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Solvent Hold Tank Sample Results for MCU-15-556-557-558: March 2015 Monthly Sample

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-15-556, MCU-15-557, and MCU-15-558), pulled on 03/16/2015 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-556-557-558 indicated a low concentration (~ 78 % of nominal) of the suppressor (TiDG) and concentrations of the extractant (MaxCalix), and of the modifier (CS-7SB) in the solvent that were slightly lower than nominal. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent in February 2015. Based on the current monthly sample, the levels of TiDG, MaxCalix, and modifier are sufficient for continuing operation without adding a trim at this time.

No impurities above the 1000 ppm level were found in this solvent by the Semi-Volatile Organic Analysis (SVOA). However, the p-nut vials that delivered the samples contained small (1 mm) droplets of oxidized modifier and amides (as detected by the FTIR analysis). In addition, up to 21 microgram of mercury per gram of solvent (or 17.4 µg/mL) was detected in this sample.

The laboratory will continue to monitor the quality of the solvent in particular for any new impurities or degradation of the solvent components.

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LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
FTIR	Fourier transform infra-red spectroscopy
HPLC	High Performance Liquid Chromatography
ISDP	Integrated Salt Disposition Project
MCU	Modular Caustic-Side Solvent Extraction Unit
MaxCalix	1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6
NGS	Next Generation Solvent
RSD	Relative Standard Deviation or the absolute value of the Coefficient of Variation
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TiDG	*N*,*N'*,*N"*–tris(3,7-dimethyloctyl)guanidine
TOA	Trioctylamine

1.0 Introduction

In late FY13, Modular Caustic-Side Solvent Extraction Unit (MCU) switched to the Next Generation Solvent (NGS) flow sheet. Facility personnel implemented the switch by adding a non-radioactive, NGS "cocktail" containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. The resulting "blend" solvent ("NGS Blend solvent") is essentially NGS with residual amounts of BOBCalixC6 and trioctylamine (TOA). SHT samples are sent to SRNL to examine solvent composition changes over time.[1] On March 16, 2015, Operations personnel pulled and delivered three samples from the SHT (MCU-15-556, MCU-15-557, and MCU-15-558) for analysis. These samples are intended to verify that the solvent is within the specified composition range. A baseline "scratch" solvent (a scratch solvent is a preparation of all 6 solvent components at the same time to generate a solution of the appropriate composition that approximates the blend of cocktail[2] and heel solvent) was prepared in the lab (May 14, 2014) and used for comparison and evaluation. The results from the analyses are presented in this document.

2.0 Experimental Procedure

2.1 Experimental Procedure

A summary of relevant and recent trims to the MCU solvent as well as the arrival date of the samples currently being studied is shown in Table 2-1. On February 22, 2015, a trim addition was made to MCU that was 2.23E4 grams of modifier, 838 grams of TiDG, and 2.23E3 grams of MaxCalix in 10 gallons of Isopar™L.

Table 2-1 Log of recent trims to the MCU solvent and sample arrivals to SRNL

Event	**Date**
February solvent trim added to MCU	February 22, 2015
SHT sample MCU-15-389-390	February 25, 2015
SHT sample MCU-15-439-440-441	February 28, 2015
10 gallons of Isopar™L added to MCU	March 6, 2015
SHT sample MCU-15-556-557-558	March 16, 2015

Samples shown in Table 2-1 were received in p-nut vials containing ~10 mL each (see Fig 1). Once taken into a radioactive hood, the samples were visually inspected and analyzed for pH. MCU-15-556, MCU-15-557, and MCU-15-558 were composited before use. Aliquots of the composited sample were removed to perform analysis by density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, Fourier-Transformed Infra-Red Spectroscopy (FTIR), and Fourier-Transformed Hydrogen Nuclear Magnetic Resonance (FT-HNMR). Results from analytical measurements were compared with the theoretical values shown in Table 2-2.

Table 2-2 Nominal concentrations of the relevant components in NGS Blend[2]

Component	**mg/L**	**Molar**
MaxCalix	~ 44,400	~ 0.0465
BOBCalixC6*	< 4,030	< 0.0035
TOA*	< 530	< 0.0015
Modifier	~ 169,000	~ 0.50
TiDG	~1440	~ 0.003
Isopar™L	~ 623,000	~ 74 wt%

*Values represent starting values when NGS blend was implemented. These components are no longer added to or refurbished in MCU

2.2 Quality Assurance

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

The p-nut vials from MCU-15-556, MCU-15-557, and MCU-15-558 were examined and found to contain a single phase liquid with no apparent solids contamination or cloudiness. However, there were droplets observed on the walls of the p-nut vials. The droplets observed on the walls of the p-nut vials were examined by FTIR. All samples had a pH value of 5.5. No unusual reactions, solids, foaming, or immiscible layers were observed after combining the samples into one (MCU-15-556-557-558). Table 3-1 contains the results for the MCU-15-556-557-558 sample.

