Source	MFC-10-2		FTIR response		Calculated Exhaust Flow		Notes
				[ppm]	Set	Flow [SLPM]	[ppm]	STD$_{[ppm]}$	[SLPM]	[SCFM]	
5/7/2018	12:39	6.1	Methane	30000	0%	0.000	1.8	0.4	-	-	• Methane background
5/7/2018	12:47	6.1	Methane	30000	20%	1.851	35.9	0.4	1630	57.5	• Exhaust flow measurement
5/7/2018	14:47	6.1	Methane	30000	20%	1.851	38.6	0.4	1511	53.3	• Exhaust flow measurement
5/14/2018	15:27	2.1	Methane	30000	0%	0.000	1.7	0.3	-	-	• Methane background
5/14/2018	15:35	2.1	Methane	30000	20%	1.851	39.3	0.4	1475	52.1	• Exhaust flow measurement
6/1/2018	12:40	1.1	Methane	30000	20%	1.851	39.0	0.5	1485	52.4	• Exhaust flow measurement

Table E.7. Test 1.1 – Acetaldehyde and Acetonitrile

Date	Time Start	Test	COPC	Source	MFC-10-2		MFC-20-1		Exhaust Flow	Exhaust Spike	PTR-MS Ionization Mode	PTR-MS response			FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	STD$_{[ppm]}$	[ppm]	STD$_{[ppm]}$			
6/1/2018	12:40	1.1	Acetaldehyde	250	0%	0	0%	0	1484.7	0	H_3O+	8194	0.3	0.01	0.29	0.08	*<none>*	D	• Exhaust baseline
6/1/2018	12:52	1.1	Acetaldehyde	250	0%	0	74.9%	14.47	1484.7	2.44		126887	4.0	0.1	3.07	0.18	Exhaust	D	
6/1/2018	13:14	1.1	Acetaldehyde	250	0%	0	0%	0	1484.7	0		0	0	0	0.38	0.13	*<none>*	D	• Exhaust baseline
6/1/2018	12:40	1.1	Acetonitrile	300	0%	0	0%	0	1484.7	0	H_3O+	405	0.01	0.002	-	-	*<none>*	D	• Exhaust baseline
6/1/2018	12:52	1.1	Acetonitrile	300	103.4%	10.29	0%	0	1484.7	2.08		120612	3.2	0.1	-	-	Exhaust	D	
6/1/2018	13:14	1.1	Acetonitrile	300	0%	0	0%	0	1484.7	0		0	0	0	-	-	*<none>*	D	• Exhaust baseline

Table E.8. Test 1.2 – Acetaldehyde and Acetonitrile

Date	Time Start	Test	COPC	Source	Inlet Flow	Predicted Inlet	PTR-MS Ionization Mode	PTR-MS response H_3O+ ionization mode			FTIR response		Injection Location	Sample Port	Notes
				[ppm]	[SLPM]	[ppm]		[cts]	[ppm]	STD$_{[ppm]}$	[ppm]	STD$_{[ppm]}$			
6/4/2018	9:51	1.2	Acetaldehyde	bubbler	1373.5	0	H_3O+	8916	0.26	0.01	0.08	0.09	*<none>*	D	• Exhaust baseline
6/4/2018	10:08	1.2	Acetaldehyde	bubbler	1373.5	0		574	0.015	0.001	0.34	0.12	*<none>*	A	• Inlet baseline
6/4/2018	10:41	1.2	Acetaldehyde	bubbler	1373.5	-		881565	62.3	0.8	85.7	0.34	Inlet	A	
6/4/2018	11:51	1.2	Acetaldehyde	bubbler	1359.4	-		17706	0.53	0.01	0.79	0.09	Inlet	C	
6/4/2018	12:05	1.2	Acetaldehyde	bubbler	1359.4	-		183988	6.2	0.05	5.1	0.15	Inlet	B	
6/4/2018	12:12	1.2	Acetaldehyde	bubbler	1359.4	-		874438	61.6	0.8	75.5	0.40	Inlet	A	
6/4/2018	13:17	1.2	Acetaldehyde	bubbler	1373.5	-		9405	0.28	0.01	0.73	0.14	Inlet	D	
6/4/2018	9:51	1.2	Acetonitrile	bubbler	1373.5	0	H_3O+	262	0.006	0.001	-	-	*<none>*	D	• Exhaust baseline
6/4/2018	10:08	1.2	Acetonitrile	bubbler	1373.5	0		57	0.001	0.0002	-	-	*<none>*	A	• Inlet baseline
6/4/2018	10:41	1.2	Acetonitrile	bubbler	1373.5	-		924161	41.2	0.2	-	-	Inlet	A	
6/4/2018	11:51	1.2	Acetonitrile	bubbler	1359.4	-		9504	0.23	0.003	-	-	Inlet	C	
6/4/2018	12:05	1.2	Acetonitrile	bubbler	1359.4	-		264752	7.1	0.0	-	-	Inlet	B	
6/4/2018	12:12	1.2	Acetonitrile	bubbler	1359.4	-		908675	40.3	0.3	-	-	Inlet	A	
6/4/2018	13:17	1.2	Acetonitrile	bubbler	1373.5	-		593	0.014	0.001	-	-	Inlet	D	

