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Antifoam Degradation Testing

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August 2015

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EXECUTIVE SUMMARY

This report describes the results of testing to quantify the degradation products resulting from the dilution and storage of Antifoam 747. Antifoam degradation is of concern to the Defense Waste Processing Facility (DWPF) due to flammable decomposition products in the vapor phase of the Chemical Process Cell vessels, as well as the collection of flammable and organic species in the offgas condensate. The discovery that hexamethyldisiloxane is formed from the antifoam decomposition was the basis for a Potential Inadequacy in the Safety Analysis declaration by the DWPF.

Antifoam 747 is diluted twenty-fold in the Additive Mix Feed Tank in preparation for use. The diluted antifoam solution is stored up to thirteen days after preparation. During storage, the antifoam slowly decomposes to form flammable organic products. When the antifoam is added during processing, the degradation products quickly vaporize, causing a sharp peak in concentration in the offgas. Some of the degradation products are very soluble and collect in the condensate generated during processing.

Three sets of experiments were completed to determine the concentration of volatile degradation products in the undiluted antifoam, in the offgas during testing, and in the condensate. Over one-hundred tests were completed in order to investigate the degradation mechanism and the decomposition products of Antifoam 747. The following conclusions can be made from this testing.

- Antifoam 747 degrades to products that include the volatile and flammable components hexamethyldisiloxane, trimethylsilanol and propanal.
- Trimethylsilanol and propanal are soluble in the condensate and were found to have much lower concentrations in offgas that has been processed through the condensers and NH_3 scrubber.
- Minimizing or eliminating the time after antifoam dilution or utilizing undiluted antifoam will greatly reduce the concentration of antifoam degradation products associated with antifoam additions, but will not completely eliminate their formation resulting from slow degradation of the antifoam during processing.
- The antifoam degradation peak was measured four days after addition, simulating an outage just after an antifoam addition. After four days, the Sludge Receipt and Adjustment Tank was returned to boiling. The resulting peaks of antifoam degradation products were small and similar or lower in magnitude to the comparable peaks just after the antifoam addition (i.e. - relatively low). Based on the results of this test, there will not be a large peak as the result of a delay in processing.
- To avoid potential downstream impacts, discarded antifoam should not be combined with any of the streams that will be returned to the tank farm.
- The Antifoam 747 being used by DWPF (lots 413 and 613D) has not degraded appreciably based on comparison with new Momentive Silwet L-77.
- The SMECT and RCT condensate testing results were inconclusive in that the tests performed could not be extrapolated to the actual vessel air purge rates. Additional testing would be required to determine realistic degradation product release rates.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
AMFT	Additive/Mix Feed Tank
ARP	Actinide Removal Process
AVU	Analysis Validation Utility
CI	Confidence Interval
CL	Confidence Limit
CPC	Chemical Process Cell
DL	Detection Limit
DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condenser
FTIR	Fourier Transform Infrared Spectrometry or Spectrometer
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
HMDSO	Hexamethyldisiloxane
IR	Infrared
MCU	Modular Caustic Side Solvent Extraction Unit
MKS	MKS Instruments, Inc.
MWWT	Mercury Water Wash Tank
MS&E	Measurement Systems and Equipment
OGCT	Offgas Condensate Tank
PISA	Potential Inadequacy of the Safety Analysis
ppm	Parts Per Million by Mole or Volume in Offgas
RCT	Recycle Collection Tank
SB	Sludge Batch
SE2SME	Strip Effluent to Slurry Mix Evaporator
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TMS	Trimethylsilanol
TNX	TNX was location of DWPF Pilot Plants
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

Antifoam degradation is of concern to the Defense Waste Processing Facility (DWPF) due to flammable decomposition products in the vapor phase of the Chemical Process Cell (CPC) vessels, as well as the collection of flammable and organic species in the offgas condensate. The Savannah River National Laboratory (SRNL) has previously shown[1] that hexamethyldisiloxane (HMDSO) is formed from the antifoam decomposition. This finding was the basis for a Potential Inadequacy in the Safety Analysis (PISA) declaration by DWPF. This report documents the antifoam degradation experimental tests.

Bench-scale Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) demonstrations performed by SRNL since the late 1990's have utilized antifoam additions and monitored the concentrations of some offgases, but the test objectives were not focused on antifoam-related factors that influence the formation of degradation products in the offgas and the equipment could not measure these offgas species. Hence, additional targeted tests were necessary where the makeup, handling, and addition of the antifoam solution have been carefully controlled and the flammable offgas species were measured with the relatively new Fourier Transform Infrared Spectrometer (FTIR) prior to and after the condenser train.

Antifoam decomposes to form flammable organic products in the vapor phase and condensate of the CPC vessels. Previous simulant experiments had shown small quantities of the decomposition products in condensate samples, primarily hexamethyldisiloxane (HMDSO) with small amounts of trimethylsilanol (TMS). See the Antifoam Timeline below for references.

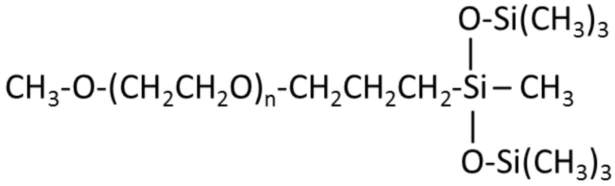
SRNL received a Technical Task Request (TTR) to determine variables that contribute to the generation of HMDSO.[2] In response, a Task Technical and Quality Assurance Plan (TTQAP) was developed that outlined a 3-phase approach to experimental testing to determine the peak HMDSO concentration resulting from antifoam decomposition.[3] The following objectives were identified for Phase-1 testing in support of the overall objective:

1. Determine the peak HMDSO concentration using the DWPF maximum antifoam addition rate based on the system design of 8 gpm.
2. Determine the peak HMDSO concentration using an addition rate of 30 gpm.
3. Determine the peak HMDSO concentration using an addition rate of 240 gpm.
4. Evaluate the impact of antifoam dilution on HMDSO concentration as a function of time.
5. Determine any antifoam degradation products in the offgas resulting from heating SME condensate at 50 and 70 °C.

After quantifying HMDSO in the initial series of experiments, it was noted that TMS and propanal were being removed by the offgas train (i.e., the condensers and scrubbers). Testing was expanded to sample the offgas directly from the SRAT/SME before the offgas train, which allowed quantification of HMDSO, TMS and propanal. In addition, testing was completed to quantify the antifoam degradation products in the raw antifoam and the degradation products if antifoam is added but no processing is completed until after a four day outage.

Antifoam Timeline

Antifoam 747 was invented by Dr. Darsh Wasan and Dr. Alex Nikolov as a replacement for Dow Corning 544. Antifoam 747 is currently produced by Siovation for DWPF by combining two Momentive wetting agents, Silwet L-77, 90% by mass, *n* ~ 8 and Y-17580, 10% by mass, *n* ~ 12. Note that Y-17580 is not a commercial product but is made as needed for DWPF. Both components are siloxane polyalkyleneoxides. The chemical structure of the two components is shown in Figure 1.1.



$$CH_3\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2CH_2CH_2\text{-}\underset{\displaystyle O\text{-}Si(CH_3)_3}{\underset{|}{\overset{\displaystyle O\text{-}Si(CH_3)_3}{\overset{|}{Si}}}} - CH_3$$

n = nominally 7-9 for Silwet L-77; n = nominally 11-13 for Y-17580

Figure 1.1. Chemical Structure of Antifoam Components Silwet L-77 (90%) and Y-17580

A brief timeline of antifoam use in DWPF is described below:

- 1988: Foaming and associated solids carryover was a notable problem encountered during Run #4 of the Full-Scale SRAT/SME at TNX, which resulted in a recommendation to DWPF to provide the capability to add antifoam periodically to both the SRAT and the SME.[4]
- 1989: Dow Corning 544 was chosen as the antifoam agent for SRAT and SME processing and was used until Antifoam 747 was deployed in November 2001.[4] Antifoam is added in the SRAT and SME to mitigate foam generation during acid addition and boiling of these vessels and the associated solids carryover and reduction in decontamination factor.
- 1995: Foam-over in run 16 of DWPF cold chemical runs.[5]
- 1997-1998: Three foam-overs in DWPF radioactive runs.[6]
- 1999: Extensive testing of antifoam 747.[7]
- 2000: Evaluation of irradiated and non-irradiated Antifoam 747. The results of these tests indicated antifoam decomposition products were present in the SRAT and SME condensates. Although these products were not identified based on molecular structure, the possibility of these products returning to the Tank Farm and concentrating in the Waste Evaporators is discussed.[8]
- 2003: The antifoam addition strategy was revised based on Sludge Batch (SB) 2 simulant testing. This addition strategy required a 200 mg/kg antifoam (34 gallons DWPF scale) addition prior to acid addition, 500 mg/kg (85 gallons DWPF scale) prior to boiling in the SRAT, and 100 mg/kg (17 gallons DWPF scale) prior to boiling in the SME.[9]
- 2004: Analyses of DWPF Slurry Mix Evaporator Condensate Tank (SMECT), Offgas Condensate Tank (OGCT), and Recycle Collection Tank (RCT) samples indicated the presence of silicon. The silicon was primarily attributed to antifoam degradation products in the condensate.[10]
- 2005: Analytical results of samples collected during SB4 simulant flowsheet studies with Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU) showed antifoam degradation products in all samples (dewater, condensate, and slurry). The compounds detected ranged from “the simplest siloxane to some of the modified siloxanes that are present in the antifoam”.[11]
- 2011: Previously reported data[7,8] from simulant tests were reviewed. A material balance based on SMECT samples post SRAT and SME was calculated which determined that 14% of the antifoam silicon added to the SRAT and 22% of the antifoam silicon added to the SME was partitioned to the offgas condensate.[12]

- 2011: DWPF issued a Potential Inadequacy in the Safety Analysis (PISA)[13] based upon an increase in Melter Offgas flammability resulting from increased antifoam additions.[14] During this timeframe, SRNL was performing flowsheet studies to determine the impact of the Next Generation Solvent on the CPC process. Additional analyses were performed to determine antifoam partitioning in the SRAT and SME. Results qualitatively identified antifoam degradation products in condensate samples.[15]
- 2011: During SB7b simulant flowsheet testing, scoping samples were obtained in an attempt to learn more concerning the fate of antifoam during the CPC process. These samples included the SRAT dewater condensates analyzed for Si. In addition, hexane extractions were performed on SRAT and SME dewater condensates, the Mercury Water Wash Tank (MWWT) and Formic Acid Vent Condenser (FAVC) condensates removed following the SRAT and SME cycles, SME product slurry, and the ammonia scrubber solution. Various compounds potentially related to antifoam were found using semi-volatile organic analysis and volatile organic analysis on the hexane extractions and hexane rinses. These included siloxanes, TMS, methoxytrimethylsilane, HMDSO, aliphatic hydrocarbons, dioctyl phthalate, and emulsifiers.[16]
- 2012: The FTIR was first used to monitor offgases from some of the SB8-A and SB8-B (SB8 with Tank 12) series of CPC simulations. HMDSO was seen in these tests, but its significance as a flammable gas was not recognized.
- 2013: The fate of organic compounds, namely glycolic acid and Antifoam 747, was examined using simulated SME product. Low concentrations of methylsiloxane products and polyethylene glycol fragments were observed.[17]
- 2013: Simulated SRAT/SME cycles were performed using the formic-nitric acid flowsheet for SB8 simulants. Offgas analysis using by FTIR spectroscopy detected HMDSO, which was reported.[18]
- 2015: Simulant studies were performed to support a flowsheet change to add strip effluent to the SRAT or SME using the SB8 formic flowsheet. During testing, hexamethyldisiloxane was detected using FTIR.[19] This was the first mention that HMDSO was potentially flammable.

2.0 Experimental Procedure

Antifoam testing was performed at the Aiken County Technology Laboratory (ACTL). Three types of tests to quantify antifoam degradation products in the offgas were completed as part of this study: 1) SME product testing; 2) condensate testing; and 3) undiluted antifoam testing.

The experiments were performed using GN78 SME product, strip effluent to SME (SE2SME) blended condensate, and various antifoam samples. Information for each of these solutions is discussed below.

The GN78 SME product was chosen because a large quantity of this material was available. Run GN78 was a 220-L scaled glycolic-nitric flowsheet test. The GN78 SME product used in experiments had been stored in sealed carboys. This slurry was produced the week of September 15, 2014 and included seven 100 mg/kg antifoam additions (Lot 613S). The SME product composition is summarized in Table 2.1. Complete analytical results are documented in the eNotebook.[20]

Table 2.1. GN78 SME Product Composition

Run	**Result**
Total Solids, wt %	49.67
Insoluble Solids, wt %	37.23
Calcined Solids, wt %	39.46
Soluble Solids, wt %	12.44
pH	5.55
Slurry Density, g/mL	1.40
Supernate Density, g/mL	1.15

The SE2SME condensate was produced by blending all remaining condensates collected during SRAT/SME simulant testing using the Nitric/Formic Acid Flowsheet (a blend from runs SB8-D6 to SB8-D9). The condensate was produced the weeks of November 11 and December 1, 2014 and included sixteen 100 mg/kg antifoam additions (Lot 613S). The condensate has been stored in sealed carboys since the completion of the SE2SME testing. The condensate samples produced during the runs were analyzed for anions, pH and density and results are recorded in the report.[21] In the current work, a blended condensate was analyzed for pH, HMDSO, TMS, and propanal.
Two DWPF lots of antifoam 747 were tested during these experiments. A lot of antifoam, 110684-0*413*, referred to as *413* throughout the report, was produced by Siovation for DWPF on 4-13-2011. This older lot of antifoam has been in use in DWPF since 2011. An unopened pail of this lot was shipped to SRNL. A sample was pulled from the pail and this sample was used for all lot *413* antifoam tests.

A second lot of antifoam, 111128-0*613*, was produced by Siovation for DWPF on 6-13-2011. There are two samples of this antifoam that were used in SRNL experiments. SRNL has an acceptance sample that has been used since 2011 (referred to as *613S*). There was concern that this sample had degraded during storage, so an unopened pail of lot *613* was shipped to SRNL. A sample was pulled from the pail and this sample was used for some lot *613* antifoam tests. This fresh sample is referred to as lot *613D* in this report.

A fresh sample of Momentive Silwet L-77 was shipped on June 4, 2015. This sample was used in several tests to compare the concentration of degradation products in the fresh sample to antifoam that was four years old. Silwet L-77 makes up 90 wt% Antifoam 747.

The SME product testing, condensate testing and undiluted antifoam testing are described in the following sections.

2.1 SME Product Testing to Determine Antifoam Degradation Products in Offgas

Testing was performed to detect and quantify antifoam degradation products in the offgas after the addition of antifoam to SME product at boiling. The initial testing used a typical offgas train (Figure 2.1) consisting of a condenser, ammonia scrubber, and FAVC.

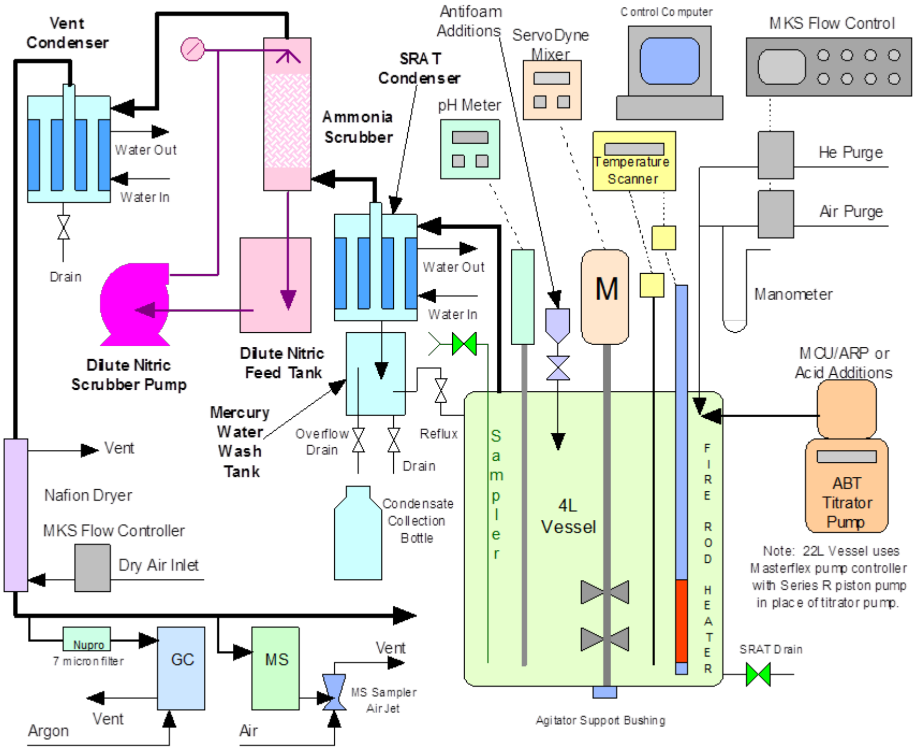


Figure 2.1. Original Test Equipment with Ammonia Scrubber

The testing equipment was changed because the condensers and scrubbers were removing condensable and soluble offgas species from the offgas such that their evolution rate could not be determined by the analyzers. Two additional offgas trains were developed based on the customer's need for analysis of the offgas directly from the SRAT/SME vessel.

In much of the subsequent testing, the offgas exiting the vessel was routed directly to the FTIR through heated offgas lines, then through the condenser and FAVC (Figure 2.2). In other tests, the offgas exiting the vessel was routed directly to the condenser and FAVC and then to the FTIR (Figure 2.3). Both of these offgas trains bypassed the ammonia scrubber due to pressure fluctuations that caused over-pressurization of the vessel and venting the offgas into the hood rather than into the offgas equipment.

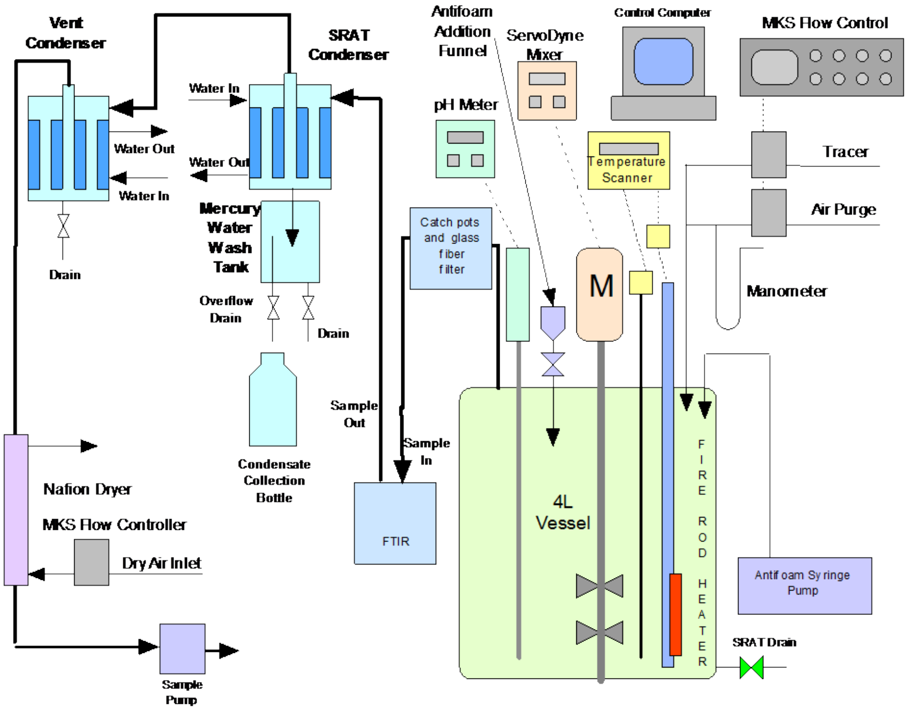


Figure 2.2. Test Equipment Configured to Sample Directly from SRAT Vessel

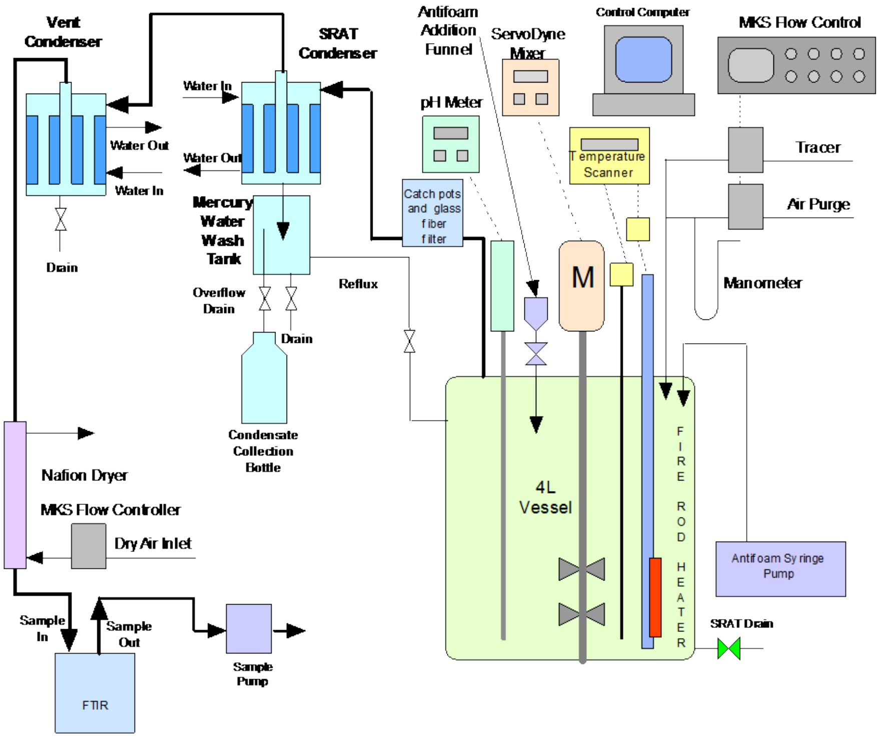


Figure 2.3. Test Equipment Configured to Sample after Condensers

For SME product experiments, 3.5 L of glycolic-nitric flowsheet GN78 SME product was used. Results using this SME product should be applicable to both the formic-nitric flowsheet and the glycolic-nitric flowsheet. Antifoam was added at several concentrations: pure antifoam, a 1:10 (antifoam:solution) dilution, and a 1:20 dilution. The air purge rates were adjusted as necessary without regard to scaling to keep the system pressure under control; for most runs, a prototypic SRAT air purge could be maintained. The prototypic SRAT air purge rate was determined from the ratio of the DWPF SRAT purge (230 scfm) to the DWPF nominal SRAT batch size (6000 gal). For both systems, this ratio was 0.286 L/min air per L of slurry. Boilup rates were scaled based on a DWPF rate of 5000 lb/hr condensate generation. This boilup rate is conservative for antifoam degradation testing as the typical DWPF SRAT boilup rate is 2700 lb/hr. The SME product had a pH of 5.84 at 25˚C.

The 4-L laboratory scale equipment designed for SRAT/SME flowsheet testing[22] was modified for antifoam addition testing. Teflon® tubing was used to route the offgas from the SRAT vessel into a J-KEM® reaction station (a heated block) and a microfiber filter cartridge (Balston 33S6 BX) heated to 120 °C. The reaction station was heated to 120 °C and held two catchpots for entrained water. These catchpots with the filter prevented any entrained offgas liquids and solids from continuing downstream. A 10 foot sample line (MKS Model 2385S) heated to 150-175 °C was used to route the offgas from the filter cartridge to either the FTIR or the SRAT condenser.

Connecting the heated sample line directly to the FTIR allowed for offgas analysis directly from the SRAT vessel (Figure 2.2). When routed from SRAT vessel to the SRAT condenser, the offgas passed through the SRAT condenser, FAVC, and Nafion® dryer prior to be analyzed (Figure 2.3).