Isopar™ L and Modifier Levels

Density measurement of the sample gave a result of 0.833 g/mL (0.1% RSD) (or 0.830 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-556-557-558 at 22 °C. The calculated density (0.830 g/mL) for MCU-15-556-557-558 is 1% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory) [1]. Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be about the same as the nominal value.

MCU-15-556 **MCU-15-557** **MCU-15-558**

Figure 1. Typical appearance of the three vials MCU-15-556, MCU-15-557, and MCU-15-558

An examination of Table 3-1 shows that the Isopar™ L concentration is at its nominal value while the modifier concentration is correspondingly slightly lower than its nominal value. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement. The last Isopar™L trim addition to MCU was on March 6, 2015.

All measurements indicate the Isopar™ L level is at nominal value while the modifier concentration level is below its nominal value. This explains why the measured density is slightly below the standard sample density. The accuracies of the different measurements were within expectation as reflected in the total mass sum of the “average” results listed in Table 3-1. They added up to 0.826 ± 0.020 g/mL. Their sum is consistent with the measured and temperature corrected (to 25 ºC) value of 0.830 g/mL, but it is below the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL).

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[1] A second standard was prepared on December 12, 2014

Table 3-1 Sample Results for MCU-15-556-557-558

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.22E+05	6.23E+05	100
Isopar® L	FTIR	NA	6.21E+05		100
Isopar® L	Density[*]	NA	6.22E+05		100
Average[$]	All	NA	6.22E+05	6.23E+05	100
Modifier	HPLC	300316271	1.56E+05	1.69E+05	92
Modifier	FT-HNMR	NA	1.64E+05		97
Modifier	FTIR	NA	1.64E+05		97
Modifier	Density[*]	NA	1.58E+05		94
Average[$]	All	NA	1.59E+05	1.69E+05	94
TiDG	Titration	NA	1.13E+03	1.44E+03	78
TiDG	FT-HNMR	NA	1.08E+03		75
Average[$]	All	NA	1.12E+03	1.44E+03	78
trioctylamine	Titration	NA	2.49E+02	5.30E+02	47
Average[$]	All	NA	2.49E+02	5.30E+02	47
MaxCalix	FT-HNMR	NA	4.72E+04	4.44E+04	106
MaxCalix	HPLC	300316271	3.95E+04		89
Average[$]	All	NA	4.18E+04	4.44E+04	94
BOBCalixC6	HPLC	300316271	2.78E+03	4.03E+03	69
Average[$]	All	NA	2.78E+03	4.03E+03	69
Density (g/mL)	Direct Measurement	NA	0.830	0.835	99

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. Titration method uncertainty is 10% for TiDG and 16% for TOA. Density results from the average of replicate volumetric trials typically have a percentage standard deviation of <3% between each value and the average. NMR analytical uncertainty is 10% for the modifier and 13% for MaxCalix, 14% for Isopar™ L, and 20% for TiDG. N/A = Not Applicable.

Density estimations assume the TiDG,

[*] Nominal value is the expected value for freshly prepared blended solvent with a target density of 0.8352 g/mL at 25 °C.

[$] $x = \frac{\Sigma_1^i \left({x_i}/{\delta_i^2} \right)}{\Sigma_1^i \left({1}/{\delta_i^2} \right)};$

Suppressors Levels

The average TiDG concentration level (1.12E3 mg/L) is at 78 % of its nominal value of 1440 mg/L despite the trim addition in February 2015. The suppressor concentration is above the minimum recommended operating level (480 mg/L) and thus, the solvent does not require a TiDG addition at this time. This data point also confirms the addition of TiDG made to the MCU solvent in February 2015. Inferring from past TiDG concentrations level trends and in the absence of new additions or new removal mechanisms, the TiDG concentration is expected to drop as shown in Fig. 2. The TOA concentration appears to have dropped to 249 mg/L (in the previous month the TOA level was 298 mg/L). These numbers are within analytical error. In addition, the TOA concentration appears not to correlate with the Isopar™ L concentration which in this case is at nominal value. Since MCU no longer adds TOA, the drop in TOA concentration is expected. Although both the TOA and TiDG concentrations are declining, there is a still a strong negative correlation between these two measurements (see Table 3-2). The correlation is perhaps due to TiDG degradation into primary amines, which have previously been identified as degradation products of the suppressor when heated.[3] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalence points coincide.[4] Prior to the December sample analysis, there was a strong positive correlation (0.78) between TiDG and TOA based on titration analysis (both components decreased with time).