Table E.8. Test 2.1 – Benzene and Propanenitrile

Date	Time Start	Test	COPC	Source	MFC-5-2		MFC-10-1		Exhaust Flow	Exhaust Spike	PTR-MS Ionization Mode	PTR-MS response H_3O+ ionization mode			Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	$STD_{[ppm]}$			
5/14/2018	16:27	2.1	Benzene	200	0.0%	0	0.0%	0	1474.9	0	H_3O+	109.6	0.0025	0.0006	*<none>*	D	• Exhaust baseline
5/14/2018	16:42	2.1	Benzene	200	2.2%	0.107	0.0%	0	1474.9	0.014		608.7	0.014	0.001	Exhaust	D	
5/14/2018	16:27	2.1	Propanenitrile	150	0.0%	0	0.0%	0	1474.9	0	H_3O+	36.9	0.0009	0.0011	*<none>*	D	• Exhaust baseline
5/14/2018	16:42	2.1	Propanenitrile	150	0.0%	0	7.4%	0.758	1474.9	0.077		8778	0.205	0.005	Exhaust	D	

Table E.9. Test 2.2 – Benzene and Propanenitrile

Date	Time Start	Test	COPC	Source	MFC-10-1		MFC-20-1		MFC-100-1		Inlet Flow	Predicted Inlet	PTR-MS Ionization Mode	PTR-MS response H_3O+ ionization mode			Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	$STD_{[ppm]}$			
15-May-18	12:27	2.2	Benzene	200	0%	0	0%	0	0%	0	1345.2	0	H_3O+	270	0.0061	0.0007	*<none>*	A	• Inlet baseline
15-May-18	13:38	2.2	Benzene	200	0%	0	0%	0	0%	0	1342.4	0		110	0.0025	0.0006	*<none>*	D	• Exhaust baseline
15-May-18	14:45	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1345.2	0.93		38764	0.87	0.01	Inlet	A	
15-May-18	14:49	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1274.4	0.98		1033	0.023	0.001	Inlet	D	
15-May-18	15:10	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1345.2	0.93		15129	0.34	0.004	Inlet	B	
15-May-18	15:14	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1345.2	0.93		1520	0.034	0.001	Inlet	C	
15-May-18	15:29	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1345.2	0.93		1052	0.024	0.001	Inlet	D	
15-May-18	15:38	2.2	Benzene	200	63.5%	6.296	0%	0	0%	0	1274.4	0.98		37743	0.85	0.01	Inlet	A	
15-May-18	12:27	2.2	Propanenitrile	150	0%	0	0%	0	0%	0	1345.2	0	H_3O+	337	0.0079	0.0011	*<none>*	A	• Inlet baseline
15-May-18	13:38	2.2	Propanenitrile	150	0%	0	0%	0	0%	0	1342.4	0		37	0.0009	0.0011	*<none>*	D	• Exhaust baseline
15-May-18	14:58	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1345.2	12.5		558795	13.0	0.1	Inlet	A	
15-May-18	14:49	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1274.4	13.1		500	0.0117	0.0014	Inlet	D	
15-May-18	15:10	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1345.2	12.5		87419	2.04	0.01	Inlet	B	
15-May-18	15:14	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1345.2	12.5		2643	0.062	0.002	Inlet	C	
15-May-18	15:29	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1345.2	12.5		358	0.0083	0.0010	Inlet	D	
15-May-18	15:38	2.2	Propanenitrile	150	0%	0	92.0%	17.72	110%	104.6	1274.4	13.1		848920	19.8	0.3	Inlet	A	

Table E.10. Test 3.1 – 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine

Date	Time Start	Test	COPC	Source	MFC-10-2		MFC-20-1		MFC-100-1		Exhaust Flow	Exhaust Spike	PTR-MS Ionization Mode	PTR-MS response			FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	$STD_{[ppm]}$	[ppm]	$STD_{[ppm]}$			
5/30/2018	9:52	3.1	1,3-Butadiene	100	0%	0	0%	0	0.0%	0	1484.7	0	NO+	11.7	0.0008	0.0047	-	-	*<none>*	D	• Exhaust baseline
5/30/2018	10:02	3.1	1,3-Butadiene	100	0%	0	0%	0	5.7%	1.375	1484.7	0.093		2096.0	0.174	0.008	-	-	Exhaust	D	
5/18/2018	15:30	3.1	Formaldehyde	30	16.3%	1.498	0%	0	0%	0	1484.7	0.030	H_3O+	3022.5	0.558	0.022	0.0189	0.0617	Exhaust	D	• FTIR data F.I.O.
5/18/2018	15:43	3.1	Formaldehyde	30	0%	0	0%	0	0%	0	1484.7	0		2806.3	0.516	0.015	-0.0119	0.0497	*<none>*	D	• Exhaust baseline
5/18/2018	15:30	3.1	2,4-Dimethylpyridine	5	0%	0	0%	0	18.4%	13.94	1484.7	0.047	H_3O+	-	-	-	-	-	Exhaust	D	• PTR-MS data not usable