The pressure drop across the cartridge filter required the use of a pump to pull a vacuum through the rest of the system. Otherwise, pressure build up in the SRAT vessel would result in the offgas exiting through the offgas manometer. Antifoam was added using a 15 mL pressure equalized addition funnel mounted to the SRAT vessel lid or using a syringe pump. For some tests, either an N_2O or CO tracer was added to the air purge to allow back calculation of the water concentrations in the gas samples.

Because the sample lines were heated to 150-175 °C and the FTIR optical cell to 191 °C, it is possible that some degradation of the organic species could occur. If TMS or propanal had been degraded, the resulting smaller organic species would have been seen by the FTIR. No such compounds were seen. The degradation that would be most possible would be for HMDSO, in the presence of water, to decompose to form two TMS molecules. The possible extent of such a reaction is not known. Testing with a pure HMDSO standard and water would be needed to determine if this degradation could occur.

2.2 Condensate Testing

Condensate testing was completed to determine the concentration of antifoam degradation species in the offgas of the SMECT or RCT. No antifoam was added during the condensate testing. A volume of 1.6 L of condensate was put into the vessel for each test. The pH of the blended condensate was 2.4 at 25 °C (pH requires correction for electrode temperature effect so pH reads 1.7 at 50 °C and 1.1 at 70 °C). The offgas system configuration shown in Figure 2.2, sampling before the condenser train, was used.

For the first set of tests, three different temperature/pH combinations were utilized. To simulate RCT condensate, the condensate was heated to 50 °C and was analyzed for an hour. To simulate the SMECT, the temperature was then increased to 70 °C and again analyzed for an hour. After completion of the 70 °C testing, sodium hydroxide was added to increase the pH to 11.2 at 25 °C (pH requires correction for electrode temperature effect so pH reads 11.9 at 50 °C and 12.5 at 70 °C). The vessel was cooled to 50 °C, to simulate the RCT after a caustic addition. The condensate temperature was held at 50 °C for an hour while the offgas was analyzed by the FTIR.

Since the same condensate was used for all of the above testing combinations, the volatile species were depleted over time and the results of the testing underestimated the subsequent offgas peaks for the antifoam decomposition products from the subsequent tests the same day. As a result, a second test was completed to determine the offgas decomposition products at 70 °C with fresh condensate. The condensate was heated to 70 °C and then was analyzed for 3 hours. Note that no caustic was added during this testing and no other testing was performed on that condensate.

2.3 Undiluted Antifoam Sparge Testing

The sparge testing was performed by bubbling inert gas (argon was used for Lot *413*, nitrogen used for Lot *613D* and Silwet L-77) through sintered glass into approximately 50 grams of undiluted antifoam at ambient temperature. An MKS mass flow controller regulated the gas flow to 100 sccm. The offgas from the headspace was directed to the FTIR for analysis. Testing was conducted for approximately two to six hours. See Figure 2.4 for the equipment setup.

Figure 2.4. Antifoam Sparging Setup

2.4 Offgas Sampling Equipment

The concentrations of HMDSO, TMS, and propanal were analyzed by FTIR (MKS MG2030). The FTIR utilizes a library calibration database and no external calibration is required. The FTIR can also quantitatively measure CO, CO_2, NO, NO_2, N_2O, H_2O, and NH_3 concentrations. Neither NO nor NO_2 was detected in these tests. CO and N_2O were only detected when they were used as tracers.

2.5 Identification and Quantification of Antifoam Degradation Products

Some possible decomposition pathways for Antifoam 747 have been previously reported.[1] HMDSO is potentially formed by the reaction of two antifoam molecules to form one polymeric siloxane ethoxylated derivative molecule and one HMDSO molecule.[23] TMS and propanal have also been found to be decomposition products. The structures and some properties of HMDSO, TMS, and propanal are shown in Table 2.2.

Table 2.2. Antifoam Degradation Products

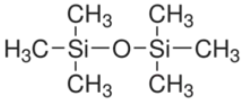
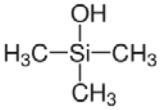
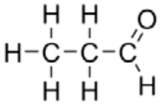
Compound	Formula	Structure	Molar Mass, g/mol	Solubility in water	Lower Flammability Limit, vol %	Boiling Point
Hexamethyl disiloxane (HMDSO)	$C_6H_{18}OSi_2$		162.38	0.933 mg/L @ 23 °C[24,25]	0.8[26]	100 °C
Trimethyl silanol (TMS)	$C_3H_{10}OSi$		90.20	35 g/L @ 25 °C [27]	1.45[26]	99 °C
Propanal	C_3H_6O		58.08	310 g/L @ 25 °C[28,29]	2.6[26,30]-2.9[31,32]	46-50 °C

Figure 2.5 displays overlaid IR spectra for compounds of interest in this study: water (dark green), TMS (light green), HMDSO (dark purple), and propanal (light purple). Due to the structural similarities of HMDSO and TMS, simultaneous resolution of the IR spectral features of these species was inaccurate in some circumstances when using the MKS FTIR automated software. This inaccuracy was most apparent when the HMDSO concentration was of similar magnitude or larger than the TMS concentration and resulted in high detection limits and uncertainties. As shown in Figure 2.5, TMS has a distinctive IR spectral feature at about 3750 cm^{-1} that is obscured by water. Similarly, propanal has a unique strong peak at about 1750 cm^{-1} that is also obscured by water. The distinctive TMS peak at about 920 cm^{-1} was used to identify TMS. The propanal peaks between 2600 and 2850 cm^{-1} were used and are unique but relatively weak, resulting in high detection limits and uncertainties. The HMDSO peak at 1075 cm^{-1} is unique and strong so HMDSO has the best detection limits and uncertainties.

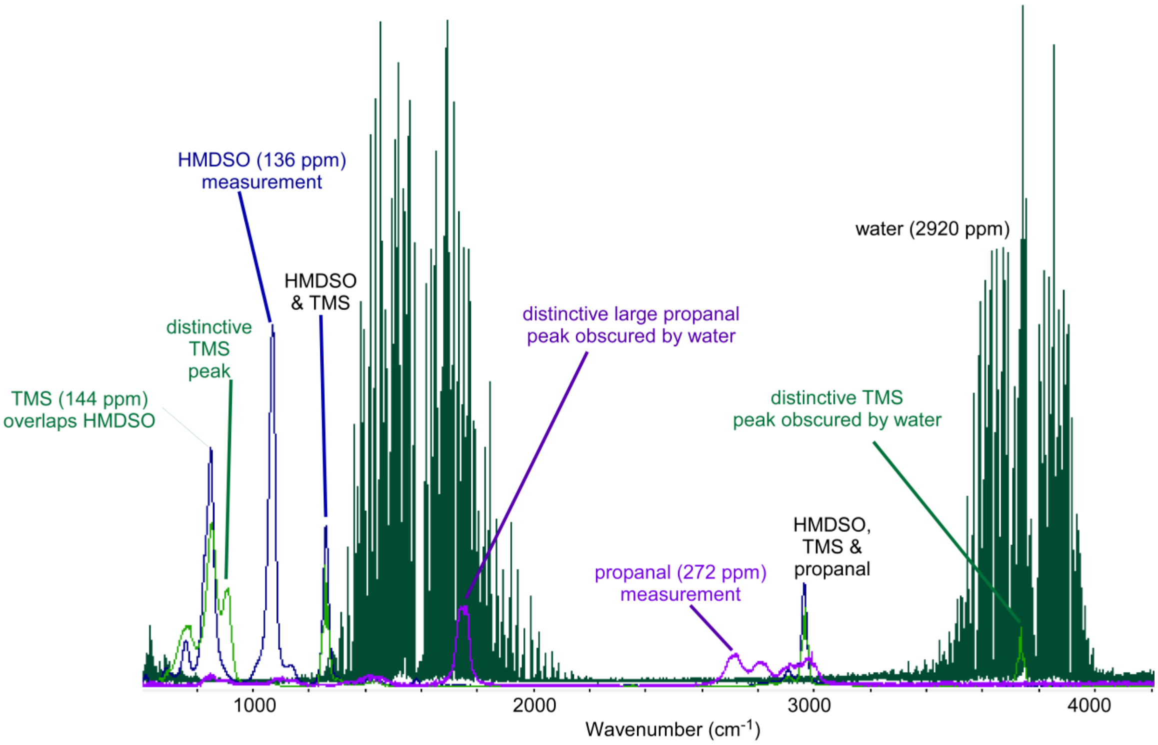


Figure 2.5. **IR Spectra for HMDSO, TMS and Propanal**

To achieve satisfactory quantification of the unique features of the three compounds and accurately determine the concentrations of each species, two different comparative analyses were performed: the MKS Analysis Validation Utility (AVU) and the Excel methods. The AVU method utilized quantification software provided by the instrument manufacturer (MKS) that uses calibration spectra (generated by MKS) to account for overlap in the species of interest. The software utilizes ASTM method D6348[33] and EPA Method 320[34] to perform statistical analysis of the spectral data and generate detection limits (DL) and confidence limits (CL). The detection and confidence limits are MKS specific and are calculated from the statistical measures in D6348. The MKS confidence limit approximates to a 95% confidence interval. In addition to measuring the species of interest, the FTIR also measured the concentrations of N_2O and CO tracers that were sometimes used, and the concentrations of CO_2, NH_3, and water.

The Excel method involved mathematically combining the pure compound calibration spectra of the species of interest and determining a least squares fit to the observed spectral data. The Excel and AVU methods were shown to agree within the confidence limits except in the cases where the AVU method was unable to resolve the concentration of TMS; in these cases the agreement between the HMDSO values was good. The detection limits determined by the AVU method matched qualitatively with the estimated detection limits in the Excel method.

The presence of water in the sample significantly affects the ability to measure HMDSO, TMS, and propanal. HMDSO is the least affected because water interferes minimally. Water interferes more with TMS, and the combination of high water concentration and relatively high HMDSO makes TMS more difficult to measure. The propanal signal, at the only unique wavenumbers, is relatively weak and has some interference from water.

Water is a common interference in interpreting IR spectra, so in order to quantify the HMDSO, TMS and propanal, the spectrum of water has to be subtracted from the sample spectra. The AVU software simultaneously subtracts the spectrum of each component from the sample spectrum to get the best overall fit. The sample spectrum minus the reference spectra should result in zero signal across the measurement wavenumbers. Successful accounting for the water spectrum depends on the calibration reference spectra used in the data processing.

Sampling before the condenser significantly increased the level of water vapor present during the analysis; in most cases at a lab-scale boilup rate of around 6 g/min and a purge rate of 1 L/min, the concentration of water was >80%. Due to the exceptional ability of water to absorb IR, this presented a significant challenge to quantifying the relatively low concentrations of any other species. Using the AVU software, the water could be entered as an interference by choosing the calibration spectra that most closely estimated the predicted water content based on the boilup rate and purge flow.

During early testing with the ammonia scrubber in the offgas train, only HMDSO was detected because all of the TMS and propanal and most of the water were removed by the offgas train. The data analysis was then simplified since no correction was needed for water and there was no interference from TMS. In these tests, both the AVU and Excel methods agreed well. In all cases, including when significant water was present, the DL and CL values for HMDSO were 3 ppm or less. Later tests that measured the composition of the offgas after the condenser train but without the ammonia scrubber installed qualitatively found TMS and propanal in addition to quantifiable HMDSO. In tests where the offgas composition was measured before the condenser train HMDSO was easily quantified but TMS and propanal were more difficult due to the water interference.

The MKS-supplied calibration spectra were generated on a spectrometer with a longer optical path length of 511 cm versus the SRNL version with a 35 cm length. This means that the absorbance of reference spectra are actually 511/35 = 14.6 times higher than the tabulated value. This difference can generally be accounted for mathematically. However, when a compound is present at high concentration in the shorter path length SRNL unit, the shape of the spectral features is broadened such that they do not fit the standard spectra well. An example is for water at 85% in the SRNL unit. The closest standard spectrum would have a concentration of 85/14.6 = 5.82%. A 5.82% water sample is a low concentration and would have relatively narrow spectral features. The actual 85% sample in the SRNL unit would have much broader features, so use of a 5.82% calibration from a 511 cm cell cannot completely account for the water spectrum. Therefore, an SRNL generated spectrum of approximately 85% water in air was used to subtract the effect of water at high concentrations. Since the water content was not exactly controlled, water concentrations determined using this “calibration” are only qualitative and probably have an error of about 5% water. At lower concentrations (below 30%), either a % calibration or a ppm calibration were used as standard spectra as appropriate.

In the Excel method, the water calibration spectra were used similarly. Depending on the water concentration, the standard water calibration spectrum that most closely matched the estimated levels could be subtracted directly from the observed spectrum to reduce the presence of the features due to water. Following water subtraction, baseline corrections were made when the baseline (where there should be no spectral features) was observed to be some value other than zero absorbance. Baseline corrections were made by increasing or decreasing the absorbances in a given range so that the signal where it should be zero is set to zero.

When antifoam additions were being performed, it was often possible to take a spectrum observed before the addition during some steady state, and subtract it from the peak concentration spectrum to be analyzed. This subtraction of the closest approximation of baseline conditions before the addition was usually more accurate than subtracting a reference spectrum. The only drawback to this method was when successive additions had been performed one after another. As more antifoam is added to the same material, the baseline offgas concentration for the species of interest remains slightly elevated even after allowing time to return to somewhat of a steady state. Therefore, subtraction of a spectrum before a later addition actually subtracts a small amount (about <2 ppm) of the desired spectral features along with the undesired water features. With the levels of uncertainty in the calculations, subtractions of this magnitude were deemed to be inconsequential to the overall concentrations determined as long as the baseline shift due to successive additions remained low (<5ppm).

In the Excel method, once the water features had been accounted for, the resolution of the other species was a matter of manipulation of the calibration spectra of the pure compounds. In the AVU, the software takes into account the interference spectra (specifically the species you believe to be present but are undesired for analysis: in this case, water, CO_2 and ammonia) and the desired analytes and generates concentrations, detection limits, confidence limits and residual spectra. To verify the AVU software was effectively separating out the interfering species, the AVU values were compared to the Excel method. When the HMDSO concentration is high and TMS concentration is low (but non-zero), the AVU method tends to overestimate the TMS concentration by fitting the residual spectra to noise. In these cases, checking the results versus the Excel method was definitely required.

In the Excel method, the water-subtracted, baseline-corrected spectrum was overlaid by the sum of the concentration adjusted spectra of the HMDSO, TMS, and propanal. Specifically, the absorbance values of each reference spectrum were multiplied by a variable value (coefficient) and the sum of all calculated absorbances were compared to the sample spectrum absorbances. From the best fit values, the concentration of each species was then the reference spectrum concentration multiplied by the coefficient. The coefficients were varied until the lowest least squares value was reached or the best visual estimation was achieved. The more conservative of the values was chosen to account for the level of uncertainty in the calculations.

The tracer gas method for determining water concentration used a known addition of N_2O or CO to the air purge. The concentration of water in the offgas is then determined:

$$W = \frac{T - C_T\ (T + A)}{C_T}$$

where W = water (sccm)
T = tracer (sccm)
A = air purge (sccm)
C_T = measured concentration of tracer in gas sample (mol frac)

$$C_{H_2O} = \frac{W}{W + A + T}$$

The water concentration in the samples was determined by several methods. For sampling after the condenser or during the condensate tests at 50 and 70 °C, the water concentrations from the AVU and tracer gas were used. The condensate values were generally about 80% of saturation for the given temperature, which when combined with the 1 L/min air purge are reasonable values.

For sampling before the condenser, there were three methods to estimate the water concentration. The AVU software provided a rough value for water. The water boilup rate was measured manually by collecting a volume of condensate over a known time period. The tracer gas concentration was measured and the tracer gas dilution was used to calculate the water concentration. The water concentration was then the moles of water divided by the sum of the moles of water and the air purge.

The as-analyzed wet basis concentrations reported for HMDSO, TMS and propanal include the estimated half widths of the two-sided 95% confidence intervals (CI). For tests at boiling, the water concentration reported is the average of the value calculated from measuring the condensate rate and from a tracer gas dilution calculation; the uncertainty was taken to be 2 times the standard deviation. The FTIR was also used to estimate the water concentration, but at 85-90% water the FTIR values have higher uncertainty. Overall, the FTIR values were within a few percent of the values from the boilup rate and the tracer gas calculations.

Dry basis concentrations for HMDSO, TMS, and propanal are reported so that values obtained at different water contents can be directly compared. Further discussion of the rationale for reporting the dry basis values is given in Section 3.1. The estimated uncertainty in the dry basis values is a combination of the uncertainty in the measured species value and the measured water value. The dry basis concentrations were calculated as follows:

$$C_{\text{dry basis}} = \frac{C_{\text{measured, wet basis}}}{1 - C_{H_2O}}$$

$$C_{H_2O} \approx \frac{\text{boilup rate (scfm)}}{\text{(boilup rate + air purge rate) (scfm)}} \text{ or from tracer gas calculation}$$

The combined absolute uncertainty $U(C_A^{dry})$ in ppm is:

$$U(C_A^{dry}) = \sqrt{\left(\frac{\Delta C_{H_2O}}{1 - C_A^{wet}}\right)^2 + \left(\frac{C_{H_2O}\ \Delta C_A^{wet}}{\left(1 - C_A^{wet}\right)^2}\right)^2}$$

where C_A^{dry} = species A dry concentration
C_A^{wet} = species A wet concentration
ΔC_A^{wet} = absolute uncertainty in species A wet concentration
ΔC_{H_2O} = absolute uncertainty in water concentration

Future improvements to the measurement of these gases exiting the SRAT/ SME vessel should be considered. Decreasing the water vapor to inert gas ratio by decreasing the boilup rate or increasing the air purge rate should be investigated. Use of equipment such as a heated Nafion® dryer to remove water to low levels should be tested. It would have to be demonstrated that the Nafion® dryer did not remove any of the degradation product species as it removes water. Alternative analytical methods should be examined such as online Raman spectroscopy or using the existing mass spectrometer with calibration gases. Mass spectrometry would not have interference from water, but would need calibration gases that were not required for the FTIR.

2.6 Calculation of Flammable Gas Generation at DWPF Scale

2.6.1 *Scaling Factors for Antifoam Addition to the SRAT/SME*

For laboratory scale SRAT/SME runs, the amount of fresh sludge used and the air purge rates used are scaled to the corresponding DWPF values. For a given volume of sludge at the laboratory scale, this volume scaled to the DWPF fresh sludge volume of 6000 gal is used to scale the air purge rates. The reason for scaling on the fresh sludge volume is that it is this material that generates the offgases, including hydrogen, that are a significant focus of the experimental work. By scaling in this manner, the offgas concentrations from the lab-scale tests should be the same as the DWPF values. This assumption assumes that the effect of the SRAT and SME heels are negligible. These values are compared in Table 2.3.

Table 2.3. Comparison of DWPF and Lab-Scale Parameters for SRAT/SME Runs

Quantity	DWPF Value	Lab-Scale Value	DWPF/Lab Scale Ratio
Fresh Sludge Volume	6000 gal	3.5 L (example)	6490
SRAT Air Purge Rate	230 scfm	1.00 L/min	6510

This is the scaling ratio that was used for the antifoam testing. However, upon further examination of what parameters affect the concentration of flammable gases from antifoam degradation, it was determined that the sludge volume basis was not the correct basis. The flammable gas concentrations do not depend on the sludge volume; they depend on the ratio of the amount of antifoam added to the air purge rate. The amount of flammable gases generated from an antifoam addition to sludge will be, for the most part, independent of the amount of sludge present. A more correct basis for scaling from DWPF to lab-scale would be to scale the antifoam addition amount to the air purge to be the same.

The nominal DWPF addition of 100 mg/kg is based on the full volume of the SRAT after fresh sludge is added to the heel. This volume is 7500 gal. At an approximate density of 1.14, this is 32,365 kg, so a 100 mg/kg antifoam addition would add 3236.5 g of undiluted antifoam, which is equal to 0.855 gal. At the historical antifoam dilution ratio of 1:20, this is a 17.1 gal addition. Ratioing the antifoam addition to the air purge is shown in Table 2.4.

Table 2.4. Comparison of DWPF and Lab-Scale Parameters for Antifoam Addition Testing

Quantity	DWPF Value	Lab-Scale Value
100 mg/kg Undiluted Antifoam Addition	0.855 gal	0.497 mL (g)
SRAT Air Purge Rate	230 scfm	1.00 L/min
Addition Volume to Purge Ratio (mL or g)/(L/min)	Target: 0.497 (0.00372 gal/scfm)	Target: 0.497 Actual: 0.355
Diluted Antifoam Addition Rate to Purge Ratio (mL or g)/min/(L/min)	0.00465 (0.0348 gpm/scfm)	0.00474

The actual SRNL additions were, due to an oversight, calculated to be 100 mg/L, or 0.355 g of undiluted antifoam. The lab scale additions were approximately 70% of the intended 100 mg/kg additions. Therefore, they were effectively 70 mg/kg additions.

At the approximate highest possible DWPF addition rate of 8 gpm of 1:20 diluted antifoam, the addition time is then 128.25 s. The lab-scale addition was 7.1 mL in 90 s, or a rate of 4.74 mL/min. Therefore, the lab-scale addition rate was equal to the DWPF addition rate within 2%.

Overall, the lab-scale additions were performed at the same rate as DWPF relative to the air purge, but only 70% of the targeted amount was added.

2.6.2 *Scaling of Lab-Scale Data to DWPF Scale*

The lab-scale peak concentration data are reported in units of "mol/min/g undiluted antifoam added" where the mol unit may be in mmol or μmol. Reporting the data in this way makes it independent of the purge rate in the vessel. These rates are calculated from the measured peak concentrations and the air purge rate:

$$\frac{\frac{\text{mmol G}}{\text{min}}}{\text{g antifoam}} = \frac{C_G \times 10^{-6}\,\frac{\text{mol frac}}{\text{ppm}} \times F\,\frac{\text{std. L}}{\text{min}} \times \frac{\text{mol offgas}}{22.414\text{ L}} \times \frac{\text{mol G}}{\text{mol offgas}} \times \frac{1000\text{ mmol}}{\text{mol}}}{\text{A g antifoam}}$$

C_G = measured peak concentration of TMS, HMDSO or propanal, ppm
F = air purge flowrate, std. L/min
A = grams undiluted antifoam added

To calculate the concentration in the SRAT or SME, only the amount of antifoam added and the purge rate is needed and the above calculation is reversed to determine the concentration.

This calculation of the concentration directly applies only to the same antifoam addition ratio that was used in the testing: 70 mg/kg. For actual additions of 100 mg/kg in the SRAT or 50 mg/kg in the SME, the mol/min/g antifoam values tabulated would be used to calculate the peak concentrations, with the following caveats:

The flammable gas concentrations versus time during an antifoam addition at a scaled rate of 8 gpm or lower had several general characteristics. The time from the start of the concentration increase until the peak concentration was always almost exactly equal to the addition time, showing that the start of gas generation was immediate. The gas generation immediately decreased upon completing the antifoam addition. The shapes of the peaks were nonlinear, with the rate of increase slowing in time as shown in Figure 2.6 for an addition of 70 mg/kg antifoam. This concentration profile is typical of what was found during testing, with some graphs having more and some having less nonlinearity.

The peak value for the 70 mg/kg addition was 306 ppm. Extrapolation to 100 mg/kg by multiplying by 100/70 gives about 437 ppm, but extrapolation of the slope of the concentration versus time gives a smaller value, 365 ppm. Therefore, it appears that extrapolation of the experimental data to higher addition amounts will be conservative. Note that extrapolation of the rates will follow the same trends as the concentrations.

However, extrapolation to lower addition amounts by ratioing is not conservative. Ratioing to a 50 mg/kg addition by 50/70 would give 218 ppm. Using the actual concentration versus time curve gives a value of 255 ppm because of the nonlinearity of the concentration profile.

As this graph is just one example, further examination of the existing experimental data would be needed to better quantify the values that should be used for a 50 mg/kg addition. To remain conservative, the 70 mg/kg concentration or rate value should be used for any smaller additions.