Table 3-2 Correlation coefficient between TiDG and TOA as determined by Titration since the NGS-CSSX implementation. HNMR does not adequately measure TOA.

	TiDG titration	*TOA titration*	*TiDG HNMR*
TiDG Titration	1		
TOA Titration	**-0.72**	1	
TiDG FT-HNMR	0.78	-0.63	1

Extractant Levels

The average MaxCalix level is 4.18 E4 mg/L (±13%) which is 6% below the nominal concentration but it is within the 95% confidence level of the analytical measurement (see Figure 3).

Gamma Level

The gamma measurement of MCU-15-556-557-558 is 4.19E+04 dpm/mL (±5%). This level is consistent with recent gamma measurement levels (see Fig. 4).

Impurities

No impurities were seen at the 1000 ppm level or higher as indicated by the SVOA method.

However, a significant concentration of droplets was observed on the wall of the p-nut vials (556-557-558). Some of these droplets were transferred onto a CaF_2 disc (initially assuming they were water droplets) and examined by FTIR. The infrared analysis showed (see Fig. 5) the presence of amides and oxidized material possibly modifier (or aliphatic acid from degraded lubricant). The oxidized material was the majority of the droplet while a relatively smaller amount of amide was detected (sources of amide can be bacteria or urea from TiDG). Coincidentally, amides were also observed in the FTIR analysis of the October 2014 Strip Effluent Feed Tank (SEFT) that was believed to be due to bacteria.

A few mL of the blended solvent was digested and analyzed for mercury (by the cold vapor method). The total mercury level in the solvent measured 21.1 $ug/g_{solvent}$ (20% st.dev.) or 17.4 $\mu g/mL_{solvent}$. This is a lot higher than the solubility of metallic Hg in dodecane (~3 ppm)[5] implying that other solubility-enhancing mechanisms are at play (like for example extraction or sorption or trapped solids) or a more soluble form of mercury is present. For 200 gallons of solvent (757.1 L) and assuming a density of 0.835 g/mL, the solvent could contain a total of 13.3 ± 3g of mercury. The oxidation state or states of this mercury is unknown at this time.

Recommendation

The current analysis indicates low modifier and TiDG levels in this solvent relative to the standard. The TiDG level is trending downwards similarly to previous trends observed after a TiDG trim addition is done to the solvent. However, the current TiDG level is above the minimum operating recommended level (958 mg/$L_{solvent}$) and above the minimum recommended level (479 mg/$L_{solvent}$). There is sufficient TiDG in the solvent for continuing operation without adding a trim until the next monthly sample and given the need to minimize the byproducts from TiDG decomposition, we don't recommend a TiDG trim at this time. Similarly, the modifier level (0.47 M) is well above the minimum modifier level at which the MaxCalix becomes insoluble in the solvent.

