Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Analysis of Condensate Samples in Support of the Antifoam Degradation Study

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January 2016

SRNL-STI-2015-00698, Rev. 0

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Prepared for
U.S. Department of Energy

SRNL-STI-2015-00698
Revision 0

Keywords: *Organics Analysis, Radionuclides*

Retention: *Permanent*

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EXECUTIVE SUMMARY

The degradation of Antifoam 747 to form flammable decomposition products has resulted in declaration of a Potential Inadequacy in the Safety Analysis (PISA) for the Defense Waste Processing Facility (DWPF). Savannah River National Laboratory (SRNL) testing with simulants showed that hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), and 1-propanal are formed in the offgas from the decomposition of the antifoam. A total of ten DWPF condensate samples from Batch 735 and 736 were analyzed by SRNL for three degradation products and additional analytes. All of the samples were analyzed to determine the concentrations of HMDSO, TMS, and propanal. The results of the organic analysis found concentrations for propanal and HMDSO near or below the detection limits for the analysis. The TMS concentrations ranged from below detection to 11 mg/L. The samples from Batch 736 were also analyzed for formate and oxalate anions, total organic carbon, and aluminum, iron, manganese, and silicon. Most of the samples contained low levels of formate and therefore low levels of organic carbon. These two values for each sample show reasonable agreement in most cases. Low levels of all the metals (Al, Fe, Mn, and Si) were present in most of the samples.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
HMDSO	Hexamethyldisiloxane
IC Anions	Ion Chromatography Anions
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
PISA	Potential Inadequacy in the Safety Analysis
RCT	Recycle Collection Tank
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TMS	Trimethylsilanol
TOC	Total Organic Carbon
TTQAP	Task Technical and Quality Assurance Plan
VOA	Volatile Organic Analysis

1.0 Introduction

The degradation of Antifoam 747 to form flammable decomposition products has resulted in declaration of a Potential Inadequacy in the Safety Analysis (PISA) for the Defense Waste Processing Facility (DWPF). Simulant testing at the Savannah River National Laboratory (SRNL) showed that hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), and 1-propanal are formed in the offgas from the decomposition of the antifoam.[1] Savannah River Remediation (SRR) requested that SRNL develop analytical methods for these antifoam degradation products and analyze radioactive samples.[2] A Task Technical and Quality Assurance Plan (TTQAP) was developed to address analysis of DWPF Chemical Process Cell (CPC) condensate samples from the Slurry Mix Evaporator Condensate Tank (SMECT) and other applicable radioactive samples.[3] Results from the analysis of Tank 22H samples were previously reported.[4] This report presents analytical results for recent SMECT samples from the DWPF.

2.0 Experimental Procedure

A total of ten DWPF CPC condensate samples were analyzed by SRNL for antifoam degradation products and other analytes. Two of the samples were from a collection of six SMECT samples that were received from Batch 735, seven of the samples were from the SMECT during Batch 736, and one of the samples was from the Recycle Collection Tank (RCT) during Batch 736. Table 2-1 provides identifying information about the samples.

Nine of the samples were transferred directly to Analytical Development (AD) for analysis. All of the samples contained a small amount of sludge solids. With the sludge solids suspended in the solution the samples exhibited low extremity dose rates. However, when the solids settled to the bottom of the sample bottles, the extremity dose rates increased significantly. The unexpectedly high extremity dose rates slowed the analysis of the samples. Therefore, when the tenth sample arrived at SRNL, the sample was placed in the SRNL Shielded Cells and aliquots were prepared for analysis by AD.

Aliquots of the samples were obtained from the sample bottles after mixing with a vortex mixer. Portions of the as-received sample were analyzed by volatile organic analysis (VOA) and semi-volatile organic analysis (SVOA). VOA provides concentrations of propanal and HMDSO in the samples, while SVOA can quantify concentrations of HMDSO and TMS.

All samples for VOA were analyzed by GC/MS with a purge and trap inlet. The purge and trap system was an OI Analytical Model 4660 instrument. GC/MS was performed using an Agilent 6890 GC equipped with a J&W DB-624 column, 18 m by 0.18 mm ID with a 1 micron film thickness. The mass spectrometer used for this study was an Agilent 5973N set for selected ion monitoring (SIM). Predominant ions for propanal, HMDS, and standards were programmed for analyte quantification. HMDS-d18 and propanal-d5 were used as isotopic diluents for the study.

All samples for SVOA were extracted with methylene chloride. Prior to extraction, saturated aqueous sodium nitrate solution was added to each sample and standard to increase the ionic strength. Anhydrous magnesium sulfate was used for drying of the extract prior to analysis. The GC/MS used for this study was an Agilent 7890 GC paired with an Agilent 5977 mass spectrometer. The GC is equipped with a J&W DB-5MS column, 25 m by 0.20 mm ID with a 0.33 micron film thickness. The mass spectrometer was set for selected ion monitoring (SIM),

and predominant ions for TMSOH and HMDS were programmed for analyte quantification. The technique of standard additions was used for analyte quantification.

The samples from Batch 736 were also analyzed by ion chromatography (IC Anions) for formate and oxalate anions, for total organic carbon (TOC), and by inductively coupled plasma-emission spectroscopy (ICP-ES) for aluminum, iron, manganese, and silicon after a mixed acid digestion of the sample. The mixed acid digestion method uses a combination of HF, HNO_3, and HCl heated in a closed vessel to dissolve solids. After heating, boric acid is added to complex the fluoride and additional HCl added to effect dissolution.

Quality Assurance
Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 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. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-07.