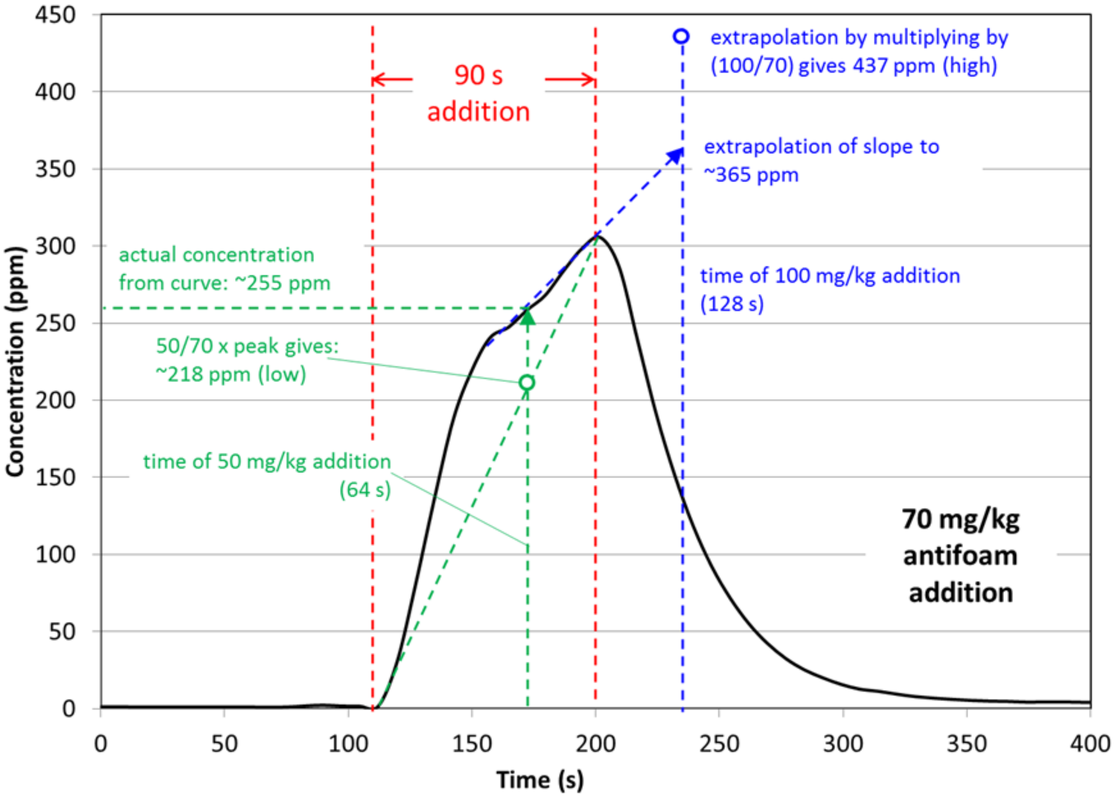


Figure 2.6. Typical Antifoam HMDSO Peak versus Time

2.6.3 *Scaling of Condensate Release of Flammable Gases Data*

The release of flammable gases from SRAT/SME condensate was studied by measuring the gases generated from heating a specific volume of condensate to a specified temperature. These tests were performed with two different (non-prototypic) air purge rates. The purge rate for the DWPF SMECT is 12 scfm and for the RCT it is 7 scfm. Lab-scale flowrates scaled to these low rates were deemed to be too small for operation of the offgas sampling system.

Just as the SRAT and SME source terms for reaction gas evolution (e.g., H_2, CO_2) are dependent on the amount of sludge, the SMECT and RCT source terms are also proportional to the amount of liquid in the tank, so scaling should be done relative to the tank inventory. The data are reported in units of "µmol/min/L of condensate" so that the data can be extrapolated from the lab-scale to DWPF scale. The proposed scaling would just involve multiplying the µmol/min/L values measured by the L of condensate in the DWPF vessel.

However, the scaling from lab-scale to DWPF scale did not turn out to be this simple. It was found that the evaporation rate of TMS was dependent on the air purge rate, so simple extrapolation could give extremely over-conservative high values.

Additional experimental work would be required to resolve this issue.

2.7 Quality Assurance

Requirements for Software Engineering and Control are established in manual 1Q 20-1 and E7 5.01. The FTIR and its software are not part of the MS&E program. The FTIR software and the AVU software have not been documented in the software QA program. To validate the FTIR data, a cross check of the calculations is completed by comparing the results of the AVU software to the Excel method.

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

Tests were performed to determine the cause of the high HMDSO concentration detected in SRAT/SME testing, to determine the concentration of flammable decomposition products in the condensate, and to determine the concentrations of HMDSO, TMS and propanal in the undiluted antifoam. As described in Section 2.1, the initial testing utilized the typical 4-L SRAT/SME offgas system including a condenser, ammonia scrubber and FAVC prior to offgas analysis. This setup removed the two soluble species TMS and propanal. As a result, only the HMDSO concentration will be reported from these tests and these concentrations are biased low due the apparent removal of some HMDSO in the offgas system. In later testing, the FTIR sampled directly from the SRAT/SME vessel and heated sample lines were used to allow measurement of HMDSO, TMS, and propanal. In each subsection, it will be clearly stated whether the data is HMDSO only or includes all three components.

This testing was designed to measure:

1. HMDSO, TMS and propanal resulting from use of diluted antifoam mixtures as a function of time after dilution
2. HMDSO, TMS and propanal that can be released upon restart after a facility outage
3. HMDSO released, comparing antifoam addition methods
4. HMDSO released, comparing antifoam addition rates
5. HMDSO released, comparing mixed and unmixed antifoam solutions
6. HMDSO, TMS and propanal in undiluted antifoam released by sparging
7. HMDSO, TMS and propanal released by heating SB8 Condensate Blend

3.1 Generation of Flammable Gases from Addition of Antifoam to SME Slurry at Boiling – Effect of Storage Time after Mixing

Testing was completed to measure the HMDSO, TMS and propanal in the offgas during boiling operations in the SRAT or SME after diluted antifoam is added. The testing utilized the equipment with heated sample lines that allowed analysis of the offgas exiting the SRAT vessel prior to any condensation. As a result, the quantification of HMDSO, TMS and propanal could be completed to determine the effect of storage time after mixing on the generation of flammable gases.

Both antifoam lots 413 and 613D were added to SME slurry at boiling after diluting 1:20 with water and storage from 0 to 31 days. All additions were 101 mg/L (0.355 g of undiluted antifoam, into 3.5 L of SME slurry). The offgas composition was monitored by FTIR both before and after the SRAT/SME condenser train in different runs, but not concurrently. The results for antifoam 413 from zero to 31 days, and antifoam 613D from zero to 7 days are shown in Table 3.1 and Table 3.2, respectively. The uncertainties (approximate 95% confidence intervals, CI) given are two sided (±) and only account for FTIR instrument uncertainty.

The concentrations measured were put on a dry basis by subtracting out the water:

$$C_{\text{dry basis}} = \frac{C_{\text{measured, wet basis}}}{1 - C_{H_2O}}$$

$$C_{H_2O} \approx \frac{\text{boilup rate (scfm)}}{\text{(boilup rate + air purge rate) (scfm)}} \text{ or from tracer gas calculation}$$

where the boilup rate (lb/hr) is converted to the equivalent gas volume at standard conditions.

These tests were run at a design basis DWPF scaled boilup rate of 5000 lb/h, whereas DWPF generally does not operate above about 2700 lb/hr. The tests were performed at the design basis because it was expected that the higher boilup rate would give conservatively high results. The reason for reporting the data on a dry basis is that DWPF will not operate at the test boilup rates, so the data will need to be adjusted to actual boilup rates used to determine the actual flammable gas concentrations.

Table 3.1. Measured Laboratory and Dry Basis Concentrations for HMDSO, TMS, and Propanal from Antifoam Batch 413 Additions to SME at Boiling

	Values Measured by FTIR (Wet Basis)							Values Adjusted to Dry Basis						
Days Post Dilution	Peak HMDSO (ppm)		Peak TMS (ppm)		Peak Propanal (ppm)		Water %	Peak HMDSO (ppm)		Peak TMS (ppm)		Peak Propanal (ppm)		Comments
	Value	CI	Value	CI	Value	CI		Value	CI	Value	CI	Value	CI	
0	11.5	3.1	<16		<37		87.9%	95	28	<131		<306		
0	12.0	3.5	17	16	<37		88.0%	101	30	139	132	<309		
0	16.5	3.2	28	14	<41		87.7%	134	32	223	116	<332		undiluted antifoam
1	10.5	2.6	44	16	<37		88.1%	88	31	370	162	<309		
1	10.8	3.2	48	16	<37		88.1%	91	35	401	167	<309		
2	12.2	2.4	65	14	48	37	87.7%	99	24	524	138	392	307	
4	16.3	2.8	89	14	87	37	87.7%	132	30	723	156	708	319	
5	21.3	2.6	82	14	54	37	87.0%	164	21	627	112	418	283	
5	20.4	2.4	82	14	54	37	87.0%	157	37	633	168	418	295	
7	37.4	3.1	98	14	57	37	86.4%	275	64	719	189	420	285	
7	43.6	2.6	107	14	65	37	86.4%	321	48	784	151	480	278	
16	71.5	2.7	137	14	87	41	85.4%	539	81	1028	226	655	411	
16	67.7	2.5	140	14	96	41	85.6%	517	79	1069	235	736	427	
16	71.4	2.7	152	14	102	41	86.7%	537	80	1145	230	768	393	
16	320	17	<20		196	36	0.98%	323	17	<20		198	36	after condenser
16	322	16	<20		209	32	0.98%	325	16	<20		211	32	after condenser
16	330	16	<20		205	32	0.99%	333	16	<20		207	32	after condenser
22	75.6	2.9	105	16	53	37	88.4%	649	160	902	258	455	337	
27	301	8	125	13	56	22	86.6%	2254	703	939	307	421	212	
27	344	9	150	13	70	22	88.0%	2860	411	1251	207	580	202	
27	321	9	168	13	91	22	88.6%	2814	724	1470	393	798	283	
27	309	8	145	13	75	22	87.8%	2525	236	1188	149	610	190	
27	1572	42	123	63	162	19	0.2%	1576	42	124	63	162	19	after condenser
27	1483	38	122	58	198	20	0.2%	1487	38	122	59	198	20	after condenser
27	1477	38	122	54	229	20	0.3%	1480	38	122	54	230	20	after condenser
31	186	6	137	13	118	33	85.6%	1292	232	953	192	819	268	
31	209	7	158	14	108	27	85.6%	1449	52	1099	94	749	188	

CI: approximate half width of the two-sided 95% confidence interval for the uncertainty in the FTIR measurement

Table 3.2. Measured Laboratory and Dry Basis Concentrations for HMDSO, TMS, and Propanal from Antifoam Batch 613D Additions to SME at Boiling

	Values Measured by FTIR (Wet Basis)							Values Adjusted to Dry Basis						
Days Post Dilution	Peak HMDSO (ppm)		Peak TMS (ppm)		Peak Propanal (ppm)		Water %	Peak HMDSO (ppm)		Peak TMS (ppm)		Peak Propanal (ppm)		Comments
	Value	CI	Value	CI	Value	CI		Value	CI	Value	CI	Value	CI	
0	11.0	3.6	21	16	<37		86.8%	83	31	158	122	<279		
0	11.0	3.7	20	16	<37		87.6%	89	30	158	128	<299		
0	12.9	3.0	25	14	<37		87.7%	105	29	204	118	<302		undiluted antifoam
1	8.2	3.0	42	16	<37		88.1%	69	26	352	138	<309		
1	9.6	2.6	52	16	<37		87.5%	77	21	414	127	<294		
2	9.5	3.0	61	14	<70		87.7%	77	27	496	135	565	313	
2	43.5	3.1	<24		112	20	0.43%	44	3	<24		113	20	after condenser
4	19.4	2.8	107	14	86	37	85.8%	136	26	754	138	604	272	
4	23.2	2.4	134	14	81	37	85.8%	163	27	943	156	566	271	
4	138	6.7	<24		170	20	0.30%	138	7	<24		170	20	after condenser
5	29.7	2.6	93	14	54	37	86.6%	221	21	697	109	406	275	
5	34.8	2.4	97	14	52	37	86.6%	260	53	726	175	386	284	
7	63.6	2.9	117	14	60	37	87.0%	490	71	898	166	460	290	
7	63.7	2.9	109	14	60	37	87.0%	490	78	838	169	460	291	

CI: approximate half width of the two-sided 95% confidence interval for the uncertainty in the FTIR measurement

Table 3.3 gives the rate of generation of the flammable gases on an antifoam added basis. These rates are given in units of mmol of gas/min/g of undiluted antifoam, so the gas concentration under any set of conditions can be calculated. For example, the DWPF SRAT with a 17 gal addition of 1:20 antifoam (or 0.85 gal of undiluted antifoam) would be 3218 g. If the peak rate of HMDSO generation were 0.0200 mmol HMDSO/min /g antifoam, then the dry basis concentration in the SRAT with a 230 scfm purge would be:

$$\text{HMDSO (ppm)} = \frac{0.0200\text{ mmol/min}}{\text{g antifoam}}\frac{3218\text{ g antioam}}{230\text{ scfm}}\frac{22.414\text{ L/mol}}{28.316\text{ L/ft}^3}\frac{\text{mol}}{1000\text{ mmol}} = 222\text{ ppm}$$

The wet basis concentration, assuming a water concentration of 75% (~2700 lb/hr boilup rate) would then be found by the following equation:

$$C_{\text{wet basis}} = C_{\text{dry basis}}\left(1 - C_{H_2O}\right) = 222\text{ ppm }(1 - 0.75) = 56\text{ ppm}$$

Table 3.3. Peak Rates of HMDSO, TMS, and Propanal Generation from Antifoam Additions to SME at Boiling

Antifoam Lot 413

Days Post Dilution	Peak HMDSO Rate (mmol/min/ g of antifoam)		Peak TMS Rate (mmol/min/ g of antifoam)		Peak Propanal Rate (mmol/min g of antifoam)	
	Value	CI	Value	CI	Value	CI
0	0.0119	0.0035	<0.0165		<0.0385	
0	0.0126	0.0038	0.0174	0.0388	<0.0388	
0	0.0168	0.0041	0.0280	0.0145	<0.0418	
1	0.0111	0.0039	0.0465	0.0204	<0.0388	
1	0.0114	0.0044	0.0504	0.0210	<0.0388	
2	0.0124	0.0030	0.0659	0.0173	0.0493	0.0386
4	0.0166	0.0037	0.0908	0.0196	0.0889	0.0401
5	0.0206	0.0027	0.0788	0.0141	0.0526	0.0356
5	0.0197	0.0046	0.0795	0.0212	0.0526	0.0371
7	0.0345	0.0081	0.0904	0.0237	0.0528	0.0359
7	0.0403	0.0061	0.0985	0.0190	0.0603	0.0350
16	0.0745	0.0112	0.142	0.031	0.0906	0.0569
16	0.0715	0.0109	0.148	0.032	0.102	0.059
16	0.0675	0.0100	0.144	0.029	0.0966	0.0494
16	0.0406	0.0021	<0.0025		0.0249	0.0045
16	0.0409	0.0020	<0.0025		0.0265	0.0040
16	0.0418	0.0021	<0.0025		0.0261	0.0040
22	0.082	0.020	0.113	0.032	0.0572	0.0423
27	0.283	0.088	0.118	0.039	0.0529	0.0266
27	0.359	0.052	0.157	0.026	0.0729	0.0254
27	0.354	0.091	0.185	0.049	0.100	0.036
27	0.317	0.030	0.149	0.019	0.0766	0.0239
27	0.198	0.005	0.0155	0.0079	0.0204	0.0024
27	0.187	0.005	0.0154	0.0074	0.0249	0.0025
27	0.186	0.005	0.0154	0.0068	0.0289	0.0025
31	0.162	0.029	0.120	0.024	0.103	0.034
31	0.182	0.007	0.138	0.012	0.0941	0.0237

Antifoam Lot 613D

Days Post Dilution	Peak HMDSO Rate (mmol/min/ g of antifoam)		Peak TMS Rate (mmol/min/ g of antifoam)		Peak Propanal Rate (mmol/min/ g of antifoam)	
	Value	CI	Value	CI	Value	CI
0	0.0104	0.0039	0.0198	0.0154	<0.0351	
0	0.0111	0.0038	0.0199	0.0376	<0.0376	
0	0.0131	0.0036	0.0257	0.0148	<0.0379	
1	0.0086	0.0033	0.0443	0.0173	<0.0388	
1	0.0096	0.0026	0.0520	0.0160	<0.0370	
2	0.0097	0.0034	0.0624	0.0170	0.0710	0.0393
2	0.0055	0.0004	<0.0030		0.0142	0.0025
4	0.0171	0.0033	0.0947	0.0173	0.0760	0.0342
4	0.0205	0.0033	0.119	0.020	0.0712	0.0340
4	0.0173	0.0009	<0.0030		0.0214	0.0025
5	0.0278	0.0027	0.0876	0.0137	0.0510	0.0345
5	0.0326	0.0066	0.0912	0.0220	0.0485	0.0357
7	0.0615	0.0090	0.113	0.021	0.0578	0.0364
7	0.0616	0.0099	0.105	0.021	0.0578	0.0366

CI: approximate half width of the two-sided 95% confidence interval for the uncertainty in the FTIR measurement

Rates are per gram of undiluted antifoam added

Shaded cells are After Condenser

The averages of the measured, dry basis, and peak rates data for HMDSO, TMS, and propanal from antifoam additions to SME at boiling are shown in Table 3.4. Here the CI values were calculated from the replicate measurements using the Student's t-statistic and the instrument uncertainty. The t-statistic brings in the random variation from test to test using the replicate measurements. The t-statistic calculation used was for an upper bound only so the CI values are upper bound limits; this makes the upper bound less uncertain.

$$\text{Upper 95\% confidence (ppm)} = \frac{t_{\alpha,n-1}\ s}{\sqrt{n}}$$

where $t_{\alpha,n-1}$ = t-statistic at tail area probability α (0.05) and n-1 degrees of freedom

s = standard deviation

n = number of data points

The CI values in Table 3.4 are actually the above upper 95% confidence value plus the instrument 95% two-sided confidence:

$$\text{Upper 95\% confidence (ppm)} = \sqrt{\left(\frac{t_{\alpha,n-1}\ s}{\sqrt{n}}\right)^2 + \left(\text{measurement uncertainty}\right)^2}$$

Using the two-sided instrument confidence makes the upper confidence conservatively high.

For example, if Value = 89, CI = 32 means the average value was 89 and the 95% upper confidence bound is 89 + 32 =121, with no lower confidence bound. A lower confidence bound is unimportant since only the maximum values expected are important. Note that this upper confidence value is value with which there is 95% confidence that the ***average***, or ***mean***, value does not exceed. This value is not a confidence interval on any given value, meaning that values greater than this can occur with greater than 5% probability.

Table 3.4. Average Measured Laboratory and Dry Basis Peak Concentrations and Rates per Antifoam Added for HMDSO, TMS, and Propanal from Antifoam Additions to SME at Boiling

		Values Adjusted to Dry Basis						**Peak HMDSO Rate**		**Peak TMS Rate**		**Peak Propanal Rate**	
Days Post Dilution	**Water %**	**Peak HMDSO (ppm)**		**Peak TMS (ppm)**		**Peak Propanal (ppm)**		**(mmol/min/ g of antifoam)***		**(mmol/min/ g of antifoam)**		**(mmol/min/ g of antifoam)**	
		Value	CI	Value	CI	Value	CI	Value	CI	Value	CI	Value	CI
0	87.6%	101	33	169	127	<305		0.0127	0.0042	0.0212	0.0159	<0.0383	
1	87.9%	81	31	384	152	<305		0.0102	0.0039	0.0483	0.0191	<0.0384	
2	87.7%	88	74	510	163	479	627	0.0111	0.0093	0.0641	0.0205	0.0602	0.0386
4	86.4%	144	39	807	251	626	313	0.0181	0.0049	0.101	0.032	0.0787	0.0393
5	86.8%	201	66	671	152	407	285	0.0252	0.0083	0.0843	0.0191	0.0512	0.0358
7	86.7%	394	148	810	191	455	288	0.0495	0.0186	0.102	0.0240	0.0572	0.0362
16	85.9%	531	82	1081	251	720	422	0.0712	0.0110	0.145	0.034	0.0963	0.0565
22	88.4%	649	NA	902	NA	455	NA	0.0816	NA	0.113	NA	0.0572	NA
27	87.7%	2613	615	1212	368	602	287	0.328	0.077	0.152	0.046	0.0757	0.0360
31	85.6%	1370	518	1026	484	784	318	0.172	0.0650	0.129	0.061	0.0985	0.0400

All values are before condenser. CI: approximate width of the upper (one-sided) 95% confidence interval. Rates are per g of undiluted antifoam.
NA: 22 days had no replicates

The detection limits and uncertainties for the before condenser measurements are high due to the difficultly in removing the interference from the IR absorption of water. This is especially true for propanal. Only after 1-2 days of dilution is enough propanal released during antifoam addition to give values above the detection limits. Note that the uncertainty in all values is significantly less for the samples taken after the condenser. The before condenser data (i.e., collected using equipment configuration shown in Figure 2.2) are plotted in Figure 3.1 (note that in Figure 3.1 to Figure 3.3, the lines shown are only to guide the eye; they are not curvefits). The inset shows the data from zero to 7 days more clearly. HMDSO could be quantified at day zero, but both TMS and propanal were below their detection limits (DL) for some of the zero, 1 and 2 day samples. (The DL's for TMS and propanal are higher than HMDSO.) Below detection limit values are plotted with open symbols. Extrapolation back to zero suggests that the concentrations of both TMS and propanal may be around their detection limits of about 200-300 ppm; however, the data do not conclusively show these values. From zero to 4 days, the concentration of HMDSO in the offgas does not increase significantly. HMDSO has increased about 5X by 16 days. The concentration of TMS increases rapidly with time and then tends to slow its increase after 16 days. Propanal increases to above its DL and then to about 500-800 ppm.

The HMDSO data at 27 and 31 days is unusual in that the concentrations at 27 days are significantly higher than at 31 days. These results are from the same sample that had been previously used at 4 and 10 days. The 27 day sample had the longest time in the closed bottle of all samples at 17 days. It appears that some of the HMDSO that built up in the diluted samples may have escaped as HMDSO vapor from the bottle when sampled. This could account for the less sampled 27 day sample having more HMDSO since none was lost from intermediate sampling. The possibility of HMDSO in the headspace of the sample bottles seems likely given the low solubility of HMDSO in water. If this is true, all of the HMDSO results would be low relative to the actual amount of HMDSO in the sample bottle, but would be representative of the amount in the liquid. The AMFT would expect to have a smaller buildup of HMDSO due to ventilation.