Table E.11. Test 3.2 – 1,3-Butadiene, Formaldehyde, and 2,4-Dimethylpyridine

Date	Time Start	Test	COPC	Source	MFC-10-1		MFC-10-2		MFC-20-1		MFC-100-1		Inlet Flow	Predicted Inlet	PTR-MS Ionization Mode	PTR-MS response			FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	$STD_{[ppm]}$	[ppm]	$STD_{[ppm]}$			
5/30/2018	9:15	3.2	1,3-Butadiene	100	0%	0	0%	0	0%	0	0%	0	1376.4	0	NO+	3.2	0.00009	0.0009	-	-	*<none>*	A	• Inlet baseline
5/30/2018	9:28	3.2	1,3-Butadiene	100	0%	0	0%	0	0%	0	0%	0	1376.4	0		11.7	0.00084	0.0047	-	-	*<none>*	D	• Exhaust baseline
5/30/2018	10:28	3.2	1,3-Butadiene	100	63.5%	6.296	0%	0	0%	0	105%	99.6	1376.4	7.1		88244.2	8.05	0.11	-	-	Inlet	A	
5/30/2018	10:31	3.2	1,3-Butadiene	100	63.5%	6.296	0%	0	0%	0	105%	99.6	1376.4	7.1		103.3	0.027	0.002	-	-	Inlet	D	
5/30/2018	10:37	3.2	1,3-Butadiene	100	63.5%	6.296	0%	0	0%	0	105%	99.6	1376.4	7.1		10901.7	0.98	0.03	-	-	Inlet	B	
5/30/2018	10:39	3.2	1,3-Butadiene	100	63.5%	6.296	0%	0	0%	0	105%	99.6	1376.4	7.1		89.3	0.026	0.001	-	-	Inlet	D	
5/30/2018	14:27	3.2	Formaldehyde	30	0%	0	0%	0	0%	0	0%	0	1359.4	0	H_3O+	4735.0	0.88	0.02	-0.031	0.065	*<none>*	A	• Inlet baseline
5/30/2018	14:43	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1359.4	0.59		6959.6	1.31	0.03	0.376	0.069	Inlet	A	• FTIR data F.I.O.
5/30/2018	14:51	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1359.4	0.59		3907.5	0.726	0.05	0.020	0.059	Inlet	D	
5/30/2018	15:05	3.2	Formaldehyde	30	0%	0	0%	0	0%	0	0%	0	1359.4	0		3902.1	0.725	0.05	0.038	0.049	*<none>*	D	• Exhaust baseline
5/30/2018	15:39	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1359.4	0.59		7296.2	1.37	0.03	0.39	0.05	Inlet	A	
5/30/2018	15:56	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1345.2	0.59		4052.9	0.753	0.05	-0.01	0.05	Inlet	D	
5/30/2018	16:05	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1345.2	0.59		14507.2	2.74	0.04	3.58	0.28	Inlet	B	
5/30/2018	16:11	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1345.2	0.59		4464.7	0.83	0.02	0.29	0.07	Inlet	C	
5/30/2018	16:22	3.2	Formaldehyde	30	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1345.2	0.59		3777.2	0.701	0.04	0.04	0.05	Inlet	D	
5/30/2018	16:32	3.2	Formaldehyde	30	0%	0	0%	0	0%	0	0%	0	1345.2	0		3613.2	0.670	0.04	0.01	0.05	*<none>*	D	• Exhaust baseline
5/31/2018	12:15	3.2	2,4-Dimethylpyridine	bubbler	0%	0	0%	0	0%	0	0%	0	1373.5	-	NO+	211.2	0.0053	0.0005	-	-	*<none>*	D	• Exhaust baseline
5/31/2018	12:19	3.2	2,4-Dimethylpyridine	bubbler	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1373.5	-		278.8	0.0071	0.0005	-	-	Inlet	D	• No PTR-MS background
5/31/2018	14:44	3.2	2,4-Dimethylpyridine	bubbler	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1350.9	-		838.3	0.021	0.001	-	-	Inlet	B	
5/31/2018	15:15	3.2	2,4-Dimethylpyridine	bubbler	0%	0	89.2%	8.858	95.0%	18.29	0%	0	1359.4	-		119.1	0.0030	0.0004	-	-	*<none>*	A	• Inlet baseline
5/31/2018	17:12	3.2	2,4-Dimethylpyridine	bubbler	0%	0	0%	0	0.0%	0	0%	0	1376.4	-		38626.7	0.978	0.096	-	-	Inlet	A	

Table E.12. Tests 4.1/5.1, 4.2/5.2, & 4.3/5.3 – N-Nitrosodimethylamine (NDMA) and Furan

Date	Time Start	Test	COPC	Source	MFC-1-3		MFC-5-2		Exhaust Flow	Exhaust Spike	PTR-MS Ionization Mode		PTR-MS response			Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts] R	[cts]	[ppm]	$STD_{[ppm]}$			
6/6/2018	14:09	4.1	NDMA	1	0%	0	0%	0	1484.7	0	NO+	94.9	73.6	0.000683	0.000130	*<none>*	D	• Exhaust baseline
6/7/2018	10:12	4.1	NDMA	1	0%	0	0%	0	1484.7	0		95.7	74.3	0.000690	0.000118	*<none>*	D	• Exhaust baseline
6/7/2018	12:54	4.1	NDMA	1	22.6%	0.221	0%	0	1484.7	0.000149		106.3	84.9	0.000781	0.000110	Exhaust	D	• 50% OEL
6/7/2018	14:09	5.1	Furan	1	0%	0	0%	0	1484.7	0	NO+	53.3	14.3	0.000108	0.000037	*<none>*	D	• Exhaust baseline
6/7/2018	10:12	5.1	Furan	1	0%	0	0%	0	1484.7	0		52.4	13.4	0.000101	0.000037	*<none>*	D	• Exhaust baseline
6/7/2018	12:54	5.1	Furan	1	0%	0	1.5%	0.072	1484.7	0.000049		58.6	19.6	0.000148	0.000039	Exhaust	D	• 10% OEL