Table 2-1. Antifoam Degradation Study Sample Information

SRNL Sample ID	Description	Bottle ID	DWPF LIMS No.
SMECT_4607_20779	Batch 736 RCT after SRAT Processing	4607	200020779
SMECT_5020_20712	Batch 736 SMECT Prior to Start of SRAT Cycle	5020	200020712
SMECT_5021_20765	Batch 736 SMECT after Nitric Addition	5021	200020765
SMECT_5022_20768	Batch 736 SMECT after Formic Addition	5022	200020768
SMECT_5023_20772	Batch 736 SMECT after SEFT Addition	5023	200020772
SMECT_5024_20775	Batch 736 SMECT End of SRAT Cycle	5024	200020775
SMECT_5025_20808	Batch 736 SMECT after 1st Frit Drop	5025	200020808
SMECT_5026_20816	Batch 736 SMECT End of SME Cycle	5026	200020816
SMECT_735_20190	Batch 735 SMECT	-	200020190
SMECT_735_20211	Batch 735 SMECT	-	200020211

3.0 Results and Discussion

Tables 3-1, 3-2, and 3-3 contain the results of the SMECT sample analyses. The results of the organic analysis in Table 3-1 show concentrations for propanal and HMDSO near or below the detection limits for the analysis. The TMS concentrations range from below detection to 11 mg/L. The results from the VOA and SVOA methods have 1-σ uncertainties of approximately 20%.

The results from the ICP-ES analysis in Table 3-2 show low levels of Al, Fe, Mn, and Si present in most of the samples. The blank from the mixed acid digestion showed a Si concentration of 197 mg/L. This value is similar in magnitude to the Si concentrations measured in the most of the samples making the sample results for silicon unreliable. The high silicon background likely results from the interaction of the HF in the mixed acid dissolution leaching silicon from the quartz torch of the ICP-ES instrument. A silicon concentration significantly higher than the blank was observed for sample SMECT_5026_20816 Although sodium was not reported in the table, the sodium concentration for the RCT sample SMECT_4607_20779 was approximately 20,000 mg/L (0.85 M) versus ~100 mg/L in the other SMECT samples. This is expected since DWPF charges the RCT heel with caustic prior to receiving a SMECT transfer.

The results in Table 3-3 indicate most of the samples contained low levels of formate and therefore low levels of organic carbon. These two values for each sample show reasonable agreement in most cases when compared on a carbon basis. The oxalate anion concentration was below detection for all samples.

Table 3-1. Results for the Organic Analysis of the SMECT Samples

Sample ID	Units	Propanal	Hexamethyldisiloxane (HMDSO)	Trimethylsiloxane (TMS)
SMECT_4607_20779	mg/L	<0.25	<0.25	9.2
SMECT_5020_20712	mg/L	<0.25	<0.25	<0.25
SMECT_5021_20765	mg/L	<0.25	<0.25	<0.25
SMECT_5022_20768	mg/L	<0.25	<0.25	<0.25
SMECT_5023_20772	mg/L	<0.25	<0.25	3.6
SMECT_5024_20775	mg/L	0.29	<0.25	2.5
SMECT_5025_20808	mg/L	0.39	0.29	8.9
SMECT_5026_20816	mg/L	0.12	<0.25	11
SMECT_735_20190	mg/L	<0.25	<0.25	1.5
SMECT_735_20211	mg/L	<0.25	<0.25	<0.25

The results from the VOA and SVOA methods have a 1-σ uncertainty of 20%.

Table 3-2. Results for the ICP-ES Analysis of the SMECT Samples

Sample ID	Units	Al	Fe	Mn	Si
SMECT_4607_20779	mg/L	15.3	77.1	3.82	261*
SMECT_5020_20712	mg/L	<9.04	40.9	2.12	122*
SMECT_5021_20765	mg/L	30.0	102	19.5	134*
SMECT_5022_20768	mg/L	<9.59	41.5	2.53	164*
SMECT_5023_20772	mg/L	<9.56	37.8	2.05	146*
SMECT_5024_20775	mg/L	<9.59	22.7	<2.10	116*
SMECT_5025_20808	mg/L	<9.43	10.8*	<2.06	139*
SMECT_5026_20816	mg/L	<12.50	122	2.68	711

* The blank run concurrently with the samples showed a value of similar magnitude as the samples. These values should be considered unreliable.

Table 3-3. Results for the IC Anions and TOC of the SMECT Samples

Sample ID	Units	Formate	Oxalate	TOC
SMECT_4607_20779	mg/L	87	<10	36.4
SMECT_5020_20712	mg/L	<10	<10	4.16
SMECT_5021_20765	mg/L	<10	<10	7.52
SMECT_5022_20768	mg/L	102	<10	30.7
SMECT_5023_20772	mg/L	77	<10	39.5
SMECT_5024_20775	mg/L	68	<10	35.4
SMECT_5025_20808	mg/L	70	<10	3.68
SMECT_5026_20816	mg/L	28	<10	15.5

4.0 Conclusions

The results of the organic analysis found concentrations for propanal and HMDSO near or below the detection limits for the analysis. The TMS concentrations ranged from below detection to 11 mg/L. Most of the samples from Batch 736 contained low levels of formate and therefore low levels of organic carbon. These two values for each sample show reasonable agreement in most cases. Low levels of metals (Al, Fe, Mn, and Si) were present in most of the samples from Batch 736.

5.0 Acknowledgements

The contributions of Rita Sullivan for preparing the samples, Chuck Coleman, Amy Ekechukwu, John Young, Steve Crump, and Tom White for providing analytical services are appreciated and acknowledged.

6.0 References

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4. C. J. Martino and C. L. Crawford, "*Results of Antifoam Degradation Product Analysis of Tank 22H*", SRNL-L3100-2015-00146, Rev. 0, August 19, 2015.

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