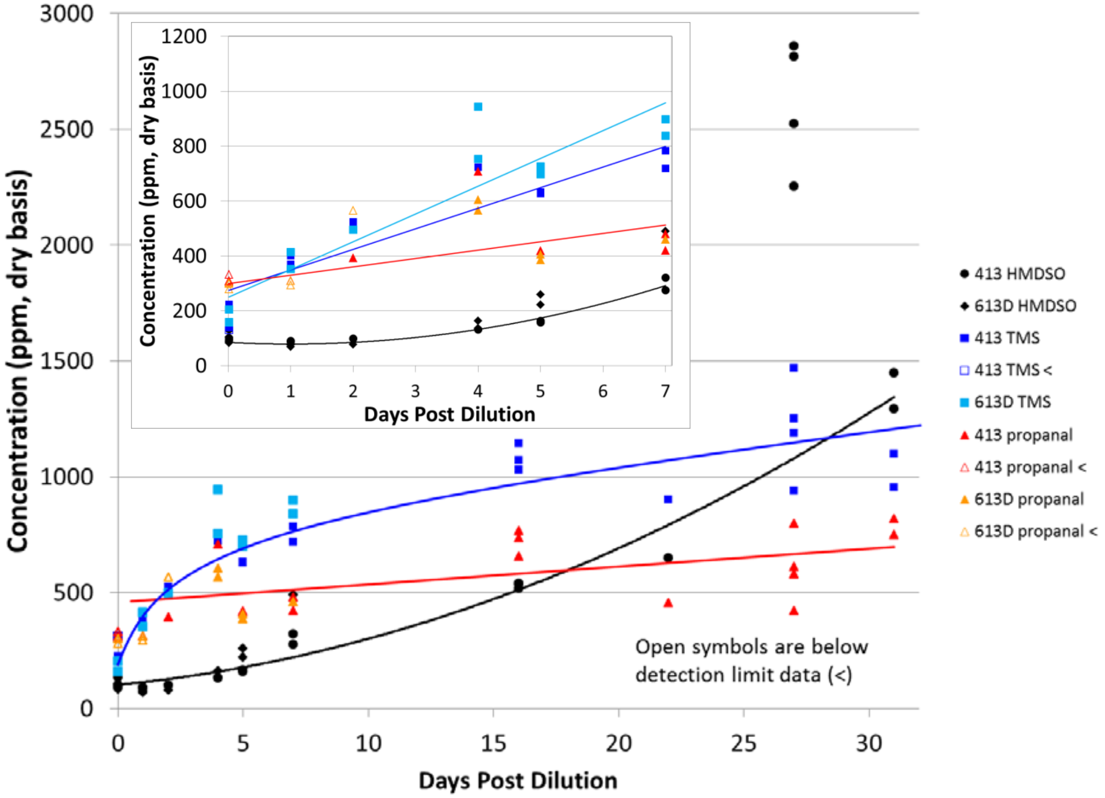


Figure 3.1. Dry Basis Concentrations of HMDSO, TMS, and Propanal Before the Condenser

The shaded rows in Table 3.1 and Table 3.2 are data for sampling after condenser (i.e., using equipment configuration shown in Figure 2.3). The HMDSO concentrations on a dry basis are similar but somewhat less than the corresponding before condenser values. The propanal values after the condenser are lower than before the condenser by a greater percentage than for HMDSO indicating that propanal is removed from the vapor phase. The TMS values are significantly lower after the condenser indicating significant removal into the condensate. These comparisons are shown graphically in Figure 3.2. Note that these values have all been put on the same dry basis. The ratios of the after-to-before concentrations are shown in Figure 3.3. About 40% of the HMDSO, 60-70% of the propanal, and 90-95% of the TMS appear to be removed in the condenser. Preliminary results that will be detailed in a future technical report show TMS concentrations of about 20 mg/L in simulant condensate.

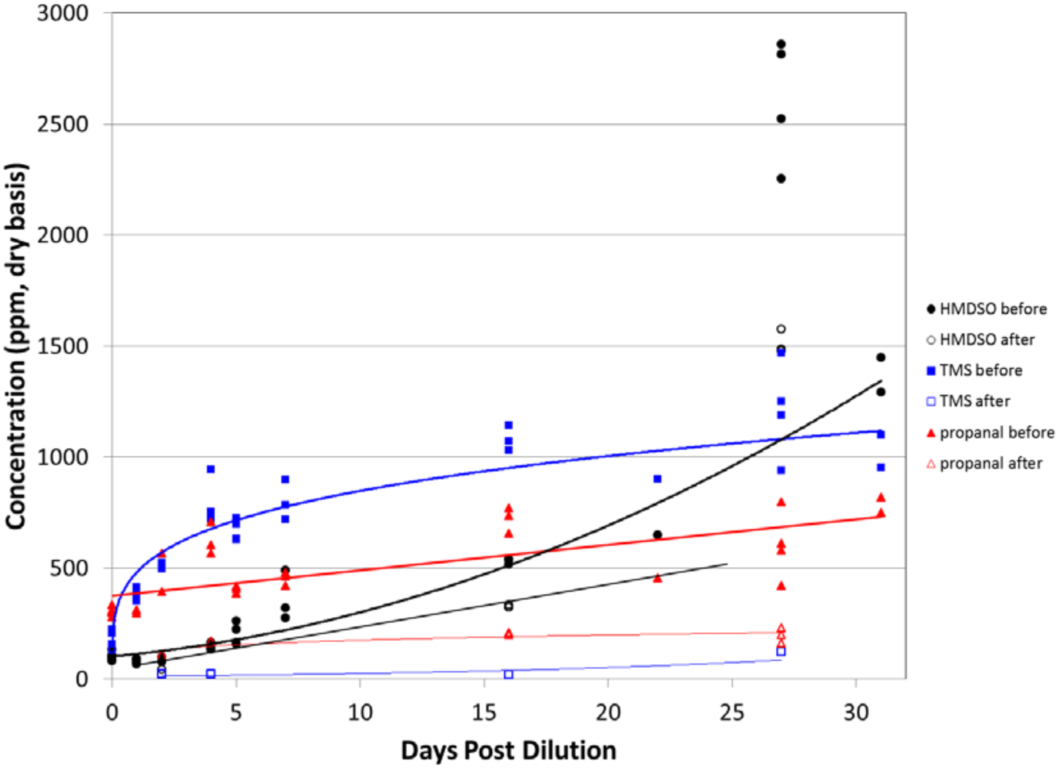


Figure 3.2. Dry Basis Concentrations of HMDSO, TMS, and Propanal Before and After the Condenser

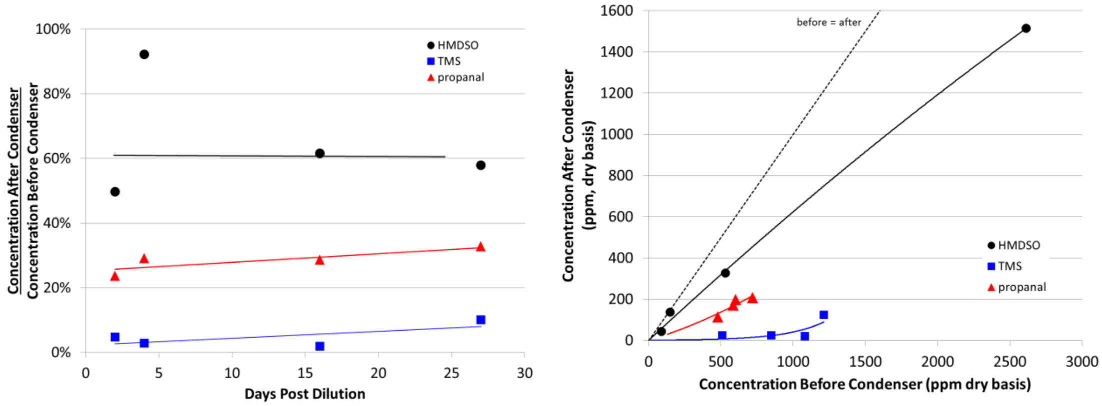
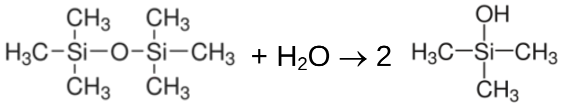


Figure 3.3. Ratio of After to Before Condenser Concentrations and After versus Before Concentrations

An HMDSO removal of 40% is not consistent with preliminary simulant condensate sample measurements of <1 mg/L, which is below the reported solubility of about 1 mg/L. There are at least two possible explanations for this discrepancy. HMDSO does condense, but since it is very insoluble, it forms an organic second phase. A second phase could be so small that it probably would not be visible in condensate samples. Another possibility is that the HMDSO decomposes in the acidic condensate by a condensation reaction to create TMS:



$$H_3C-Si(CH_3)_2-O-Si(CH_3)_2-CH_3 + H_2O \rightarrow 2\ H_3C-Si(OH)(CH_3)-CH_3$$

HMDSO TMS

The results for propanal suggest that there should be a measurable amount of propanal in condensate samples. Preliminary results for condensate samples indicate there might be only ~1 mg/L quantities at most. This value is inconsistent with the data showing 60-70% removal of the propanal. It is possible that in the acidic oxidizing conditions of the condensate that propanal is oxidized to propanoic acid and so would not be detected as propanal;[35] no propanoic acid has been detected by the FTIR in any gas samples. Further investigation of the fate of HMDSO and propanal in the condensate is warranted.

3.2 Effect of Antifoam Addition Method and Rate on HMDSO Concentration Peak

These tests utilized the original equipment setup with the offgas routed through the condenser, ammonia scrubber, FAVC and Nafion® dryer prior to FTIR analysis (Figure 2.1) and the setup without the scrubber (Figure 2.3). In both configurations sampling after the condenser, all TMS and most propanal would have been scrubbed out of the offgas. Some HMDSO may have also been scrubbed out in the condenser and scrubber (see Section 3.1).

3.2.1 *Effect of Antifoam Addition Method on HMDSO Concentration Peak*

SRNL has previously reported peak HMDSO concentrations in experiments where antifoam was added more quickly than can be accomplished in DWPF.[20,21] In the SRNL addition method, a 1:10 antifoam solution is quickly dumped (~1.5 seconds) through an addition funnel, followed by equal mass of flush water. After both additions are complete, it is equivalent to adding a 1:20 antifoam solution. The result is that a scaled antifoam addition approximately 84 times faster than it is added in DWPF. The maximum rate that DWPF can pump a 1:20 antifoam solution is ~8 gpm. Initial testing of the addition method was completed with the typical offgas system that removes some or all of the TMS and propanal from the offgas.

The measured HMDSO (after offgas train) peaks from the 1:10 antifoam solution dump were compared to identical runs where a 1:20 solution was pumped at a scaled rate of approximately 8 gpm. The results of the testing are summarized in Table 3.5. Note that the air purge rate for the data shown in Table 3.5 was 1.41 L/min versus the 1.0 L/min rate used in most of the data reported later in this document. When more than one data point was available, the average concentration is reported and the variability is estimated from the standard deviation. In all cases the pumping method gave higher peak concentrations of HMDSO than the funnel dump method. Although the peaks from the pumping method were higher, the width of these peaks was narrower than for the funnel dump method. The areas under the peaks were approximately the same indicating that the amount of HMDSO released was about the same. To determine if the TMS and propanal peaks act similarly to the HMDSO peaks, sampling before the condenser would be required.

Table 3.5. Comparison of DWPF Scaled Addition Rate vs Funnel Dump on HMDSO Peak Concentration in Testing with SRAT Condenser, Ammonia Scrubber and FAVC

Lot	Days Post Dilution	Addition Rate	Peak of HMDSO (ppm) Value	Peak of HMDSO (ppm) CI	HMDSO Generation Peak (mmol/min/ g antifoam) Value	HMDSO Generation Peak (mmol/min/ g antifoam) CI
613S	0	Funnel	8	±5 [a]	0.00141	±0.00087 [a]
613S	0	8 gpm	16	±8 [a]	0.00274	±0.00130 [a]
413	4	Funnel	13	±4 [b]	0.00230	±0.00075 [b]
413	4	8 gpm	50	±4 [b]	0.00883	±0.00075 [b]
413	8	Funnel	95	±4 [b]	0.01677	±0.00075 [b]
413	8	8 gpm	135	±4 [b]	0.02384	±0.00075 [b]
413	12	Funnel	200	±4 [b]	0.03531	±0.00075 [b]
413	12	8 gpm	296	±32 [a]	0.05217	±0.00570 [a]

[a] These approximate half widths of the two-sided 95% confidence interval include variation from multiple measurements. [b] These single analyses include only the analysis error and therefore are smaller.

3.2.2 *Effect of Addition Rate on HMDSO Concentration Peak*

Tests of pumping at rates from 4 to 21 gpm were performed to determine the effect of pumping rate on the HMDSO peak concentration. In DWPF, the maximum antifoam addition rate is ~8 gpm with the needle valve installed in the antifoam addition line. Testing was also completed at ~21 gpm, the maximum scaled flowrate of the syringe pump. The 4 gpm rate was chosen to approximate the normal DWPF addition rate with the needle valve partially closed. Testing was completed at these three scaled addition rates using a four day old 1:20 antifoam solution. The FTIR sampled after the full offgas train, so most of the TMS and propanal were removed and only HMDSO is reported. Single tests were completed at both 4 and 21 gpm scales, so the error reported includes only the analysis error. The results are summarized in Table 3.6 and shown graphically in Figure 3.4. The confidence intervals (CI) include only FTIR instrument uncertainty.

Table 3.6 Comparison of Antifoam Addition Rate on Peak HMDSO Concentration in Testing with Condenser, Ammonia Scrubber and FAVC

Lot	Days Post Dilution	Scaled Addition Rate	Peak of HMDSO (ppm)		HMDSO Generation Peak (mmol/min/g antifoam)	
			Value	CI	Value	CI
613D	4	4 gpm	35	±4	0.0062	±0.0007
613D	4	8gpm	58	±4	0.0102	±0. 0007
613D	4	21 gpm	60	±4	0.0106	±0.0007

CI: approximate half width of the two-sided 95% confidence interval

The results of this set of single experiments are somewhat inconclusive since there are no replicate data points to provide statistics on the repeatability of the tests. Assuming similar statistics to other tests with replicates would lead to concluding that the 4 gpm concentration was actually less than the 8 and 21 gpm values, and that the 8 and 21 gpm values are indistinguishable.

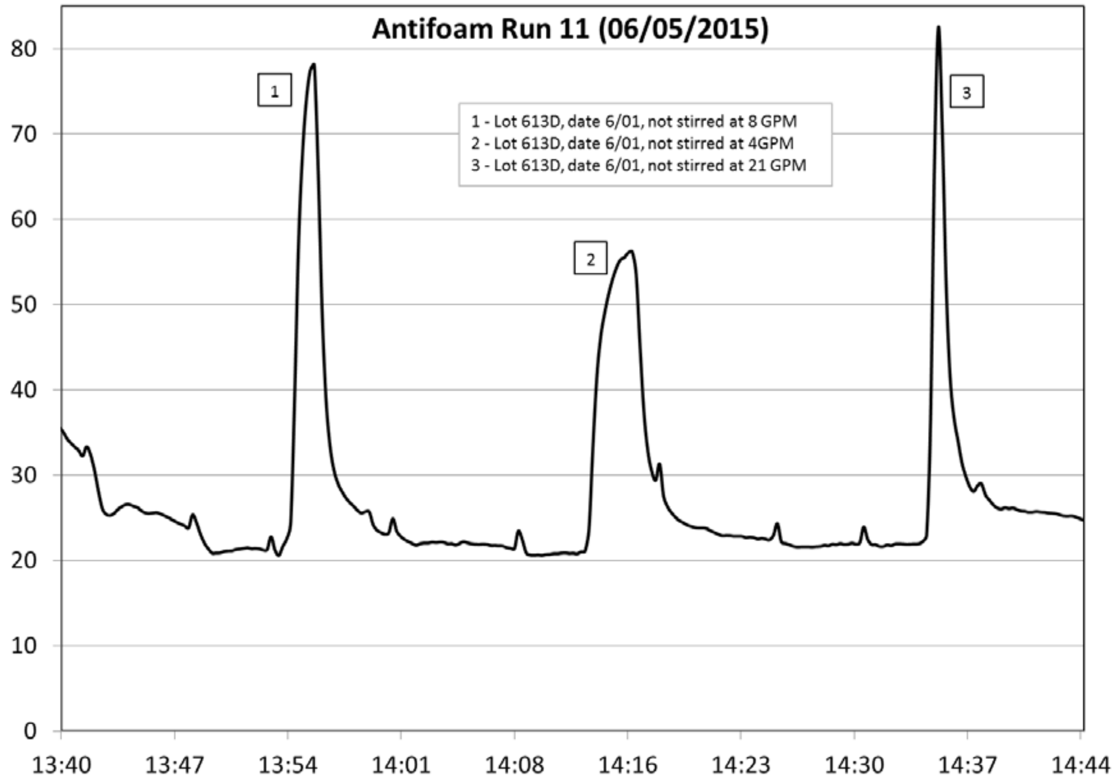


Figure 3.4. Effect of Addition Rate on HMDSO Concentration Peak

3.3 Effect of Mixing or Not Mixing as Antifoam Mixture Ages

In DWPF, the 1:20 antifoam solution is prepared in the Additive/Mix Feed Tank (AMFT) as needed. Typically, antifoam is prepared by adding 95 gallons of process water to 5 gallons (one pail) of Antifoam 747.[36] The AMFT is agitated for one hour after the antifoam is added. In addition, the AMFT is agitated for 5 minutes prior to addition if the AMFT has not been stirred in the past hour. In practice, 5 or 6 antifoam additions are made over several days, so the total mixing time is less than one hour per day.

In contrast, during prior SRNL testing, a 1:10 antifoam solution was prepared in a polyethylene bottle. A stir bar was added to a bottle and placed on a stir plate. The diluted antifoam was continuously mixed after preparation for the duration of a SRAT and SME test (typically 3-5 days). Continuous mixing of the dilute antifoam could increase its degradation rate due to the oxygen content in air, temperature increases, or by physical destruction by shearing. In addition, over-mixing of the antifoam solution can create a foamy liquid which separates the antifoam from the water. A photo of 1:20 antifoam solution that had been overmixed for 31 days using a stir plate is shown in Figure 3.5. Note the separation of the antifoam (floating) from the water. Samples pulled from this bottle likely have a much lower antifoam concentration than targeted. It was also noted during testing that some of the antifoam solutions separated into two phases (water rich and antifoam rich). If dilute antifoam continues to be used in DWPF, it is important to minimize mixing and mix well before transferring, which is consistent with DWPF’s current antifoam mixing and transfer procedures.

Figure 3.5. Photo of Continuously Stirred Lot 613D 1:20 Antifoam 747 Solution Showing Separation of Antifoam from Water

Tests were performed to compare a 1:20 antifoam solution stirred on a stir plate and 1:20 antifoam solutions that remained unmixed except for just prior to extracting the sample for each test. Tests were performed on two different days, with both 4 day old and 10 day old antifoam solutions. In the 4 day old antifoam tests, the full offgas system of Figure 2.1 was used. In the 10 day old antifoam tests, the modified offgas system of Figure 2.3 without the ammonia scrubber was used. Both 1:20 antifoam solutions were pumped at a scaled rate of 8 gpm. A graph showing the data for the 10 day tests is shown in Figure 3.6. The results are summarized in Table 3.7. There is no apparent change in degradation rate due to mixing.

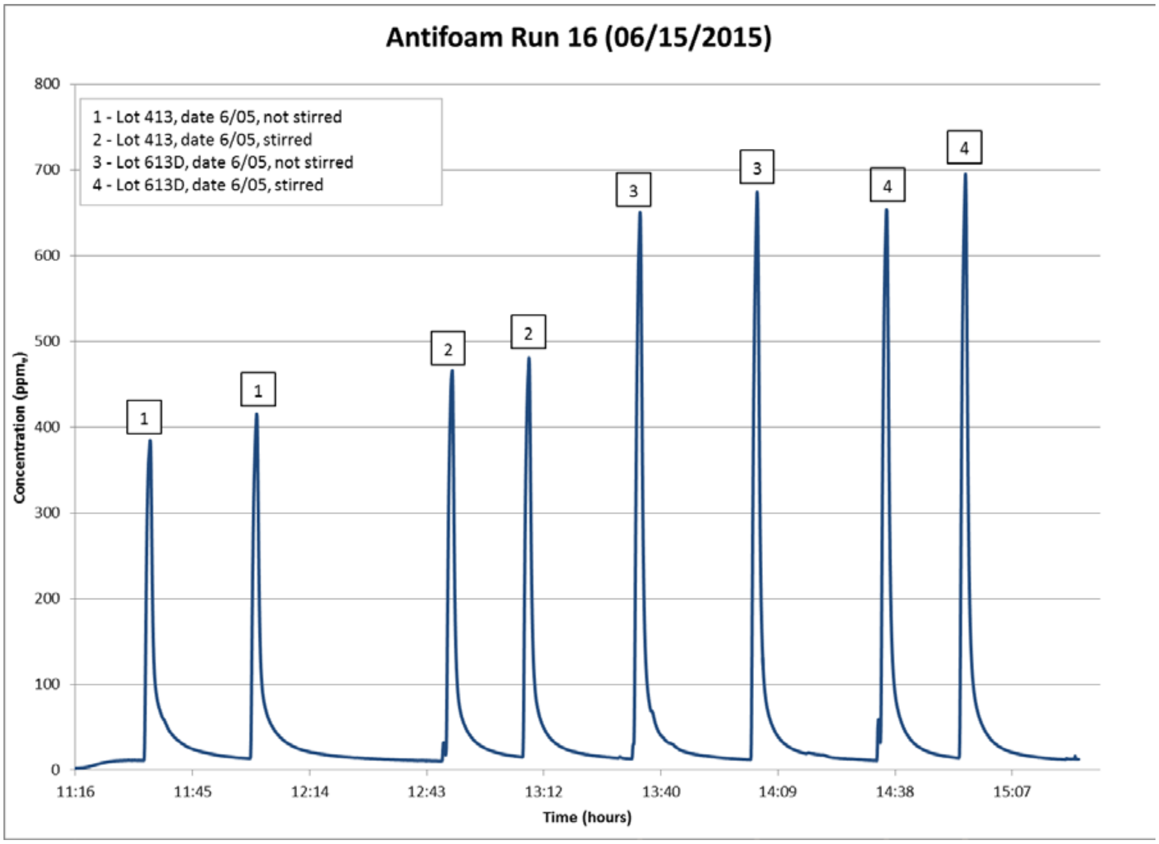


Figure 3.6. **Comparison of HMDSO peaks, ppm for Stirred vs Unstirred 10 day old 1:20 Antifoam 747 Solutions**

Table 3.7. Comparison of Mixed versus Unmixed 1:20 Antifoam Solutions on HMDSO Peak Concentration in Testing with SRAT Condenser, Ammonia Scrubber and FAVC

Lot	Days Post Dilution	Mixed or Not	Peak of HMDSO (ppm)		HMDSO Generation Peak (mmol/min/ g antifoam)	
			Value	CI	Value	CI
413	4	Mix	61	±4 [b]	0.0069	±0.0005
413	4	Not	59	±4 [b]	0.0067	±0.0005
613D	4	Mix	81	±4 [b]	0.0092	±0.0005
613D	4	Not	77	±4 [b]	0.0087	±0.0005
413	10	Mix	457	±119 [a]	0.0517	±0.0135
413	10	Not	388	±182 [a]	0.0439	±0.0206
613D	10	Mix	662	±246 [a]	0.0749	±0.0278
613D	10	Not	650	±163 [a]	0.0735	±0.0184

[a] These approximate half widths of the two-sided 95% confidence interval include variation from multiple measurements. [b] These single analyses include only the analysis error and therefore are much smaller.

3.4 Estimation of HMDSO, TMS, and Propanal Content in Raw Undiluted Antifoam

Analyses were completed on two lots of Antifoam 747 (413 and 613D) to determine the amount of HMDSO, TMS, and propanal contained in the undiluted antifoam. Both lots have been stored at SRS for four years. The older lot, 413, has been used in DWPF since 2011. In addition, a fresh sample of Momentive Silwet L-77, the 90% ingredient in Antifoam 747, was tested to compare with the Antifoam 747 lots.

In order to determine the concentrations of HMDSO, TMS and propanal, undiluted samples were sparged with 100 mL/min of a dry inert gas (argon or nitrogen), and the resulting offgas was routed to the FTIR for quantification. Graphs of the HMDSO, TMS, and propanal gas concentrations are shown in Figure 3.7, Figure 3.8, and Figure 3.9, respectively. The dotted lines show extrapolation of the data to longer times than the actual test duration so that the total gas evolved could be estimated. The rate of release of TMS was much slower than the other species. Water was detected in the offgas from each sample; this amount of water was greater than the amount in the inert gas purge.