Table E.13. Tests 4.2/5.2 – N-Nitrosodimethylamine (NDMA) and Furan

Date	Time Start	Test	COPC	Source	MFC-1-3		MFC-5-2		Inlet Flow	Predicted Inlet	PTR-MS Ionization Mode	PTR-MS response			Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	STD$_{[ppm]}$			
6/12/2018	9:36	4.2	NDMA	1	0%	0	0%	0	1373.5	0	NO+	32.5	0.000459	0.000089	*<none>*	A	• Inlet baseline
6/12/2018	9:52	4.2	NDMA	1	92.9%	0.906	0%	0	1373.5	0.00066		38.9	0.000619	0.000098	Inlet	A	
6/12/2018	10:21	4.2	NDMA	1	92.9%	0.906	0%	0	1359.4	0.00067		67.9	0.00108	0.00010	Inlet	D	
6/12/2018	10:21	4.2	NDMA	1	92.9%	0.906	0%	0	1359.4	0.00067		69.9	0.00111	0.00010	Inlet	D	
6/12/2018	12:45	4.2	NDMA	1	92.9%	0.906	0%	0	1359.4	0.00067		79.3	0.00126	0.00010	Inlet	C	
6/12/2018	13:25	4.2	NDMA	1	92.9%	0.906	0%	0	1359.4	0.00067		72.5	0.00115	0.00020	Inlet	D	
6/12/2018	13:40	4.2	NDMA	1	92.9%	0.906	0%	0	1359.4	0.00067		264.6	0.00421	0.00008	Inlet	B	
6/12/2018	14:10	4.2	NDMA	1	92.9%	0.906	0%	0	1345.2	0.00067		36.5	0.000580	0.000093	Inlet	A	
6/12/2018	14:47	4.2	NDMA	1	92.9%	0.906	0%	0	1345.2	0.00067		73.0	0.00116	0.00009	Inlet	D	
6/12/2018	15:52	4.2	NDMA	1	92.9%	0.906	0%	0	1345.2	0.00067		90.0	0.00143	0.00009	Inlet	C	
6/12/2018	17:25	4.2	NDMA	1	0%	0	0%	0	1345.2	0		69.5	0.00111	0.00004	<none>	D	• Exhaust baseline
6/12/2018	18:08	4.2	NDMA	1	0%	0	0%	0	1359.4	0		5.8	0.000040	0.000145	<none>	A	• Inlet baseline
6/12/2018	9:21	5.2	Furan	1	0%	0	0%	0	1373.5	0	NO+	68.5	0.000499	0.000084	*<none>*	D	• Exhaust baseline
6/12/2018	9:36	5.2	Furan	1	0%	0	0%	0	1373.5	0		61.1	0.000437	0.000055	*<none>*	A	• Inlet baseline
6/12/2018	9:52	5.2	Furan	1	0%	0	59.5%	2.937	1373.5	0.00213		298.7	0.00228	0.00012	Inlet	A	
6/12/2018	10:21	5.2	Furan	1	0%	0	59.5%	2.937	1359.4	0.00216		31.8	0.000195	0.000046	Inlet	D	
6/12/2018	10:21	5.2	Furan	1	0%	0	59.5%	2.937	1387.7	0.00211		35.1	0.000222	0.000061	Inlet	D	
6/12/2018	12:45	5.2	Furan	1	0%	0	59.5%	2.937	1416.0	0.00207		199.5	0.00158	0.00010	Inlet	C	
6/12/2018	13:25	5.2	Furan	1	0%	0	59.5%	2.937	1444.3	0.00203		44.8	0.000303	0.000061	Inlet	D	
6/12/2018	13:40	5.2	Furan	1	0%	0	59.5%	2.937	1359.4	0.00216		9455.0	0.0733	0.0014	Inlet	B	• Above PTR-MS calibration
6/12/2018	14:10	5.2	Furan	1	0%	0	59.5%	2.937	1345.2	0.00218		352.4	0.00269	0.00011	Inlet	A	
6/12/2018	14:47	5.2	Furan	1	0%	0	59.5%	2.937	1345.2	0.00218		47.6	0.000326	0.000050	Inlet	D	
6/12/2018	15:52	5.2	Furan	1	0%	0	59.5%	2.937	1345.2	0.00218		247.6	0.00198	0.00011	Inlet	C	
6/12/2018	17:25	5.2	Furan	1	0%	0	0%	0	1345.2	0		73.7	0.000542	0.000040	*<none>*	D	• Exhaust baseline
6/12/2018	18:08	5.2	Furan	1	0%	0	0%	0	1359.4	0		25.7	0.000188	0.000034	*<none>*	A	• Inlet baseline