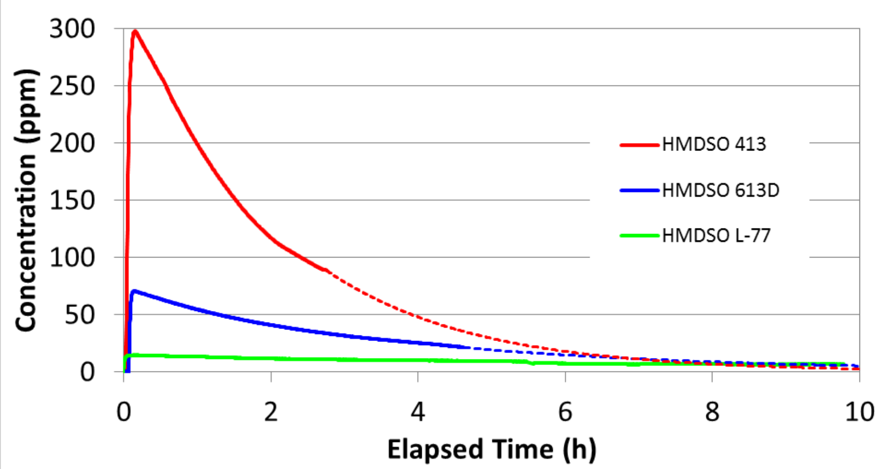


Figure 3.7. HMDSO Concentration in Purge Gas during Sparging of Undiluted Antifoam Samples

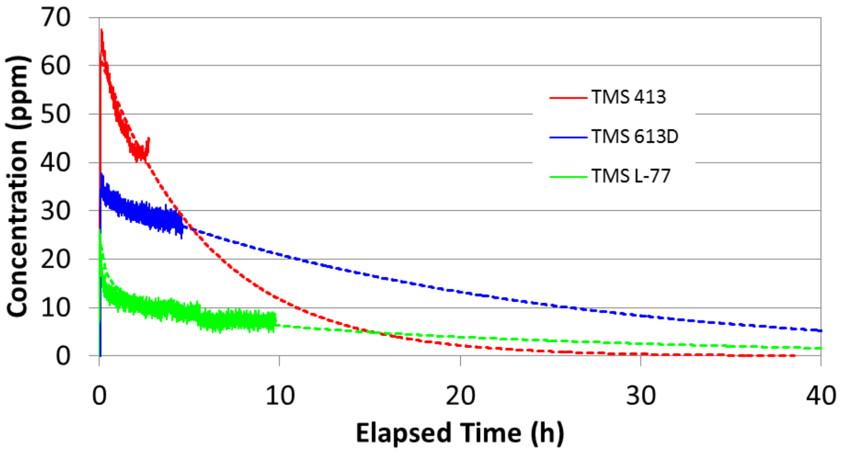


Figure 3.8. TMS Concentration in Purge Gas during Sparging of Undiluted Antifoam Samples

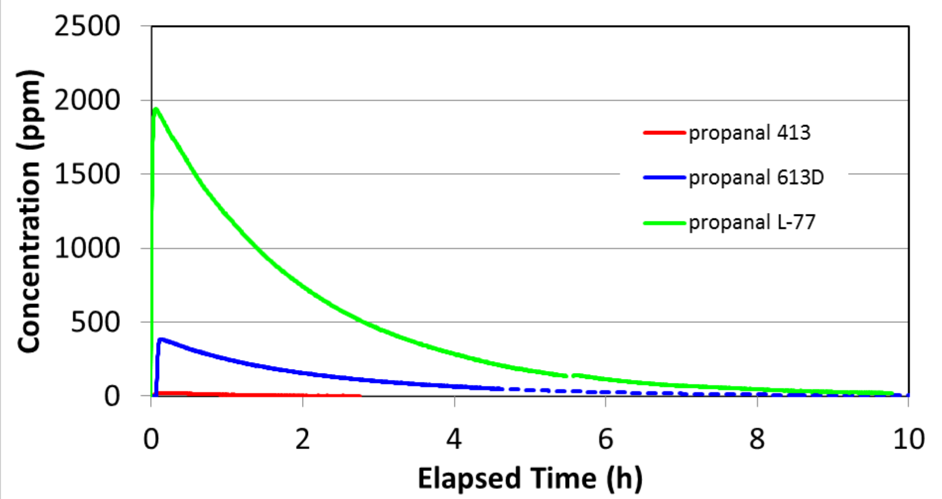


Figure 3.9. **Propanal Concentration in Purge Gas during Sparging of Undiluted Antifoam Samples**

The total gas generation for each component was calculated from the purge gas flowrate (0.1 std. L/min) and the concentrations. The small amount of water in the gas samples was neglected in the calculation. The area under the curve (ppm·hr) was determined and converted to a total amount of gas by this equation:

$$\text{Gas (mmol)} = \text{Gas}\left(\text{ppm} \times \text{h}\right) \times \frac{10^{-3}\ \text{mmol fraction}}{\text{ppm}} \times \frac{0.1\ \text{std. L}}{\text{min}} \times \frac{\text{mol offgas}}{22.414\ \text{L}} \times \frac{60\ \text{min}}{\text{hr}} \times \text{Time (h)}$$

The micromoles of each flammable gas evolved per gram of antifoam in the three antifoam samples are shown in Table 3.8.

Table 3.8. **Flammable Gases Generated from Raw Antifoam at Room Temperature**

	µmol of Gas per Gram of Antifoam		
Sample	**HMDSO**	**TMS**	**Propanal**
Antifoam 413*	3.41	1.94	<0.12
Antifoam 613D	1.42	3.88	4.53
Silwet L-77	0.83	1.18	24.6

* Some decomposition may have occurred due to introduction of water impurity during the test.

The Silwet L-77 sample analyzed may not have been as pure as the L-77 that is used to make the Antifoam 747 antifoam. Propanal is one of the raw materials used to make Silwet L-77. Relatively small quantities of propanal impurity may not be an issue for the normal use of Silwet L-77 as an agricultural chemical additive. The water evolved from these antifoam samples was also monitored. The fresh L-77 generated a constant ~100 ppm of water in the vapor. (Note dry N_2 read about zero on the FTIR.) The older 613D antifoam initially gave off ~2500 ppm of water that tapered off to ~1600 ppm at the end of about 5 hours, indicating that eventually the water evolved would become zero.

The water in the 413 antifoam was not quantified because there was some water in the sparging system before the test. This water may have resulted in some additional degradation of the antifoam in this test beyond any present in the antifoam sample. Therefore, the 413 results should be looked at as high bounds, especially for HMDSO.

3.5 Flammable Gas Release from CPC Condensates

Testing was completed to measure the HMDSO, TMS and propanal in the condensate stored in the SMECT or RCT during purged operations. No antifoam was added in these experiments. The testing utilized the equipment in the configuration shown in Figure 2.2, with heated sample lines that allowed analysis of the offgas exiting the SRAT vessel prior to any condensation. As a result, the quantification of HMDSO, TMS and propanal could be completed in order to determine the concentration of these gases in the offgas.

A blend of condensate collected during the SE2SME testing (SB8 nitric-formic flowsheet testing)[18] was used as a source of condensate for testing. This condensate sample was an SB8 condensate blend of all condensate from runs SB8-D6 to SB8-D9. These condensates were produced in November and December of 2014, so the condensate was about seven months old when analyzed.

Preliminary GCMS analysis of this condensate gave around 20 mg/L TMS, <1 mg/L propanal and <1 mg/L HMDSO. Propanal was identified in the SB8 condensate sample, but its concentration was below the lower quantitation limit of 1 mg/L. Based on the results of the antifoam additions to SRAT/SME testing done for this report, propanal is expected to be found in the condensate. It is possible that some propanal evaporated during the seven months of storage , as its vapor pressure is higher than TMS or HMDSO. It might also be possible that it was oxidized to propanoic acid or reacted with itself or other species to form compounds that were not analyzed; at this time, the possible fate of propanal in the condensate is not known. HMDSO is not expected to be present in condensate to any appreciable extent due to its low solubility. TMS is expected to be present because of its high solubility. The stability of TMS in condensate is not known

Note that this condensate was not sparged to simulate the sparging in the SMECT, so no stripping of HMDSO, TMS or propanal occurred after the condensate was generated. No pH adjustment of the condensate was needed as the measured condensate pH was 2.4 at 25 ˚C.

The testing was performed by adding 1.6 L of condensate to the same SRAT vessel that was used for the SME product testing. A lower volume was used due to the limited volume of blended condensate available. For each test, the condensate was heated to the required temperature and the FTIR measured the HMDSO, TMS, and propanal in the offgas before the condenser.

Tests were conducted at 70 °C with acidic condensate to simulate the SMECT. Since the RCT receives acidic condensate and is also pH adjusted to pH 12.5, testing was completed at 50 °C under both acidic and caustic conditions. The SMECT and RCT temperatures were specified as the maximum temperatures that could be seen in the DWPF process. Testing was not completed using a prototypic purge, because it was too low for the equipment setup used.

The first set of condensate runs (AF17) was performed with acidic condensate at 50 °C, then with the same acidic condensate at 70 °C, and then caustic was added and measurements were made at

50 °C. Only TMS was detected in the offgas. No HMDSO or propanal was quantified above the detection limits in these experiments. Trace amounts of ammonia were detected in the acidic condensate tests, while a significant amount of ammonia was released into the offgas after the pH was raised. Because these three consecutive runs were done with the same condensate solution, the solution became depleted in TMS as the test progressed. The concentration of TMS versus time in this test is shown in Figure 3.10. The air purge rate in this test was 0.20 L/min. Several concentrations measured during the test are shown in Table 3.9 on a wet and dry basis. The results shown are for the higher of the spreadsheet or AVU method of analyzing the FTIR data to be conservative. The uncertainties (CI) shown for TMS are from the AVU analyses.

The concentration of TMS at 50 °C and acidic conditions was approximately constant at around 63 ppm (dry basis). When the temperature was raised to 70 °C, the concentration peaked at about 213 ppm (spreadsheet value) and then steadily decreased. Caustic was then added to simulate the caustic RCT and the temperature was dropped to 50 °C. The concentration of TMS here was about 45 ppm. Because the solution was being depleted of TMS versus time, it is unknown if the lower concentration of TMS at the higher pH was due to the higher pH or to a lower source concentration.

The 70 °C test with acidic condensate was repeated with fresh condensate (Run AF25). The air purge rate was increased to 1.0 L/min for this test. Figure 3.11 shows the concentration versus time. The peak concentration was about 150 ppm.

From the concentrations and purge rates, the molar flow of TMS was calculated for each run. These results in μmol/min were normalized on the amount of condensate in L to give units of μmol/min/L condensate. The data were normalized to the condensate volume because the condensate is the source term for the TMS and determines the total amount of dissolved TMS that could be evolved into the vapor. These rates are shown in Figure 3.12.

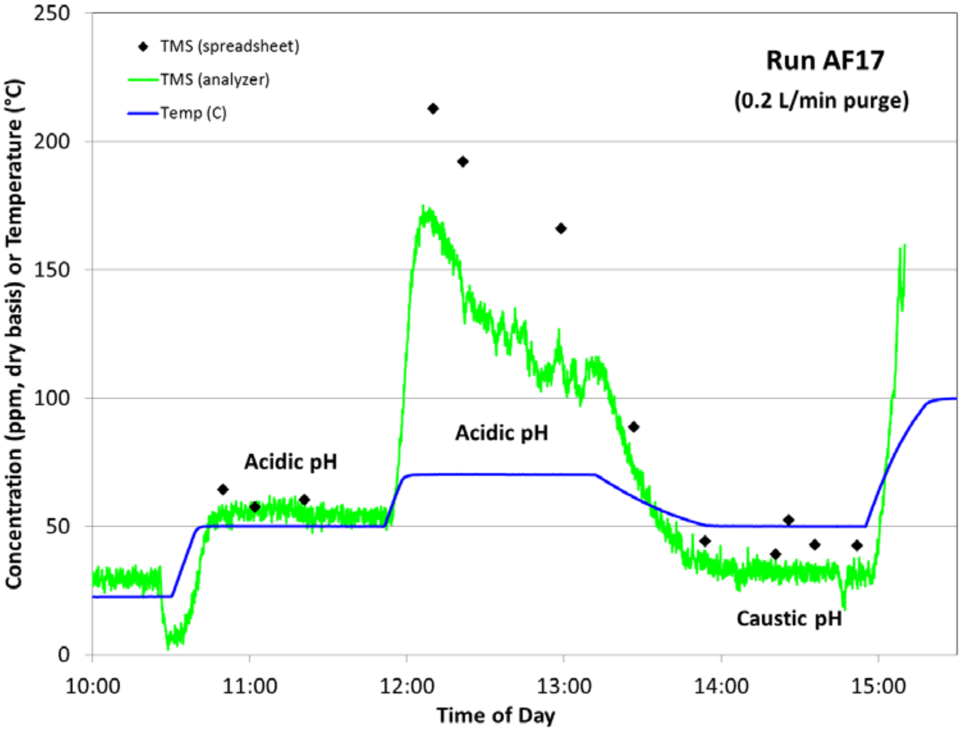


Figure 3.10. Lab-Scale Concentrations (Run AF17) of TMS from Condensate at 50 & 70 °C

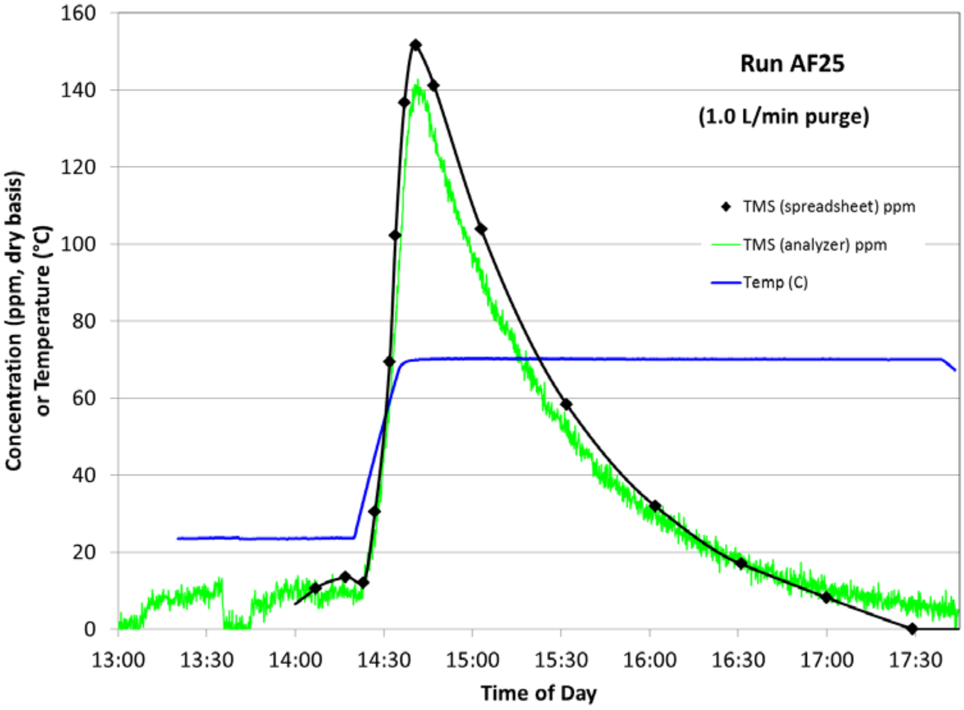


Figure 3.11. Lab-Scale Concentrations (Run AF25) of TMS from Condensate at 70 °C

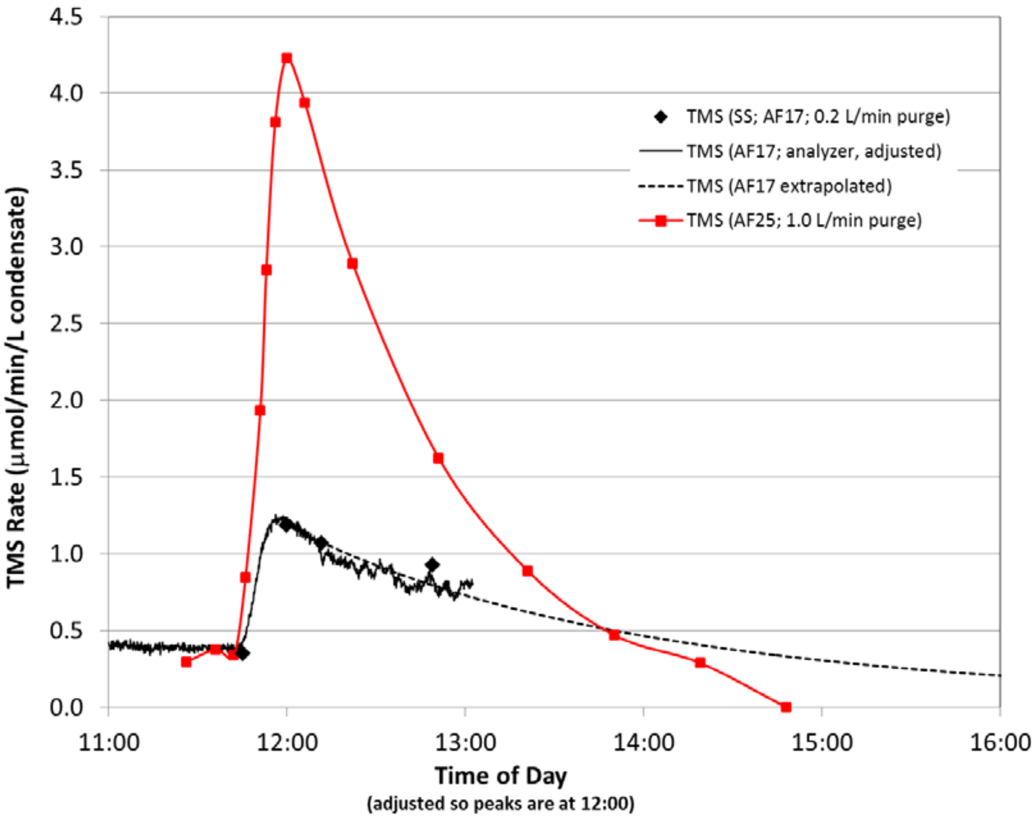


Figure 3.12. **Rate of TMS Evolution from SMECT Condensate at 70 °C**

Table 3.9. Flammable Gas Concentrations (Lab-Scale) from Condensate

			Wet Basis	Dry Basis	Wet Basis		Dry Basis		Wet Basis	Dry Basis	
Vessel	**Temp. (°C)**	**Acidic or Caustic**	**HMDSO (ppm)**		**TMS (ppm)**		**TMS (ppm)**		**Propanal (ppm)**		**Water**
Run AF17					Value	CI	Value	CI			
SMECT	50	Acidic	<2.2	<2.4	59	13	64	14	<33	<36	7.5%
	50	Acidic	<2.2	<2.3	60	13	63	14	<33	<35	5.6%
	50	Acidic	<2.2	<2.3	59	13	62	14	<33	<35	5.2%
RCT	50	Caustic	<2.2	<2.4	41	13	44	14	<33	<36	7.3%
	50	Caustic	<2.2	<2.4	36	13	39	14	<33	<36	8.3%
	50	Caustic	<2.2	<2.4	48	13	52	14	<33	<36	8.0%
	50	Caustic	<2.2	<2.4	39	13	43	14	<33	<36	8.0%
	50	Caustic	<2.2	<2.4	39	13	42	14	<33	<36	9.0%
SMECT	70	Acidic	<2.2	<2.4	198	13	213	14	<33	<35	7.0%
	70	Acidic	<2.2	<2.7	158	13	192	16	<33	<40	17.6%
	70	Acidic	<2.2	<2.5	144	13	166	15	<33	<38	13.3%
Run AF25											
SMECT	23.6	Acidic	<2.2	<2.3	<13		<14		<33	<34	4.6%
	23.6	Acidic	<2.2	<2.3	<13		<14		<33	<34	3.6%
	33.7	Acidic	<2.2	<2.3	<13		<14		<33	<34	2.9%
	46.0	Acidic	<2.2	<2.3	29	13	30	14	<33	<35	3.7%
	61.1	Acidic	<2.2	<2.3	66	13	69	14	<33	<35	4.2%
	66.7	Acidic	<2.2	<2.3	96	13	102	14	<33	<35	6.0%
	69.3	Acidic	<2.2	<2.4	127	13	137	14	<33	<36	7.7%
	69.9	Acidic	<2.2	<2.5	137	15	152	16	<33	<38	9.5%
	70.1	Acidic	<2.2	<2.5	123	13	141	15	<33	<38	13.2%
	70.2	Acidic	<2.2	<2.7	83	13	104	16	<33	<41	21.2%
	70.1	Acidic	<2.2	<2.7	48	13	58	16	<33	<41	19.7%
	70.1	Acidic	<2.2	<2.7	26	13	32	17	<33	<41	20.9%
	70.1	Acidic	<2.2	<2.7	14	13	17	17	<33	<42	21.3%
	70.1	Acidic	<2.2	<2.8	<13		<17		<33	<42	21.5%
	70.1	Acidic	<2.2	<2.7	<13		<16		<33	<41	20.3%

CI: approximate half width of the two-sided 95% confidence interval

The total amount of TMS was estimated for the condensate tests from the area under the concentration versus time curves, the air purge rates, and the water content in the gas samples. For AF25, the total TMS released from the start to the end of the test was calculated; for AF17, the total released is the amount at 50 °C and acidic pH plus the amount at 70 °C extrapolated until the TMS concentration would have been about 5 ppm. The extrapolation is shown in Figure 3.9. The approximate total TMS amounts released in the AF17 and AF25 tests would have been equivalent to the condensate containing ~18 and ~25 mg/L, respectively (note that both tests used the same blended condensate sample). These values compare well with the approximate value determined for the condensate of ~20 mg/L.

The rates of TMS generation are summarized in Table 3.10. The peak rate at 1.0 L/min purge was 4.23 μmol/min/L condensate and the peak at 0.2 L/min purge was 1.19 μmol/min/L condensate. The peak TMS generation rate appears to be a function of the purge flowrate, which was not expected. The ratio of the generation rates is 4.23/1.19, or 3.6. This value is similar to the purge rate ratio of 5.0. The rate of evaporation of TMS at a constant temperature may be dependent on the rate of purge sweeping over the liquid surface, much like evaporation of a water puddle is increased by increased air flow. For both cases, the concentrations measured were reasonably close (0.2 L/min: 213 ppm, 1.0 L/min: 152 ppm). These data suggest that the approach to equilibrium by Henry’s Law may limit the evaporation rate such that lower purge rates would result in lower evaporation rates and similar peak concentrations.

Henry's Law: $y\,P = H\,x$
where y = saturation mol frac in vapor
P = pressure
H = Henry's Law constant
x = mol frac in liquid

As the concentration in the vapor approaches the saturation concentration, the rate of evaporation of the solute tends to decrease.

The purge rate to condensate volume ratios in these tests were 0.625 min^{-1} for 1.0 L/min and 0.125 min^{-1} for 0.2 L/min. The DWPF ratio is 12 scfm/6000 gal which gives a ratio of 0.015 min^{-1} which is an order of magnitude lower than that in the 0.2 L/min tests. Therefore, the evaporation rate of TMS might be expected to be lower than in any of the lab-scale tests. This extrapolation is shown in Figure 3.13. The DWPF value shown could be much smaller since the line given is only based on two data points that both have probably ±20% error. This possible interpretation of the condensate data would be beneficial to DWPF because the actual evaporation rate could be much smaller than calculated from just taking the highest rate observed and scaling for purge flowrate.

Additional experimental evaporation tests at the same purge to condensate volume ratio as in DWPF would be required to resolve this question. Without a test at a significantly lower purge rate than what was performed, the uncertainty in Figure 3.13 would lead to large uncertainties in the concentration values adjusted to SMECT conditions.

Table 3.10. Flammable Gas Generation Rates from Condensate

Vessel	Temp. (°C)	Acidic or Caustic	HMDSO (µmol/min/ L condensate)	TMS (µmol/min/ L condensate) (Value | CI)		Propanal (µmol/min/ L condensate)
Run AF17						
SMECT	50	Acidic	<0.013	0.358	0.078	<0.199
	50	Acidic	<0.013	0.352	0.077	<0.195
	50	Acidic	<0.013	0.346	0.076	<0.194
RCT	50	Caustic	<0.013	0.246	0.095	<0.199
	50	Caustic	<0.013	0.218	0.096	<0.201
	50	Caustic	<0.013	0.292	0.096	<0.200
	50	Caustic	<0.013	0.239	0.096	<0.200
	50	Caustic	<0.013	0.236	0.097	<0.202
SMECT	70	Acidic	<0.013	1.19	0.08	<0.198
	70	Acidic	<0.015	1.07	0.09	<0.223
	70	Acidic	<0.014	0.926	0.084	<0.212
Run AF25						
SMECT	23.6	Acidic	<0.064	<0.382		<0.928
	23.6	Acidic	<0.064	<0.381		<0.928
	33.7	Acidic	<0.064	<0.382		<0.928
	46.0	Acidic	<0.064	0.847	0.384	<0.928
	61.1	Acidic	<0.064	1.94	0.39	<0.928
	66.7	Acidic	<0.065	2.85	0.39	<0.928
	69.3	Acidic	<0.066	3.81	0.40	<0.928
	69.9	Acidic	<0.068	4.23	0.409	<0.929
	70.1	Acidic	<0.071	3.94	0.43	<0.929
	70.2	Acidic	<0.077	2.89	0.46	<0.930
	70.1	Acidic	<0.075	1.62	0.45	<0.929
	70.1	Acidic	<0.077	0.889	0.460	<0.930
	70.1	Acidic	<0.077	0.471	0.461	<0.930
	70.1	Acidic	<0.077	<0.464		<0.930
	70.1	Acidic	<0.076	<0.457		<0.929

CI: approximate half width of the two-sided 95% confidence interval

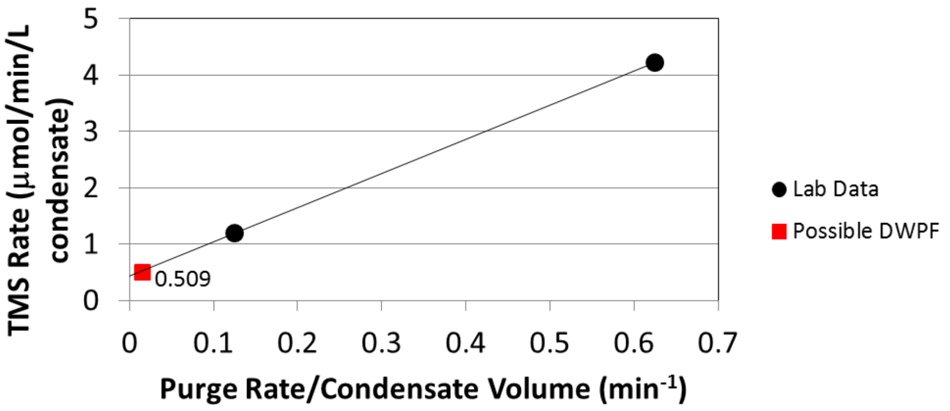


Figure 3.13. Extrapolation of TMS Evaporation Rate from Condensate

3.6 Effect of Antifoam Addition Prior to a 4-Day Facility Outage

Two tests were performed to address the antifoam degradation product peak concentrations for a scenario where antifoam is added to the CPC vessel but an unexpected facility outage prevents immediate processing. The generation of HMDSO, TMS and propanal in the offgas after addition at 93°C to the SRAT followed by an immediate 4 day outage was simulated. The first test data were collected with the equipment configuration shown in Figure 2.2, with sampling directly from the SRAT vessel. As a result, the peak concentrations of HMDSO, TMS and propanal in the offgas can be quantified.

These tests were performed due to concern that upon restarting, at the return to boiling, the flammable gas concentrations would exceed those previously measured because of antifoam degradation during the outage. Tests were performed with 5-day old antifoam and freshly made solution. For the 5-day old solution, 505 mg/L of a 1:20 solution of antifoam 747 (85 gallons DWPF scale) was added to the GN78 SME product at 93 °C. After adding the antifoam solution, the heat was turned off and the SME product temperature dropped to ambient for four days unmixed and unpurged. After four days, mixing and the air purge were reestablished, and the SME product was heated to boiling. The concentration of HMDSO, TMS and propanal that were measured, which was configured to sample directly from the SRAT vessel, are summarized in Table 3.11.

The second test was performed with freshly made antifoam 1:20 antifoam solution. A SME product (previously used for seven previous 100 mg/L antifoam tests that day) was cooled to 90 °C. A 100 mg/L addition of the 1:20 antifoam solution was pumped at scaled flowrate of 8 gpm. Heating was turned off and the slurry dropped to ambient temperature for four days unmixed and unpurged. After four days, mixing and the air purge were reestablished and the SME product was heated to boiling. For the initial antifoam addition, sampling was performed after the condenser as shown in Figure 2.3. The remainder of the data was collected with the equipment configuration shown in Figure 2.2. The results are summarized in Table 3.11.

Table 3.11. Antifoam Degradation Concentration from Antifoam Addition after 4 Days of Delayed Processing

		Experimental Values (Dry Basis)						Generation Rates (mmol/min/g antifoam)		
Days Post Dilution	**Comments**	**Peak HMDSO ppm**	**CI**	**Peak TMS ppm**	**CI**	**Peak Propanal ppm**	**CI**	**Peak HMDSO**	**Peak TMS**	**Peak Propanal**
First Test with 505 mg/L 1:20 diluted antifoam addition										
5	Addition at 93 °C	580	36	1659	92	1015	79	0.0146	0.0417	0.0255
9	Turning on Purge	71	5	41	18	<31		0.0018	0.0010	0.0008
9	Boiling at ~100 °C	20	6	317	38	125	62	0.0005	0.0080	0.0031
Second Test with 105 mg/L undiluted antifoam addition										
0 *	Addition at 90 °C	22*	2	NR		NR		0.0028*	NR	NR
4	Turning on Purge	<2.9		<14		<42		<0.0004	<0.0022	<0.0059
4	Boiling at ~100 °C	22	18	<89		<157		0.0028	<0.0111	<0.0198

CI: approximate half width of the two-sided 95% confidence interval. * NR, sampling performed after the condensers, thus TMS and propanal are not reported.

In the first test, the largest HMDSO, TMS, and propanal peaks occurred immediately after the antifoam was added at 93 °C. The peaks after sitting for four days prior to resuming boiling were much lower than the peaks immediately after antifoam addition.

In the second test, the HMDSO was approximately equal when the purge was resumed. The TMS and propanal were below the detection limits after turning on the purge and returning to boiling. No comparison can be made to values at the addition because this sample was analyzed after the condenser that would have removed all of the TMS and some of the propanal.

Based on the results of this testing, there will not be a large peak as the result of a delay in processing. Neither fresh nor aged diluted antifoam led to HMDSO, TMS or propanal concentrations when boiling was resumed that were higher than when added at ~90 °C.

4.0 Conclusions

Over one-hundred tests were completed in order to investigate the degradation mechanism and the decomposition products of Antifoam 747. The following conclusions can be made from this testing.

- Antifoam 747 degrades to HMDSO, TMS and propanal as detected in the offgas exiting the SRAT or SME. The concentrations of HMDSO, TMS and propanal vary drastically depending on time of dilution.
- Trimethylsilanol and propanal are soluble in the condensate and were found to have much lower concentrations in offgas that has been processed through the condensers and NH_3 scrubber.
- The high HMDSO concentrations reported in previous reports were primarily caused by dilution of the antifoam, which leads to degradation of the antifoam. Minimizing the time after dilution of the antifoam or utilizing undiluted antifoam will greatly reduce, but not totally eliminate, the HMDSO, TMS and propanal peaks in the SRAT/SME offgas associated with antifoam additions.
- Flammable gas generation rates from antifoam additions were measured and can be used by DWPF to estimate actual generation rates and concentrations in the SRAT and SME vessels.
- For conservatism, the tabulated gas generation rates should be linearly extrapolated from the data at 70 mg/kg addition to higher addition amounts. Lower addition amounts should use the 70 mg/kg data with no reduction in the rates.
- The Antifoam 747 being used by DWPF (lots 413 and 613D) has not degraded appreciably based on comparison with new Momentive Silwet L-77.
- The condensate blend from SB8 (Runs D6 to D9) is low in TMS (approximately 20 mg/L) and propanal (detectable but below quantitation limit of 1 mg/L). In condensate testing at elevated temperatures and acidic and caustic pHs, TMS was the only detectable component in the offgas.
- The measurements of release rates of TMS from condensate were inconclusive. Extrapolation of the measured rates at relatively high air purge rates to the low purge rates of the SMECT and RCT will result in significant overestimation of the rates.
- Since TMS and propanal are soluble in the condensate, they are largely removed by the condensers and scrubbers. Any testing that needs the generation rate of the TMS and propanal should be completed by analyzing the offgas exiting the SRAT/SME vessel.
- The antifoam degradation gas generation peak concentrations were measured four days after addition at 90-93 °C, simulating an outage just after an antifoam addition. After four days, the SRAT was returned to boiling. The resulting peaks of antifoam degradation products were comparable to or lower than the peaks after the antifoam addition.

5.0 Recommendations

Antifoam 747 degrades due to both a 1:20 dilution with process water and processing in the SRAT or SME. Antifoam 747 degradation during processing cannot be significantly decreased under current conditions. However, the antifoam degradation that occurs post dilution (during storage) could be minimized or eliminated by:

1. Adding the antifoam without dilution. This could be done by either adding undiluted antifoam or by diluting the antifoam as it is being added.

2. Adding the diluted antifoam soon after combining with water. This method will minimize the degradation caused by dilution while still allowing the same addition equipment. Antifoam solution should be discarded, including the heel of the AMFT, when the solution has been stored too long, especially after an outage.

The discarded diluted antifoam solutions should not be combined with any of the streams that will be returned to the tank farm. Transfers from the 221-S Floor Drain Catch Tank suspected of having diluted antifoam should not be allowed to the RCT (without prerequisite sample analysis). This measure is to avoid transfer of antifoam solution that may have been drained from the 3rd level AMFT into the RCT and returned to the Tank Farm.

6.0 Future Study

Work is recommended in several areas to increase the understanding of antifoam degradation and to improve the antifoam for future processing. These include:

- With the information learned from Phase 1, revisit the testing in the Task Plan and determine what additional testing should be completed.
- Complete the following experiments to better understand antifoam degradation
    - If DWPF continues to use diluted antifoam, sparge diluted, stored antifoam solution with inert offgas and measure the concentration of HMDSO, TMS and propanal.
    - Complete experiments at different antifoam addition amounts (mg/kg) to the SRAT/SME to determine the effect of addition amount on the concentrations of the flammable gases at boiling in the SRAT or SME.
- Determine if HMDSO can decompose in the FTIR heated sample lines.
- Determine if HMDSO can decompose in SMECT condensate.
- Improve the ability to measure the flammable gas concentrations before the condenser.
- Determine whether propanoic acid is formed in the acidic SMECT.
- Work with Drs. Alex Nikolov and Darsh Wasan to modify the antifoam to improve its resistance to hydrolysis. Antifoam that doesn’t decompose so quickly after dilution would likely improve the antifoam effectiveness and lead to lower generation rate of potentially flammable offgas components.
- Replacement antifoam should be developed in case hydrolysis resistant antifoam doesn’t have the antifoaming efficiency needed for DWPF.
- Determine concentrations of antifoam degradation products in offgas and condensate during lab-scale SRAT and SME testing.
- Determine concentration of antifoam degradation products in prototypic condensate that has been purged during storage. A DWPF SMECT and RCT sample would be ideal.
- Analyze DWPF SMECT and RCT samples to determine the HMDSO, TMS and propanal concentrations.
- Perform experiments with Dow Corning 544 antifoam to measure the flammable gases at boiling in the SRAT or SME.
- Perform experiments with hydrolysis-resistant Silwet L-77 replacements to determine whether possible antifoam replacements produce lower amounts of flammable gases.
- The measurements of release rates of TMS from condensate were inconclusive. The SMECT and RCT condensate testing results were inconclusive in that the tests performed could not be extrapolated to the actual vessel air purge rates. Extrapolation of the

measured rates at relatively high air purge rates to the low purge rates of the SMECT and RCT will result in significant overestimation of the rates. Additional testing would be required to determine realistic degradation product release rates.

7.0 References

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Appendix A. FTIR HMDSO Graphs from All Experiments

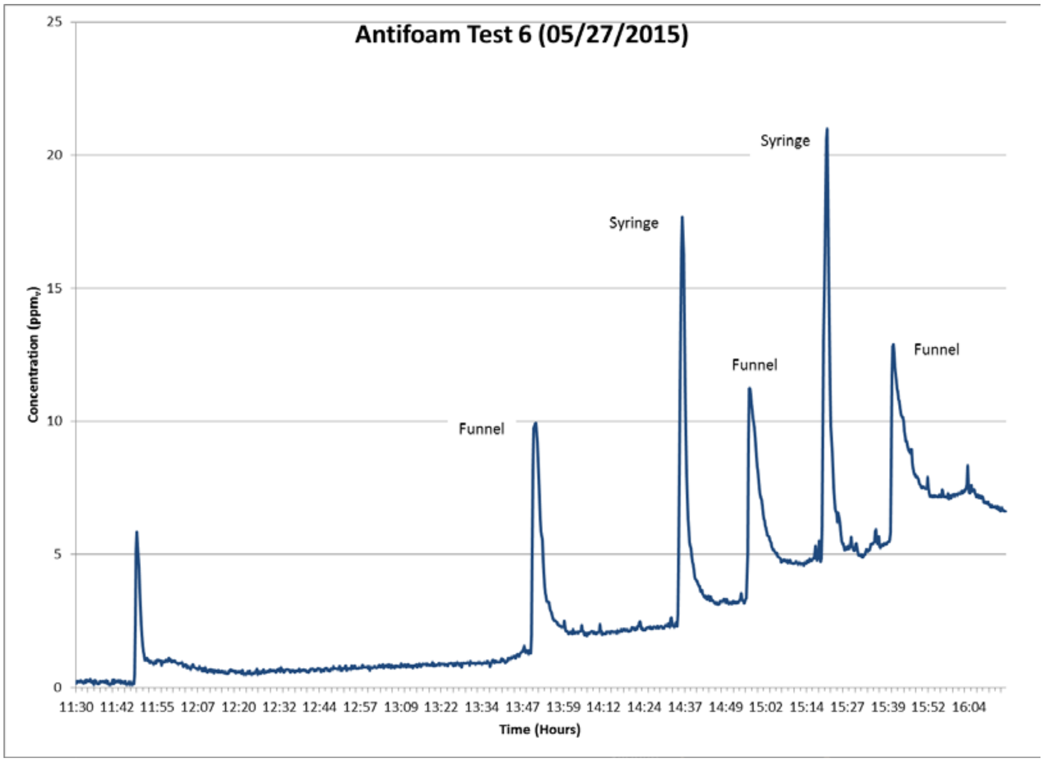
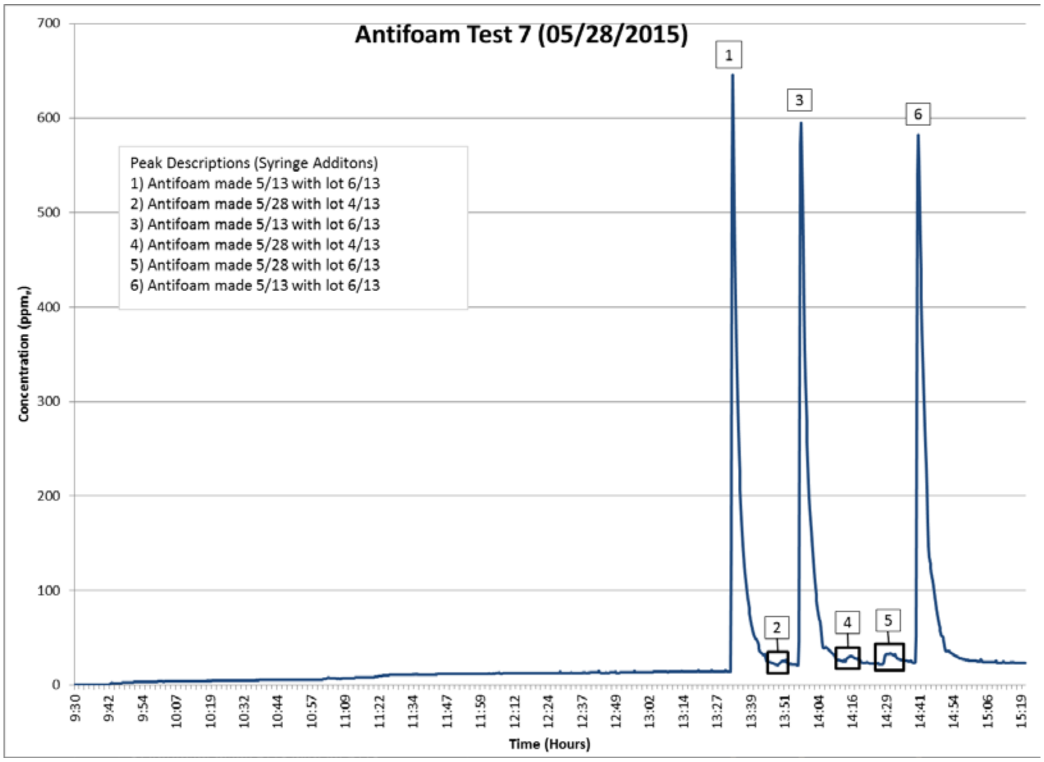


Figure A-1. Run 6



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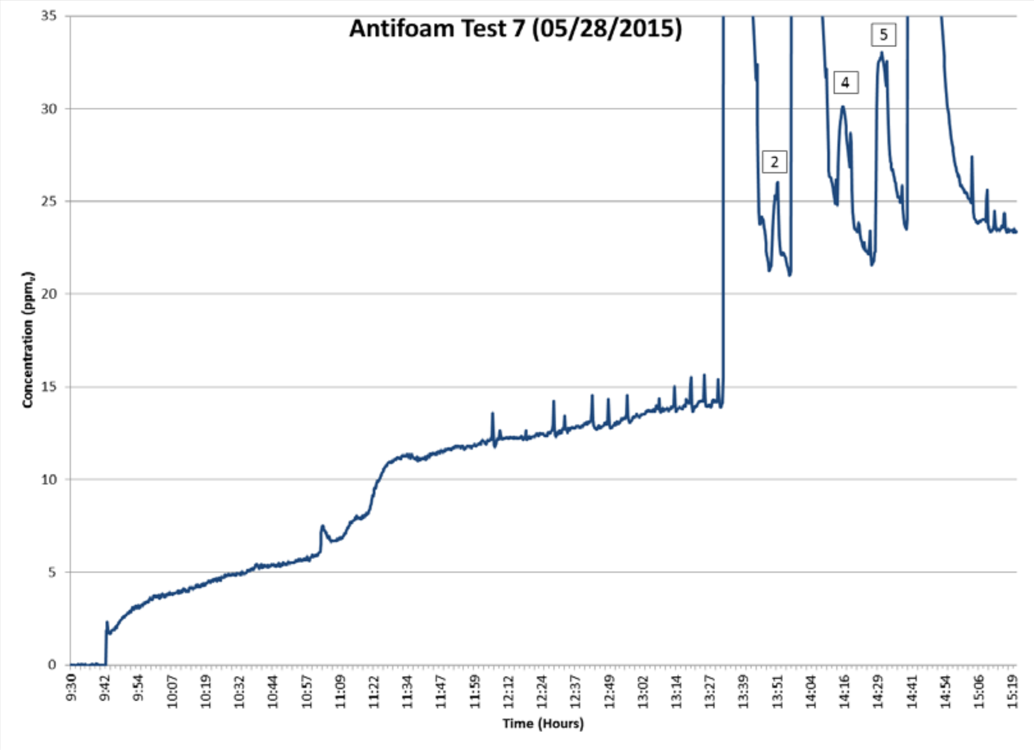
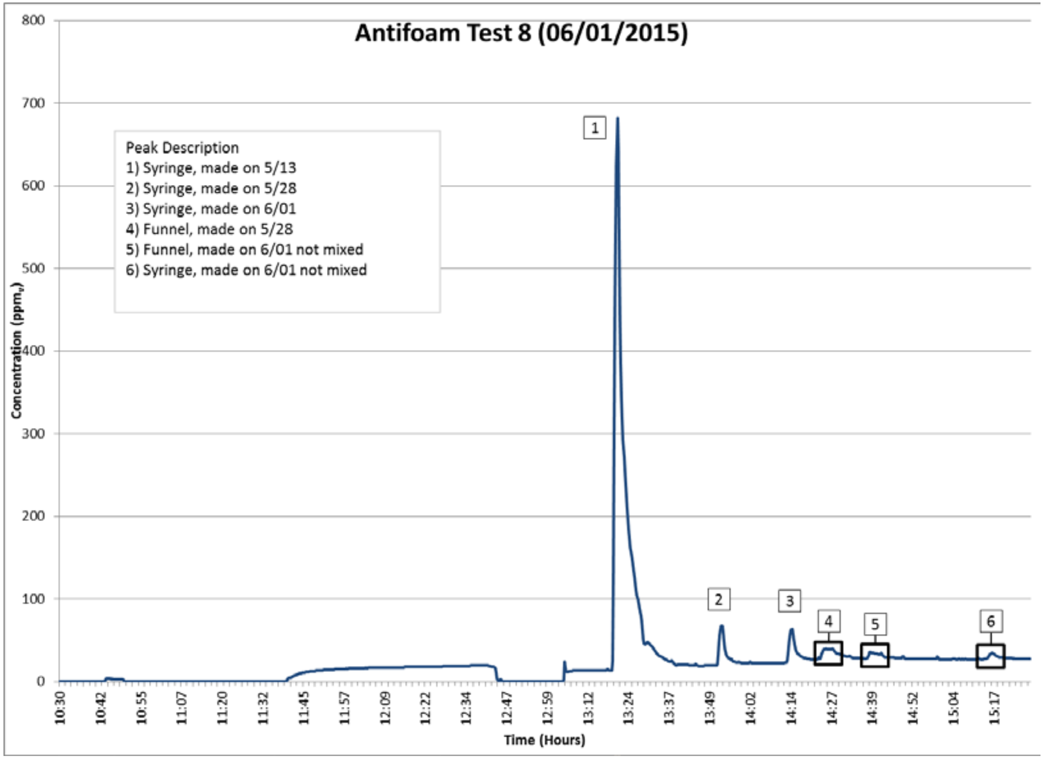