Table E.14. Tests 4.3/5.3 – N-Nitrosodimethylamine (NDMA) and Furan

Date	Time Start	Test	COPC	Source	MFC-10-1		MFC-100-1		Inlet Flow	Predicted Inlet	PTR-MS Ionization Mode	PTR-MS response			Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]		[cts]	[ppm]	STD$_{[ppm]}$			
6/13/2018	9:41	4.3	NDMA	10	0%	0	0%	0	1345.2	0	NO+	82.6	0.00131	0.00012	*<none>*	A	- Inlet baseline
6/13/2018	10:20	4.3	NDMA	10	80.2%	7.944	0%	0	1345.2	0.05906		3112.6	0.0495	0.0006	Inlet	A	
6/13/2018	10:45	6.3	NDMA	10	80.2%	7.944	0%	0	1345.2	0.05906		360.8	0.00574	0.00038	Inlet	B	
6/13/2018	10:48	4.3	NDMA	10	80.2%	7.944	0%	0	1345.2	0.05906		73.8	0.00117	0.00009	Inlet	D	
6/13/2018	11:43	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		0	0	0	Inlet	C	- PTR-MS < baseline
6/13/2018	12:22	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		3758.5	0.0598	0.0006	Inlet	A	
6/13/2018	13:04	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		3852.5	0.0613	0.0008	Inlet	A	
6/13/2018	13:23	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		394.1	0.00627	0.00086	Inlet	B	
6/13/2018	13:40	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		64.6	0.00103	0.00008	Inlet	D	
6/13/2018	14:59	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		65.6	0.00104	0.00009	Inlet	D	
6/13/2018	15:42	4.3	NDMA	10	80.2%	7.944	0%	0	1316.9	0.06033		61.7	0.000982	0.000081	Inlet	D	
6/13/2018	16:11	4.3	NDMA	10	0%	0	0%	0	1316.9	0		60.3	0.000959	0.000081	<none>	D	- Exhaust baseline
6/13/2018	9:41	5.3	Furan	1	0%	0	0%	0	1345.2	0	NO+	1.6	0.000018	0.00003	*<none>*	A	- Inlet baseline
6/13/2018	10:20	5.3	Furan	1	0%	0	26.3%	21.76	1345.2	0.0159		1589.5	0.0133	0.00031	Inlet	A	
6/13/2018	10:45	5.3	Furan	1	0%	0	26.3%	21.76	1345.2	0.0159		8082.0	0.0636	0.00254	Inlet	B	- Above PTR-MS calibration
6/13/2018	10:48	5.3	Furan	1	0%	0	26.3%	21.76	1345.2	0.0159		25.6	0.000187	0.00005	Inlet	D	
6/13/2018	11:43	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		7.9	0.000065	0.00014	Inlet	C	- PTR-MS < baseline
6/13/2018	12:22	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		2552.5	0.0210	0.00030	Inlet	A	
6/13/2018	13:04	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		2632.6	0.0216	0.00034	Inlet	A	
6/13/2018	13:23	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		13595.2	0.102	0.00568	Inlet	B	- Above PTR-MS calibration
6/13/2018	13:40	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		42.0	0.000279	0.00005	Inlet	D	
6/13/2018	14:59	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		37.1	0.000239	0.00005	*<none>*	D	- Exhaust baseline
6/13/2018	15:42	5.3	Furan	1	0%	0	26.3%	21.76	1316.9	0.0163		37.2	0.000240	0.00007	*<none>*	D	- Exhaust baseline
6/13/2018	16:11	5.3	Furan	1	0%	0	0%	0	1316.9	0		29.8	0.000218	0.00005	<none>	D	- Exhaust baseline

Table E.15. Test 6.1 – Nitrous Oxide and Ammonia

Date	Time Start	Test	COPC	Source	MFC-1-3		MFC-10-1		Exhaust Flow	Exhaust Spike	FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]	[ppm]	STD$_{[ppm]}$			
5/7/2018	12:55	6.1	Nitrous oxide	30000	0%	0	0%	0	1629.8	0	0.80	0.02	*<none>*	D	- Exhaust baseline
5/7/2018	16:00	6.1	Nitrous oxide	30000	20.1%	0.197	0%	0	1510.5	3.91	4.58	0.03	Exhaust	D	
5/7/2018	16:14	6.1	Nitrous oxide	30000	15.0%	0.147	0%	0	1510.5	2.92	3.57	0.04	Exhaust	D	
5/7/2018	12:55	6.1	Ammonia	30000	0%	0	0%	0	1629.8	0	0.07	0.03	*<none>*	D	- Exhaust baseline
5/7/2018	15:22	6.1	Ammonia	30000	10.1%	0.099	0%	0	1510.5	1.97	1.36	0.02	Exhaust	D	
5/7/2018	15:33	6.1	Ammonia	30000	20.0%	0.196	0%	0	1510.5	3.89	2.93	0.02	Exhaust	D	

Table E.16. Test 6.2 – Nitrous Oxide and Ammonia

Date	Time Start	Test	COPC	Source	MFC-10-1		MFC-100-1		Inlet Flow	Predicted Inlet	FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	Set	Flow [SLPM]	[SLPM]	[ppm]	[ppm]	$STD_{[ppm]}$			
5/9/2018	10:43	6.2	Nitrous oxide	30000	0%	0	0%	0	1373.5	0	0.32	0.03	*<none>*	A	• Inlet baseline
5/9/2018	11:53	6.2	Nitrous oxide	30000	0%	0	0%	0	1373.5	0	0.90	0.02	<none>	D	• Exhaust baseline
5/9/2018	12:18	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	103.4	0.2	Inlet	A	
5/9/2018	12:32	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	28.7	0.05	Inlet	D	
5/9/2018	15:27	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	27.9	0.1	Inlet	B	
5/9/2018	16:10	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	29.3	0.1	Inlet	C	
5/9/2018	16:48	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	108.5	0.3	Inlet	A	
5/9/2018	17:15	6.2	Nitrous oxide	30000	0%	0	8.7%	4.344	1373.5	94.6	29.2	0.4	Inlet	D	
5/9/2018	10:43	6.2	Ammonia	30000	0%	0	0%	0	1373.5	0	3.2	0.6	*<none>*	A	• Inlet baseline
5/9/2018	11:53	6.2	Ammonia	30000	0%	0	0%	0	1373.5	0	0.04	0.02	<none>	D	• Exhaust baseline
5/9/2018	12:18	6.2	Ammonia	30000	21.7%	2.170	0%	0	1373.5	47.3	54.8	0.1	Inlet	A	
5/9/2018	12:32	6.2	Ammonia	30001	21.7%	2.170	0%	0	1373.5	47.3	1.3	0.1	Inlet	D	
5/9/2018	15:27	6.2	Ammonia	30002	21.7%	2.170	0%	0	1373.5	47.3	3.2	0.3	Inlet	B	
5/9/2018	16:10	6.2	Ammonia	30003	21.7%	2.170	0%	0	1373.5	47.3	0.11	0.07	Inlet	C	
5/9/2018	16:48	6.2	Ammonia	30004	21.7%	2.170	0%	0	1373.5	47.3	54.9	0.2	Inlet	A	
5/9/2018	17:15	6.2	Ammonia	30000	21.7%	2.170	0%	0	1373.5	47.3	0.06	0.03	Inlet	D	