Figure A-2. Run AF7 Zoomed for smaller peaks



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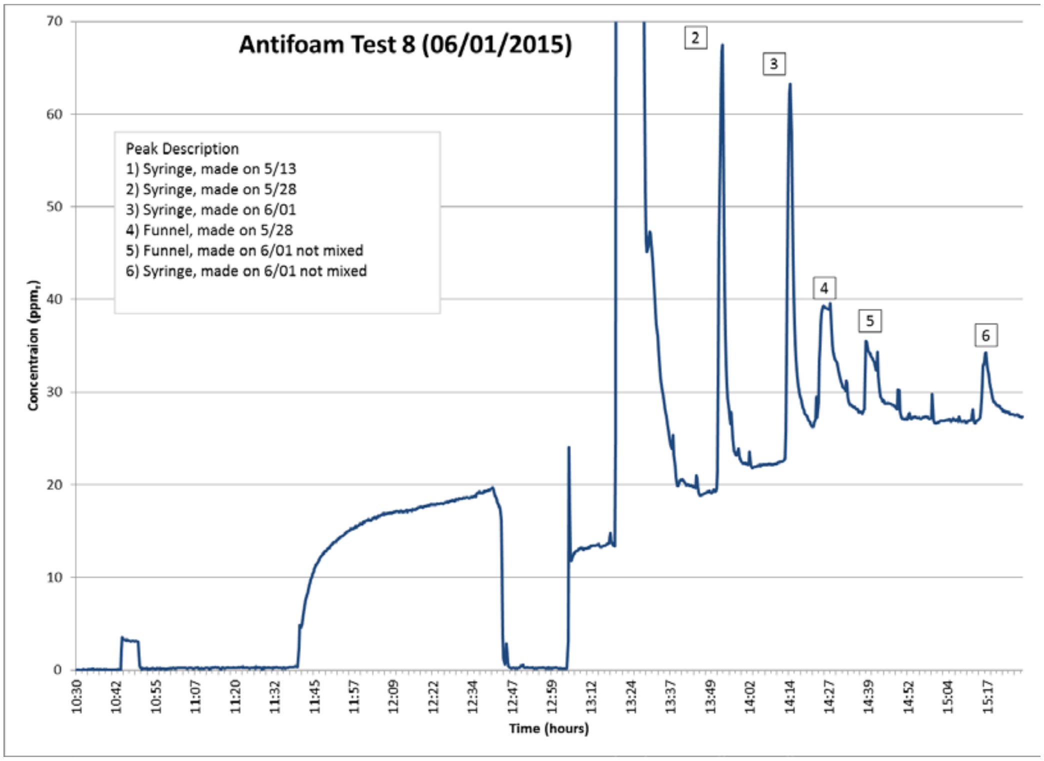
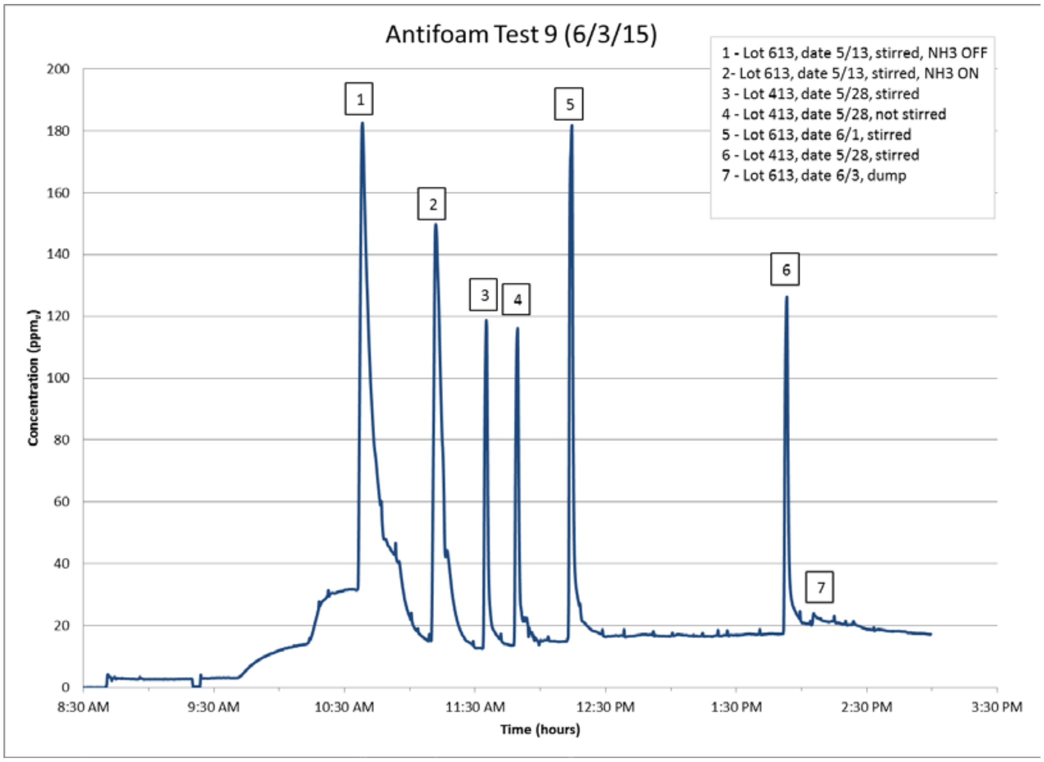


Figure A-4. Run AF8 Zoomed for smaller peaks



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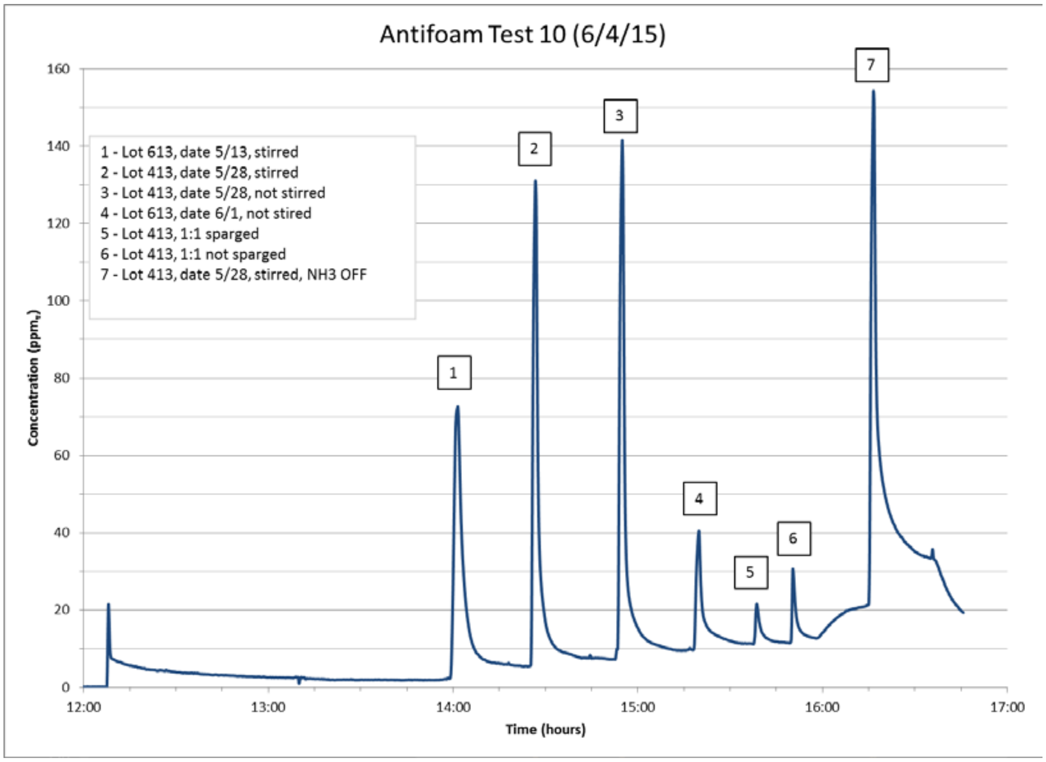

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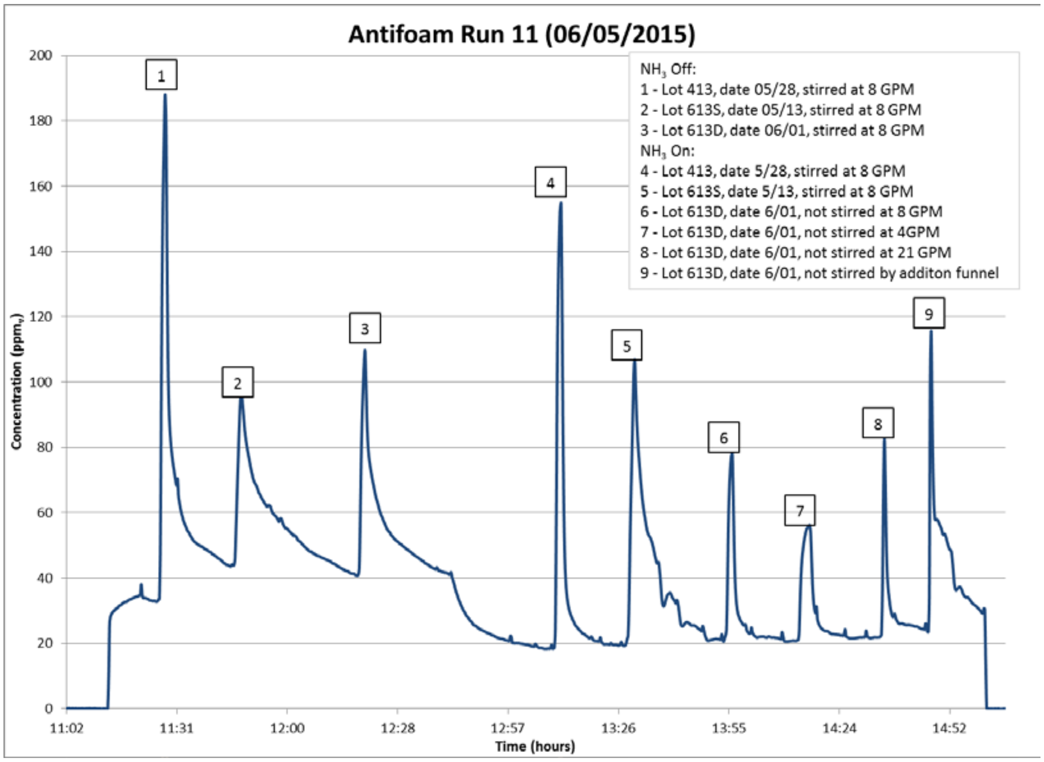

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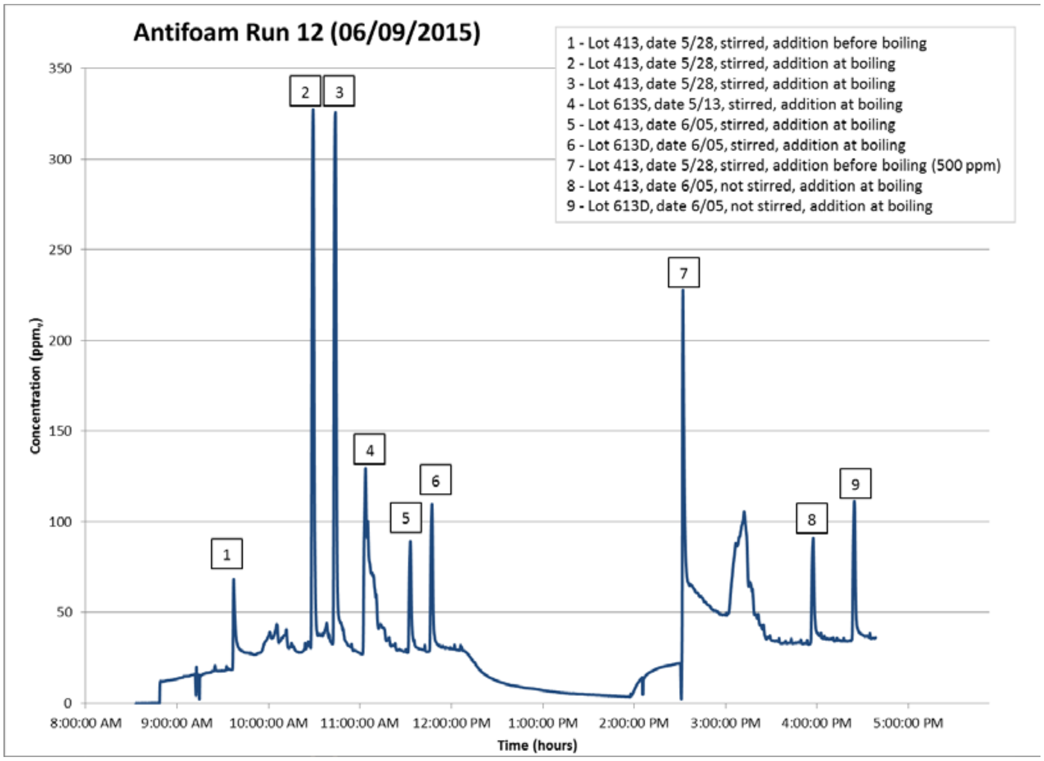

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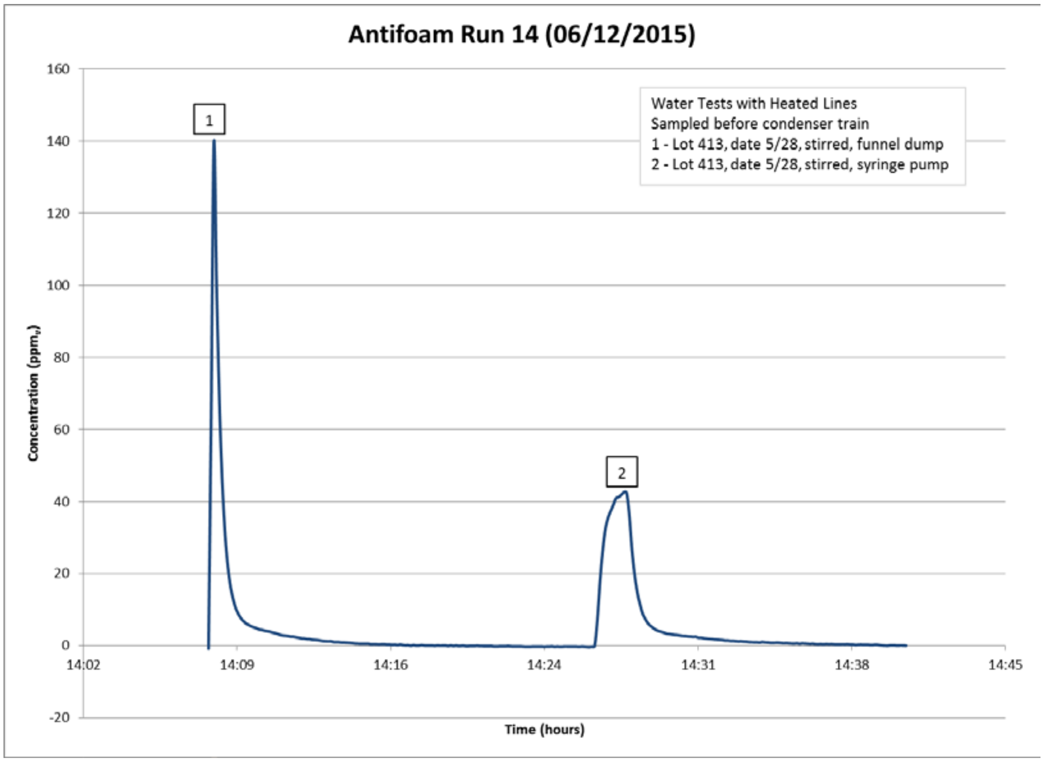

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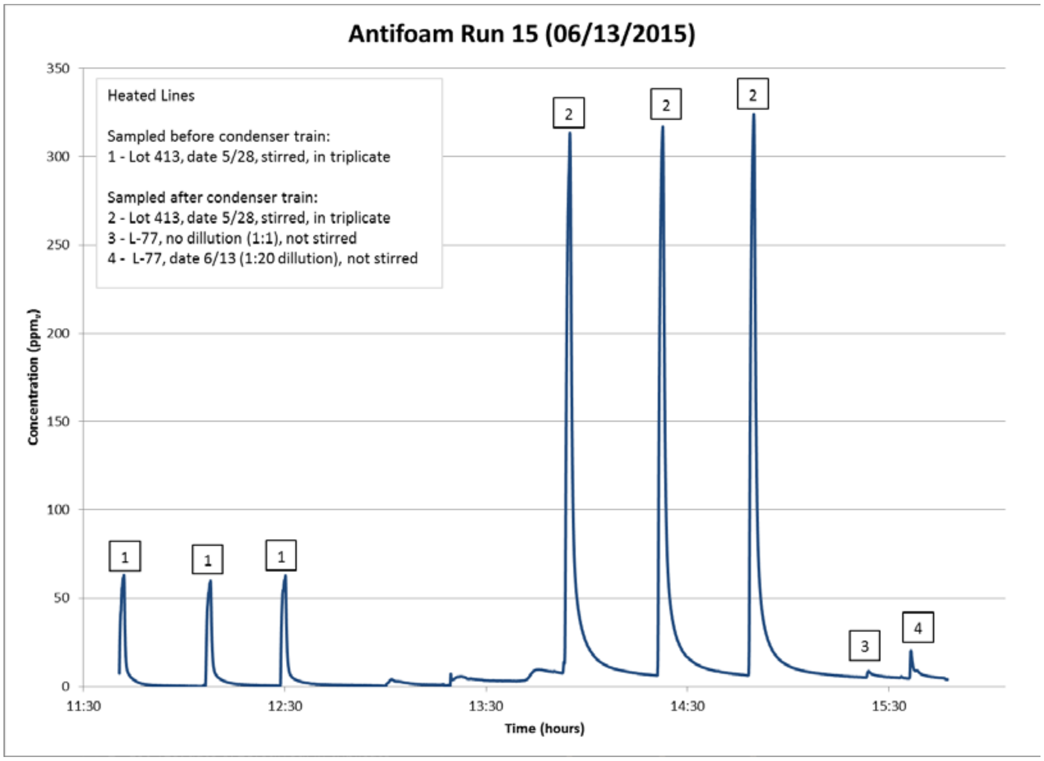

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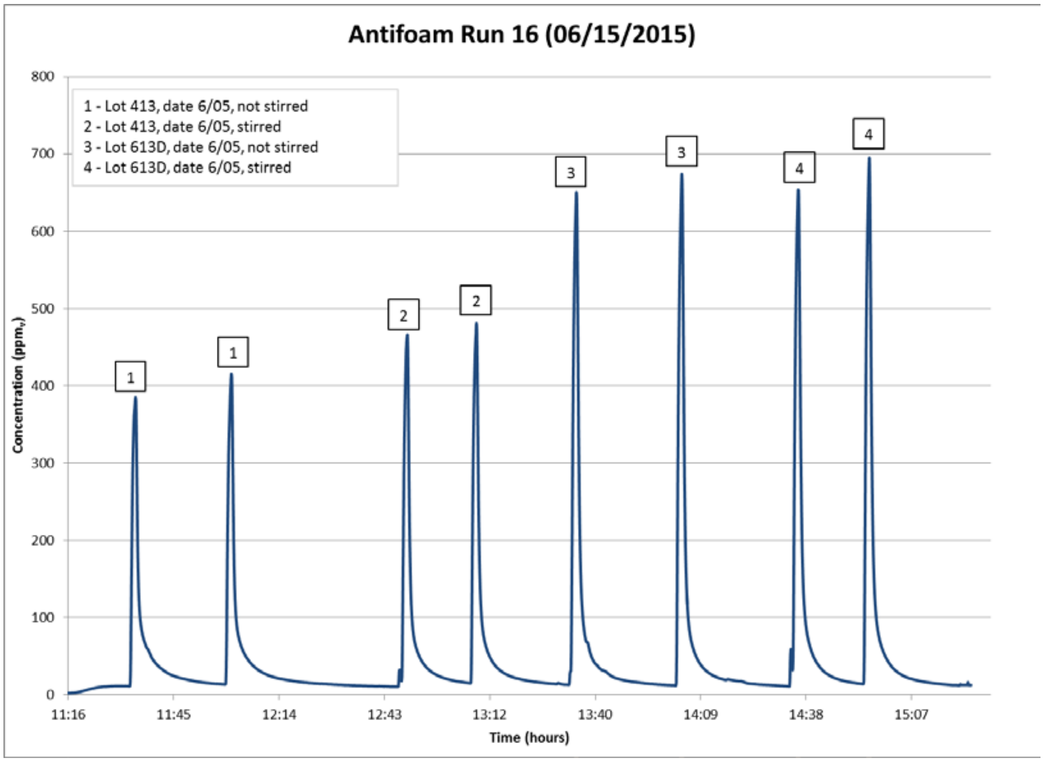

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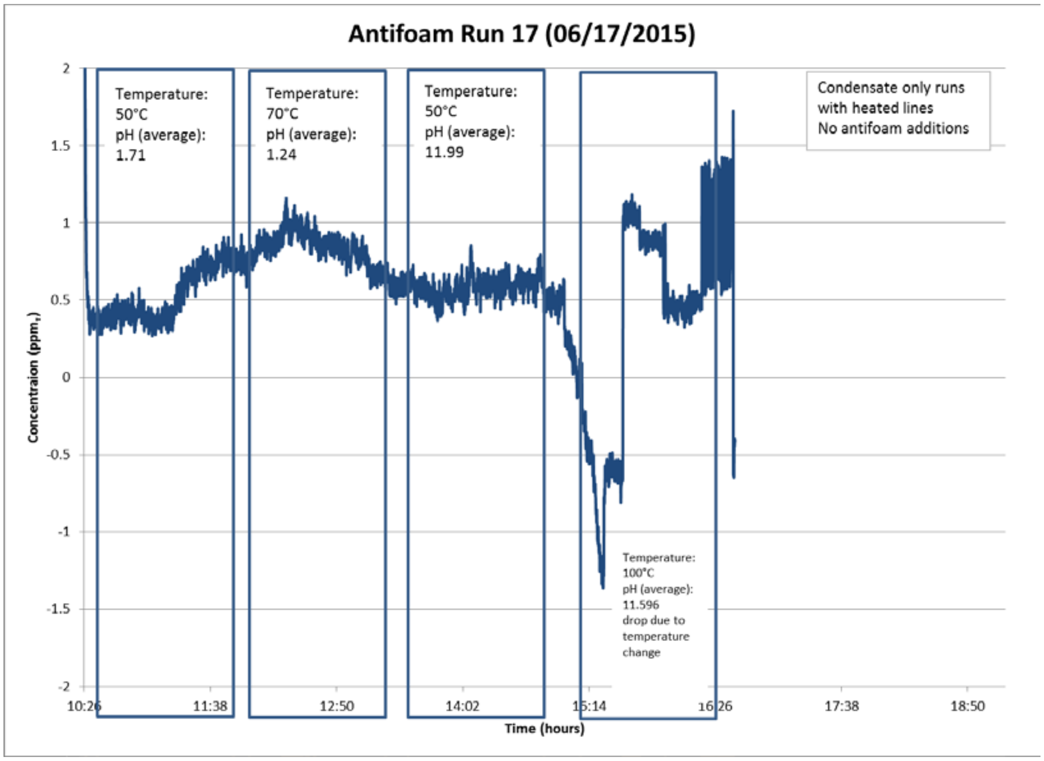

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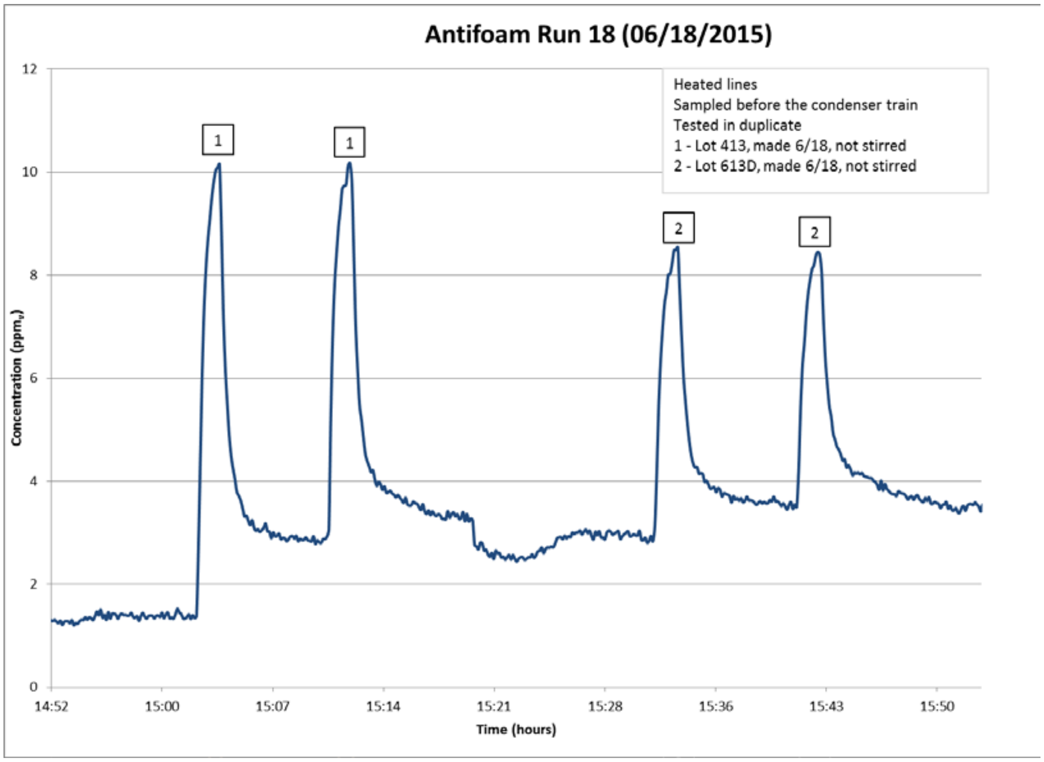