Table E.17. Test 6.3 – Nitrous Oxide and Ammonia

Date	Time Start	Test	COPC	Source	MFC-100-1		Inlet Flow	Predicted Inlet	FTIR response		Injection Location	Sample Port	Notes
				[ppm]	Set	Flow [SLPM]	[SLPM]	[ppm]	[ppm]	$STD_{[ppm]}$			
5/10/2018	11:56	6.3	Nitrous oxide	30000	45.6%	40.86	1359.4	875.5	865.0	1.6	Inlet	A	
5/10/2018	12:01	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	259.6	0.9	Inlet	D	
5/10/2018	12:04	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	257.3	0.4	Inlet	C	
5/10/2018	12:10	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	236.2	0.8	Inlet	B	
5/10/2018	12:45	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	261.6	0.9	Inlet	D	
5/10/2018	13:04	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	260.4	0.9	Inlet	C	
5/10/2018	13:15	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	841.7	2.0	Inlet	A	
5/10/2018	13:22	6.3	Nitrous oxide	30000	45.6%	40.86	1345.2	884.4	4.6	0.7	*<none>*	A	• Inlet baseline
5/10/2018	13:24	6.3	Ammonia	30000	0%	0	1359.4	0	-0.1	0.6	<none>	A	• Inlet baseline
5/10/2018	13:43	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	654.2	1.1	Inlet	A	
5/10/2018	14:13	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	76.3	1.1	Inlet	B	
5/10/2018	15:05	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	0.32	0.04	Inlet	D	
5/10/2018	16:15	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	675.4	1.1	Inlet	A	
5/10/2018	17:20	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	0.95	0.11	Inlet	C	
5/10/2018	18:00	6.3	Ammonia	30000	34.8%	30.17	1359.4	651.4	0.3	0.04	Inlet	D	

Appendix F

Additional Test Summary and Results

Appendix F

Additional Test Summary and Results

Table F.1. Select Inlet Background COPC Concentrations

COPC	Test	Inlet Background PTR-MS [ppm]	Inlet Background FTIR [ppm]	Instrument
Acetaldehyde	1.2	0.015	0.34	PTR-MS (H_3O+)
Acetonitrile	1.2	0.0014	-	PTR-MS (H_3O+)
Benzene	2.2	0.0061	-	PTR-MS (H_3O+)
Propanenitrile	2.2	0.0079	-	PTR-MS (H_3O+)
1,3-Butadiene	3.2	0.00009	-	PTR-MS (NO+)
Formaldehyde	3.2	0.88	-	PTR-MS (H_3O+)
2,4-Dimethylpyridine	3.2	0.0030	-	PTR-MS (NO+)
NDMA	4.2	0.00012	-	PTR-MS (NO+) + VOCUS PTR-TOF
Furan	5.2	0.00024	-	PTR-MS (NO+) + VOCUS PTR-TOF
Ammonia	0.1	-	1.6	FTIR
Nitrous Oxide	0.1	-	2.4	FTIR

Table F.2. Detailed Summary Test Results

COPC	Test	200% OEL Inlet Target	Measured at Inlet (port A)		Measured at port B		A → B DRE	Measured at port C		B → C DRE	Measured at Outlet (port D)		C → D DRE	VAU DRE	95% DRE Target met?	10% OEL Target met?
			PTR-MS [ppm]	FTIR [ppm]	PTR-MS [ppm]	FTIR [ppm]		PTR-MS [ppm]	FTIR [ppm]		PTR-MS [ppm]	FTIR [ppm]				
Acetaldehyde[a]	1.2	50	61.9	75.5	6.2	5.1	90.0%	0.53	0.79	9.1%	0.28	0.73	0.4%	99.6%	Yes	Yes
Acetonitrile	1.2	40	40.8	-	7.1	-	82.6%	0.23	-	16.9%	0.014	-	0.5%	>99.9%	Yes	Yes
Benzene	2.2	1	0.86	-	0.34	-	60.5%	0.034	-	35.6%	0.023	-	1.2%	97.3%	Yes	Yes
Propanenitrile	2.2	12	16.4	-	2.0	-	87.6%	0.062	-	12.0%	0.010	-	0.3%	>99.9%	Yes	Yes
1,3-Butadiene	3.2	3.4	8.05	-	0.98	-	87.8%	*N.M.*	-	-	0.026	-	11.8%	99.7%	Yes	Yes
Formaldehyde[a]	3.2	0.6	1.34	0.38	2.74	3.58	-105%	0.83	0.29	143%	0.727	0.031	7.8%	45.7%	No	No
2,4-Dimethylpyridine	3.2	1	0.98	-	0.021	-	97.8%	*N.M.*	-	-	0.0071	-	1.4%	99.3%	Yes	Yes
NDMA[b]	4.2	0.0006	0.00034	-	0.00025	-	25.7%	-	-	-	0.000151	-	29.9%	55.6%	No	No
	4.3	0.062	0.0603	-	0.00205	-	96.6%	-b	-	-	0.000042	-	3.3%	>99.9%	Yes	No
Furan[b]	5.2	0.002	0.00234	-	0.0578	-	-2367%	-	-	-	0.000017	-	2466%	99.3%	Yes	Yes
	5.3	0.017	0.0212	-	0.0869	-	-311%	-b	-	-	0.000035	-	411%	99.8%	Yes	Yes
Ammonia	6.2	50	-	54.9	-	3.2	94.2%	-	0.11	5.6%	-	0.70	-1%	98.7%	Yes	Yes
	6.3	630	-	665	-	76.3	88.5%	-	0.9	11.3%	-	0.32	0.1%	>99.9%	Yes	Yes
Nitrous Oxide	6.2	100	-	105.9	-	27.9	73.7%	-	29.3	-1%	-	28.9	0.4%	72.7%	No	No
	6.3	831	-	853	-	236	72.3%	-	259	-3%	-	261	-0.2%	69.5%	No	No

[a] FTIR results are For Information Only.

[b] Reflects combined results from the PTR-MS and the TOFWERK VOCUS-PTR

N.M. - not measured

Table F.3. Engine + Exhaust Aftertreatment (DOC + DPF) Individual DREs

COPC	**Test**	**Individual Component DRE**		**200% OEL Overall DRE**
		Engine	**Combined DOC + DPF**	
Acetaldehyde	1.2	90.0%	95.5%	99.6%
Acetonitrile	1.2	82.6%	99.8%	>99.9%
Benzene	2.2	60.5%	93.1%	97.3%
Propanitrile	2.2	87.6%	99.5%	>99.9%
1,3-Butadiene	3.2	87.8%	97.4%	99.7%
Formaldehyde	3.2	-105%	73.5%	45.7%
2,4-Dimethylpyridine	3.2	97.8%	66.7%	99.3%
NDMA	4.2	26%	40.2%	56%
NDMA	4.3	97%	98.0%	>99.9%
Furan	5.2	-2367%	2466%	99.3%
Furan	5.3	-311%	411%	99.8%
Ammonia	6.2	94.2%	77.7%	98.7%
Ammonia	6.3	88.5%	99.6%	>99.9%
Nitrous Oxide	6.2	73.7%	-4%	72.7%
Nitrous Oxide	6.3	72.3%	-10%	69.5%

Table F.4. Effect of Exhaust Background Subtraction on Overall VAU DRE

COPC	Test	200% OEL	
		No subtraction	Exhaust background subtracted
Acetaldehyde	1.2	99.6%	99.97%
Acetonitrile	1.2	>99.9%	> 99.99%
Benzene	2.2	97.3%	97.6%
Propanenitrile	2.2	>99.9%	99.94%
1,3-Butadiene	3.2	99.7%	99.7%
Formaldehyde	3.2	45.7%	99.9%
2,4-Dimethylpyridine	3.2	99.3%	99.8%
NDMA	4.2	55.6%	99.2%
NDMA	4.3	>99.9%	99.99%
Furan	5.2	99.3%	> 99.99%
Furan	5.3	99.8%	99.99%
Ammonia	6.2	98.7%	98.8%
Ammonia	6.3	>99.9%	99.96%
Nitrous Oxide	6.2	72.7%	73.5%
Nitrous Oxide	6.3	69.5%	69.6%