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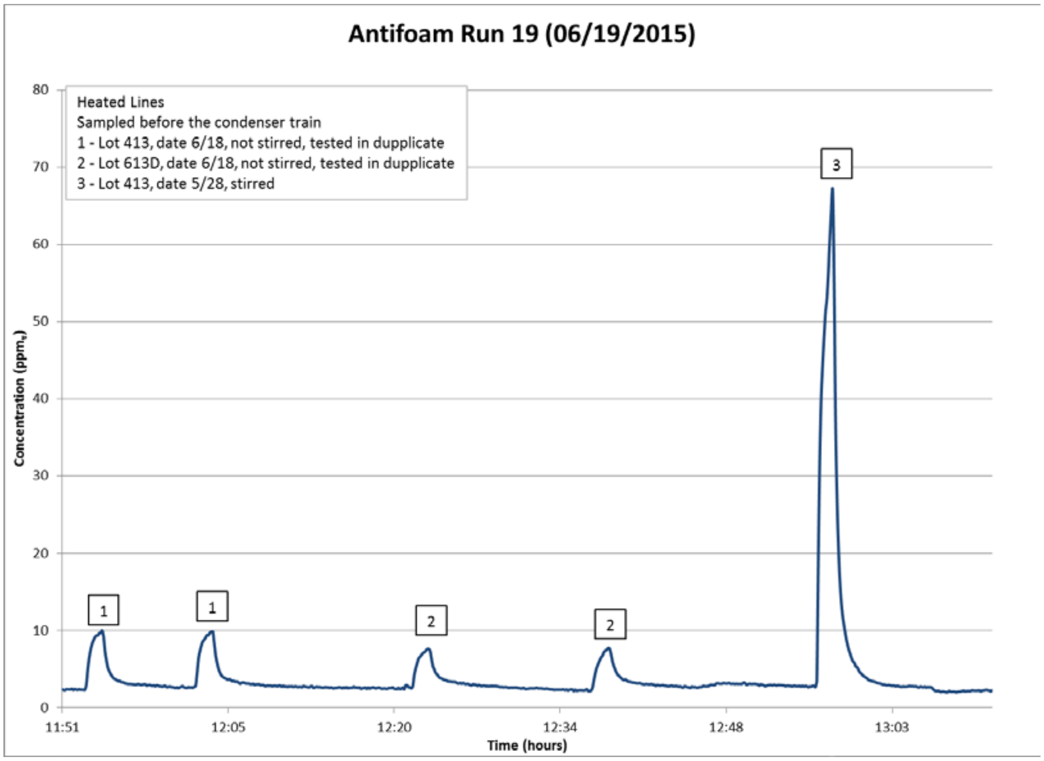

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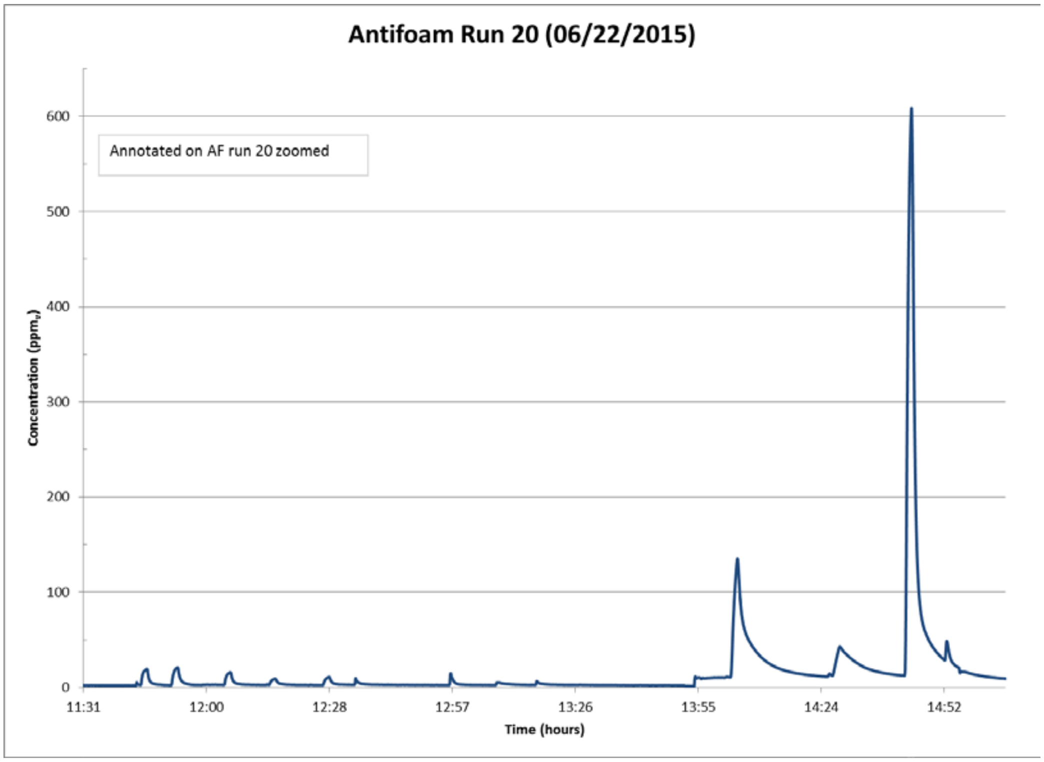

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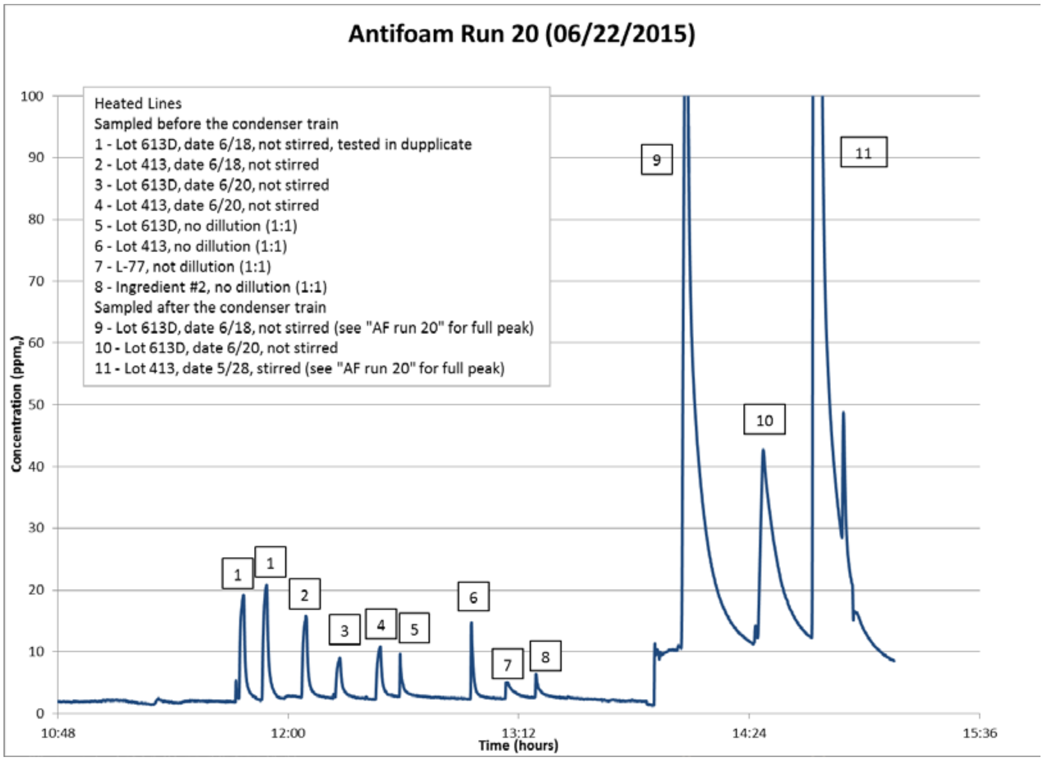
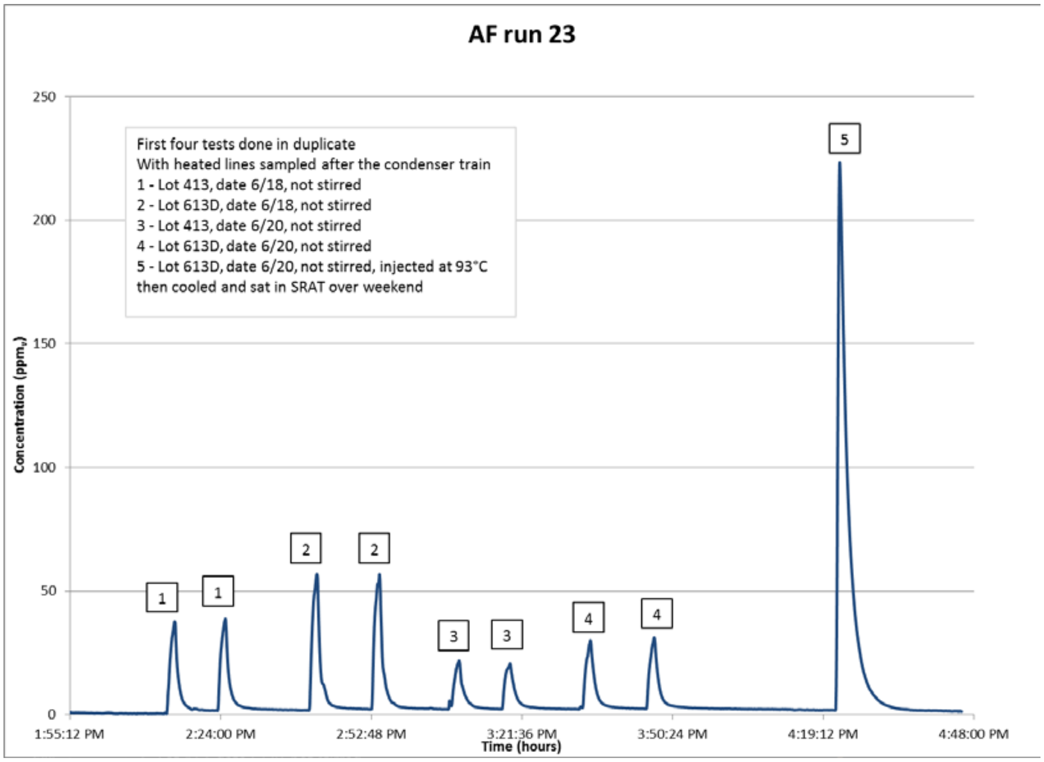


Figure A-16. Run AF20 Zoomed for smaller peaks



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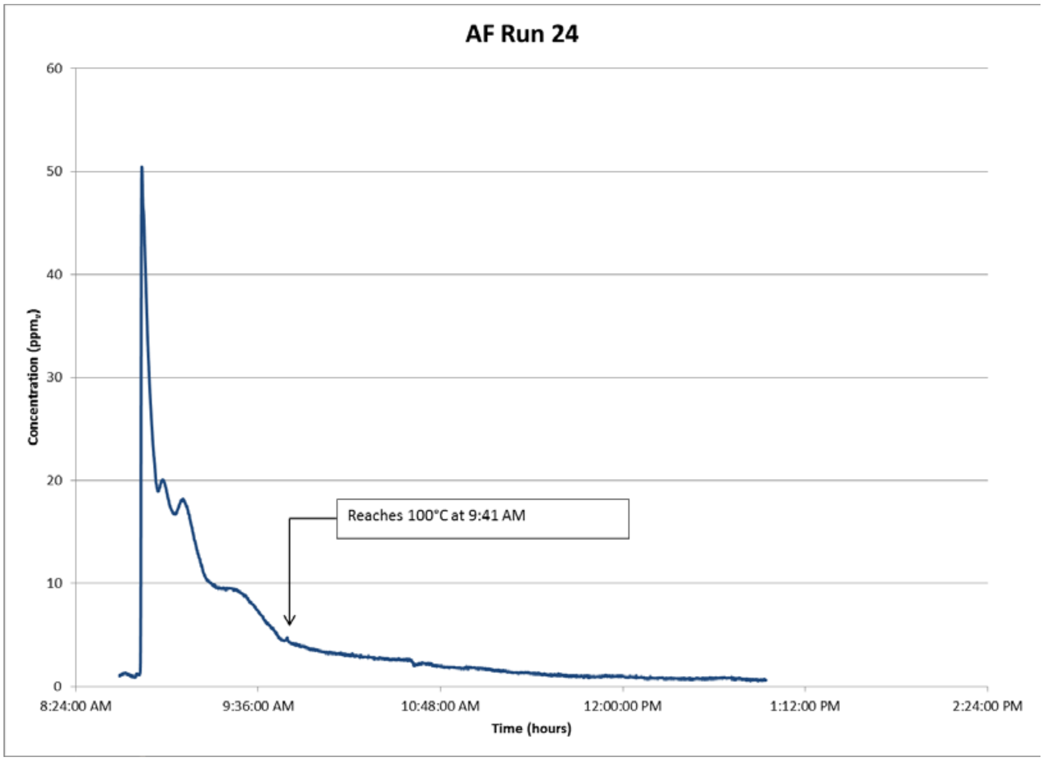


Figure A-18. Run AF24, After 5 day old antifoam sat in the kettle for 4 days

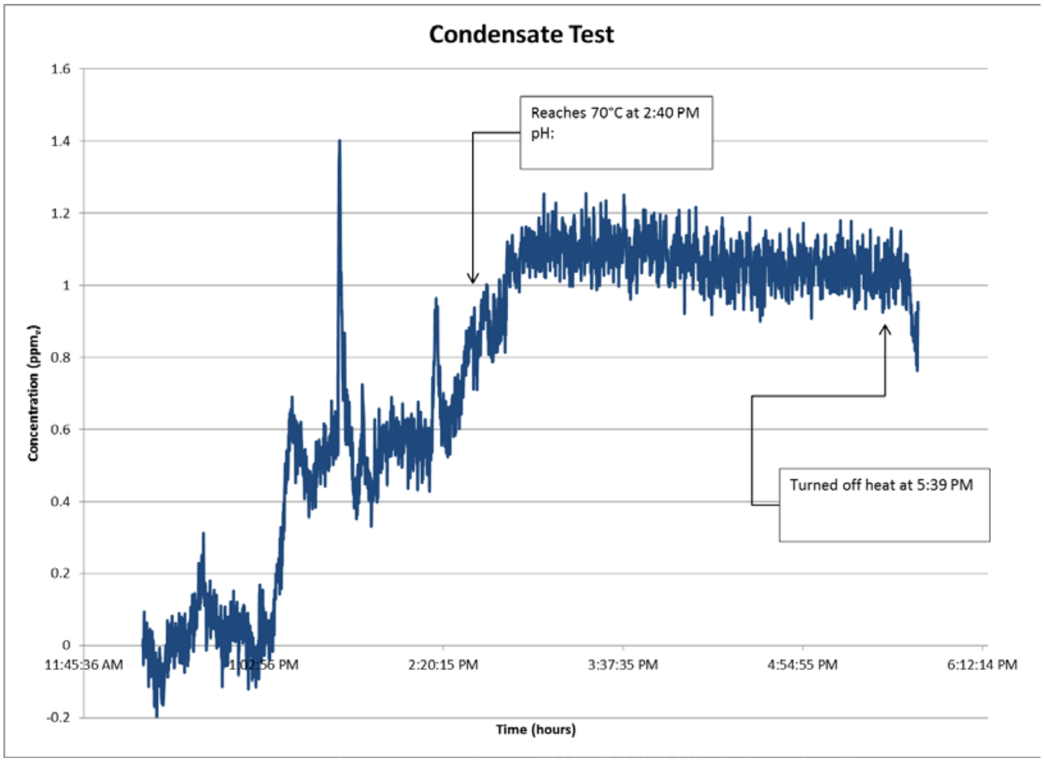
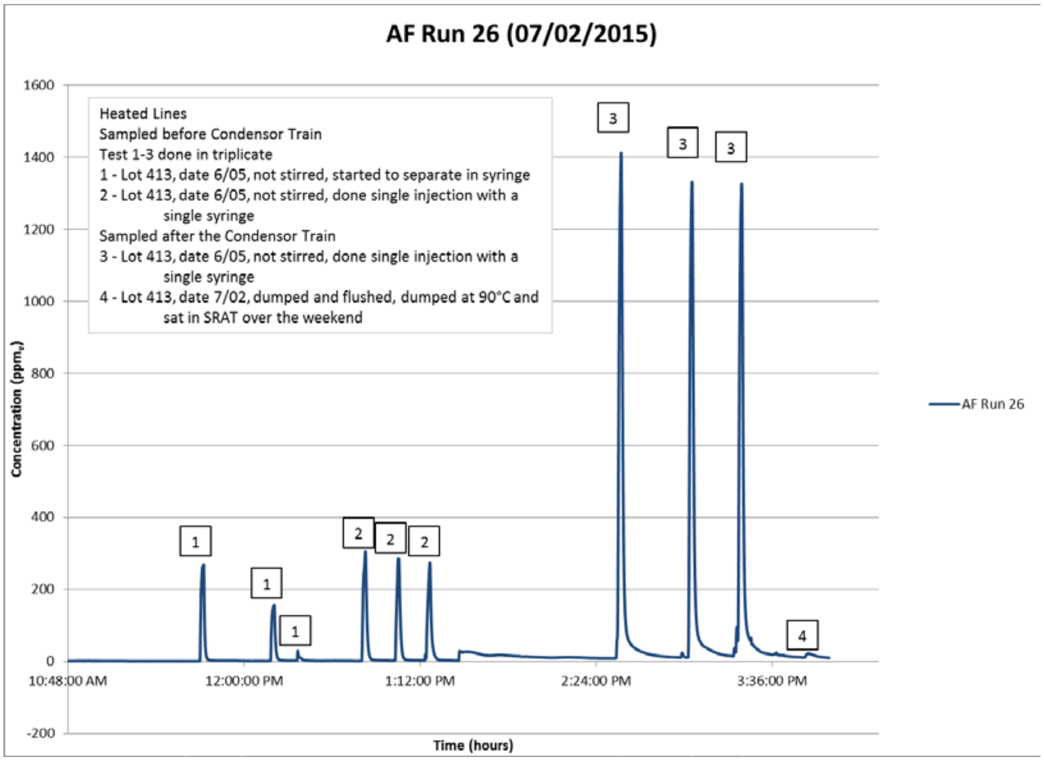


Figure A-19. Run AF25, Condensate Test



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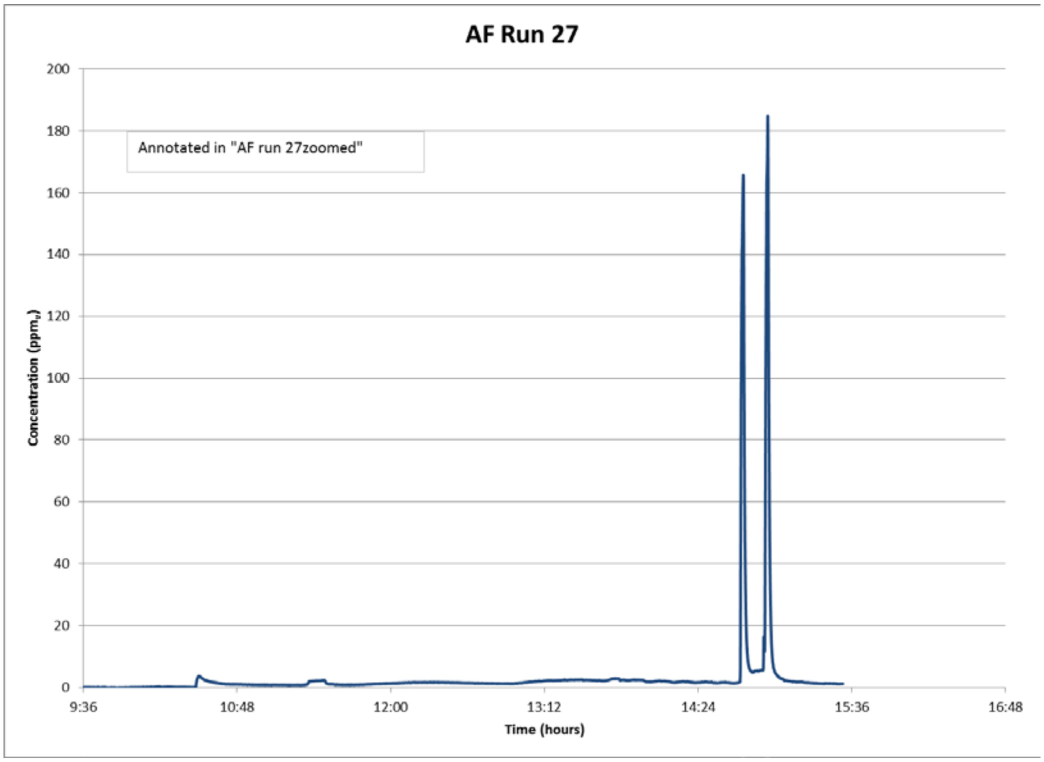

Figure A-21. Run AF27, After fresh antifoam sat in the kettle for 4 days

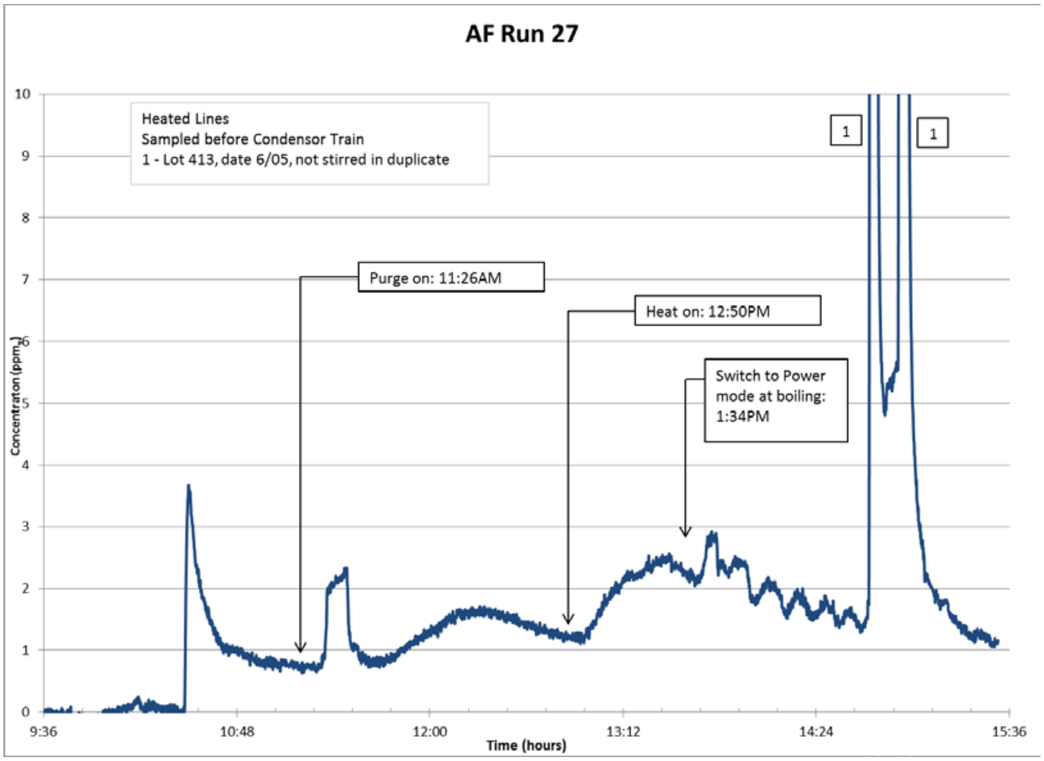

Figure A-22. Run AF27 Zoomed for smaller peaks

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