Appendix G

Hanford Tank Farm COPCs and Test Surrogate

Appendix G

Hanford Tank Farm COPCs and Test Surrogate

Table G.1. Hanford Tank Farm COPCs and Test Surrogate

COPC #	Chemical Name	CAS #	OEL[1]	Test Surrogate
1	1,1'-Biphenyl	92-52-4	0.2 ppm	Benzene, Acetaldehyde
2	1,3-Butadiene	106-99-0	1 ppm	1,3-Butadiene
3	1,3-Dinitrate-1,2,3-propantriol	623-87-0	0.05 ppm	Formaldehyde, Acetaldehyde
4	1,4-Butanediol dinitrate	3457-91-8	0.05 ppm	1,3-Butadiene
5	1-Butanol	71-36-3	20 ppm	Formaldehyde, Acetaldehyde
6	2,4-Dimethylpyridine	108-47-4	0.5 ppm	2,4-Dimethylpyridine
7	2,4-Pentadienenitrile	1615-70-9	0.3 ppm	Acetonitrile, Propanenitrile
8	2-Ethylhex-2-enal	645-62-5	0.1 ppm	Formaldehyde, Acetaldehyde
9	2-Fluoropropene	1184-60-7	0.1 ppm	1,3-Butadiene
10	2-Hexanone	591-78-6	5 ppm	Formaldehyde, Acetaldehyde
11	2-Methylbut-2-enal	1115-11-3	0.03 ppm	Formaldehyde, Acetaldehyde
12	2-Methylene butanenitrile	1647-11-6	0.3 ppm	Acetonitrile, Propanenitrile
13	2-Nitro-2-methylpropane	594-70-7	0.3 ppm	1,3-Butadiene
14	3-Buten-2-one	78-94-4	0.2 ppm	Formaldehyde, Acetaldehyde
15	3-Methyl-3-buten-2-one	814-78-8	0.02 ppm	Formaldehyde, Acetaldehyde
16	4-Methyl-2-hexanone	105-42-0	0.5 ppm	Formaldehyde, Acetaldehyde
17	6-Methyl-2-heptanone	928-68-7	8 ppm	Formaldehyde, Acetaldehyde
18	Acetaldehyde	75-07-0	25 ppm	Acetaldehyde
19	Acetonitrile	75-05-8	20 ppm	Acetonitrile
20	Ammonia	7664-41-7	25 ppm	Ammonia
21	Benzene	71-43-2	0.5 ppm	Benzene
22	Butanal	123-72-8	25 ppm	Formaldehyde, Acetaldehyde
23	Butanenitrile	109-74-0	8 ppm	1,3-Butadiene
24	Butyl nitrate	928-45-0	8 ppm	1,3-Butadiene
25	Butyl nitrite	544-16-1	0.1 ppm	1,3-Butadiene
26	Chlorinated biphenyls	---	0.03 mg/m^3	Benzene
27	Dibutyl butylphosphonate	78-46-6	0.007 ppm	1,3-Butadiene
28	Diethyl phthalate	84-66-2	5 mg/m^3	Benzene
29	Ethylamine	75-04-7	5 ppm	Acetonitrile, Propanenitrile

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[1] COPC Hanford Tank Farm occupational exposure limit form Appendix A of the Test Plan. Rappe KG. 2018. PNNL Assessment of "*NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)*". Test Plan TP-71248-01, Rev. 0, April 2018, Pacific Northwest National Laboratory, Richland, Washington.

COPC #	Chemical Name	CAS #	OEL[1]	Test Surrogate
30	Formaldehyde	50-00-0	0.3 ppm	Formaldehyde
31	Furan	110-00-9	0.001 ppm	Furan
32	2,3-Dihydrofuran	1191-99-7	0.001 ppm	Furan
33	2,5-Dihydrofuran	1708-29-8	0.001 ppm	Furan
34	2-Methylfuran	534-22-5	0.001 ppm	Furan
35	2,5-Dimethylfuran	625-86-5	0.001 ppm	Furan
36	2-Ethyl-5-methylfuran	1703-52-2	0.001 ppm	Furan
37	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	0.001 ppm	Furan
38	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	0.001 ppm	Furan
39	2-Pentylfuran	3777-69-3	0.001 ppm	Furan
40	2-Heptylfuran	3777-71-7	0.001 ppm	Furan
41	2-Propylfuran	4229-91-8	0.001 ppm	Furan
42	2-Octylfuran	4179-38-8	0.001 ppm	Furan
43	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	0.001 ppm	Benzene, Acetaldehyde, Furan
44	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	0.001 ppm	Furan, Acetaldehyde
45	Heptanenitrile	629-08-3	6 ppm	Acetonitrile, Propanenitrile
46	Hexanenitrile	628-73-9	6 ppm	Acetonitrile, Propanenitrile
47	Mercury	7439-97-6	0.025 mg/m^3	Not Tested[1]
48	Methanol	67-56-1	200 ppm	Formaldehyde
49	Methyl isocyanate	624-83-9	0.02 ppm	Formaldehyde, Acetaldehyde
50	Methyl nitrite	624-91-9	0.1 ppm	Formaldehyde
51	Nitrous oxide (N_2O)	10024-97-2	50 ppm	Nitrous oxide (N_2O)
52	N-Nitrosodiethylamine	55-18-5	0.0001 ppm	N-Nitrosodimethylamine
53	N-Nitrosodimethylamine	62-75-9	0.0003 ppm	N-Nitrosodimethylamine
54	N-Nitrosomethylethylamine	10595-95-6	0.0003 ppm	N-Nitrosodimethylamine
55	N-Nitrosomorpholine	59-89-2	0.0006 ppm	N-Nitrosodimethylamine
56	Pentanenitrile	110-59-8	6 ppm	Acetonitrile, Propanenitrile
57	Propanenitrile	107-12-0	6 ppm	Acetonitrile, Propanenitrile
58	Pyridine	110-86-1	1 ppm	Benzene, 2,4-Dimethylpyridine
59	Tributyl phosphate	126-73-8	0.2 ppm	1,3-Butadiene, Benzene
60	Dimethylmercury	593-74-8	0.01 mg/m^3	Not Tested[2]
61	2-Propenal	107-02-8	0.1 ppm	Formaldehyde, Acetaldehyde

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[1] The data to complete a preliminary assessment of MERSORB® performance was provided in the MERSORB® Mercury Adsorbents Bulletin 11B28-2012 "MERSORB® Mercury Adsorbents Design and Performance Characteristics" by NUCON International Columbus, Ohio.

[2] MERSORB® has also been evaluated for removal of dimethyl mercury and was selected as the best available control technology for mercury abatement (both elemental mercury and dimethyl mercury) in the AP stack (Evaluation of Best Available Control Technology for Toxics (tBACT) Double Shell Tank Farms Primary Ventilation Systems Supporting Waste Transfer Operations, RPP-ENV-46679, Rev. 0).

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