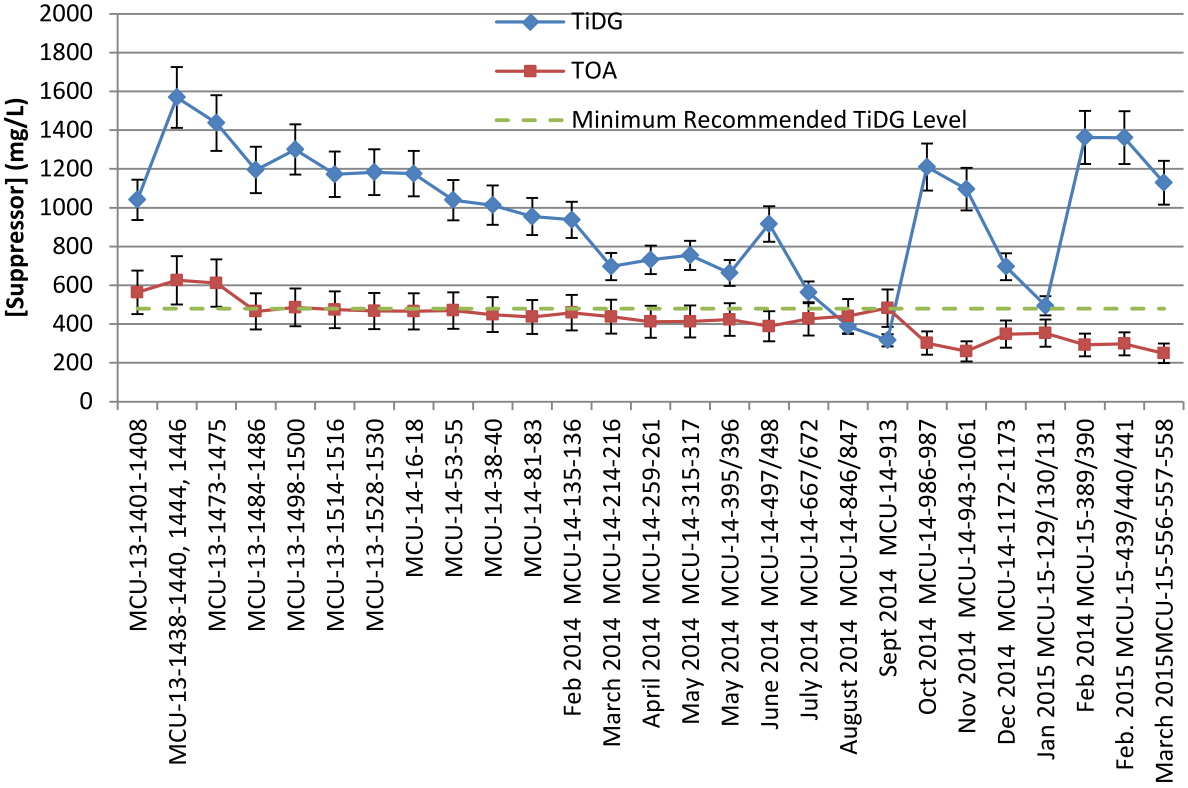

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 480 mg/L for TiDG.

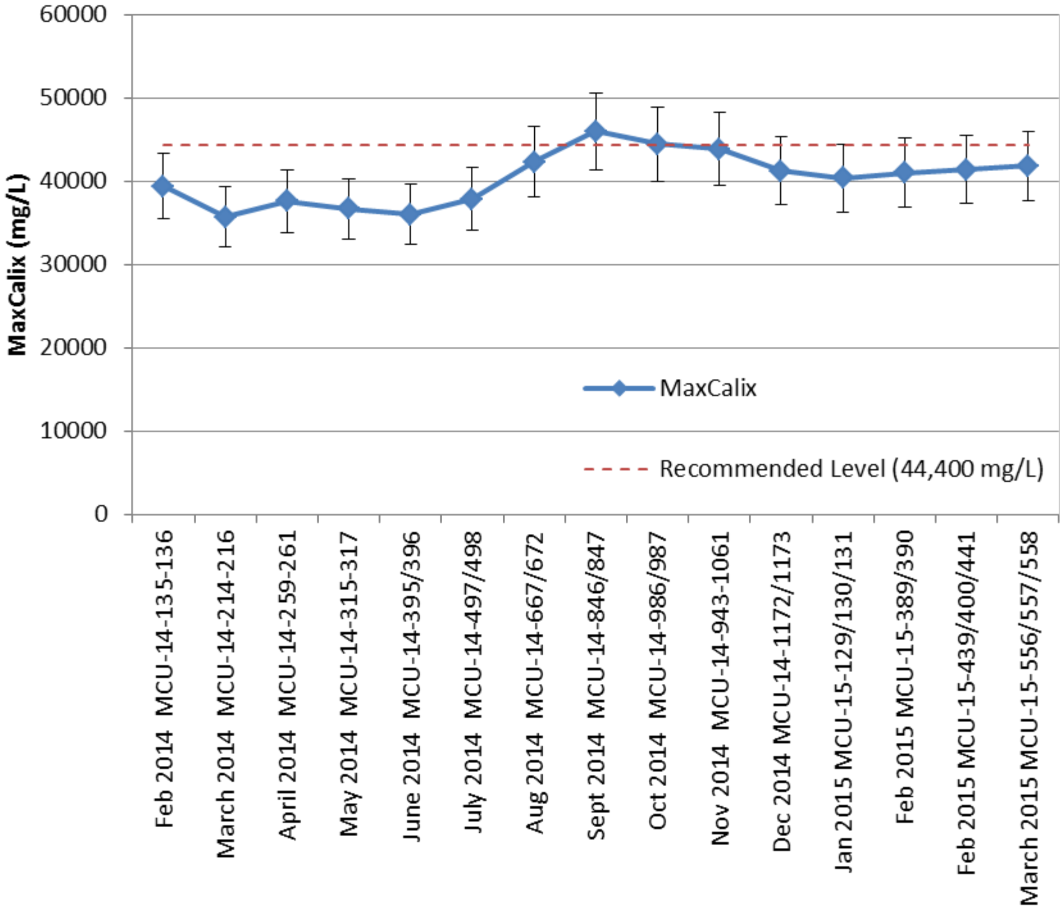

Figure 3. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

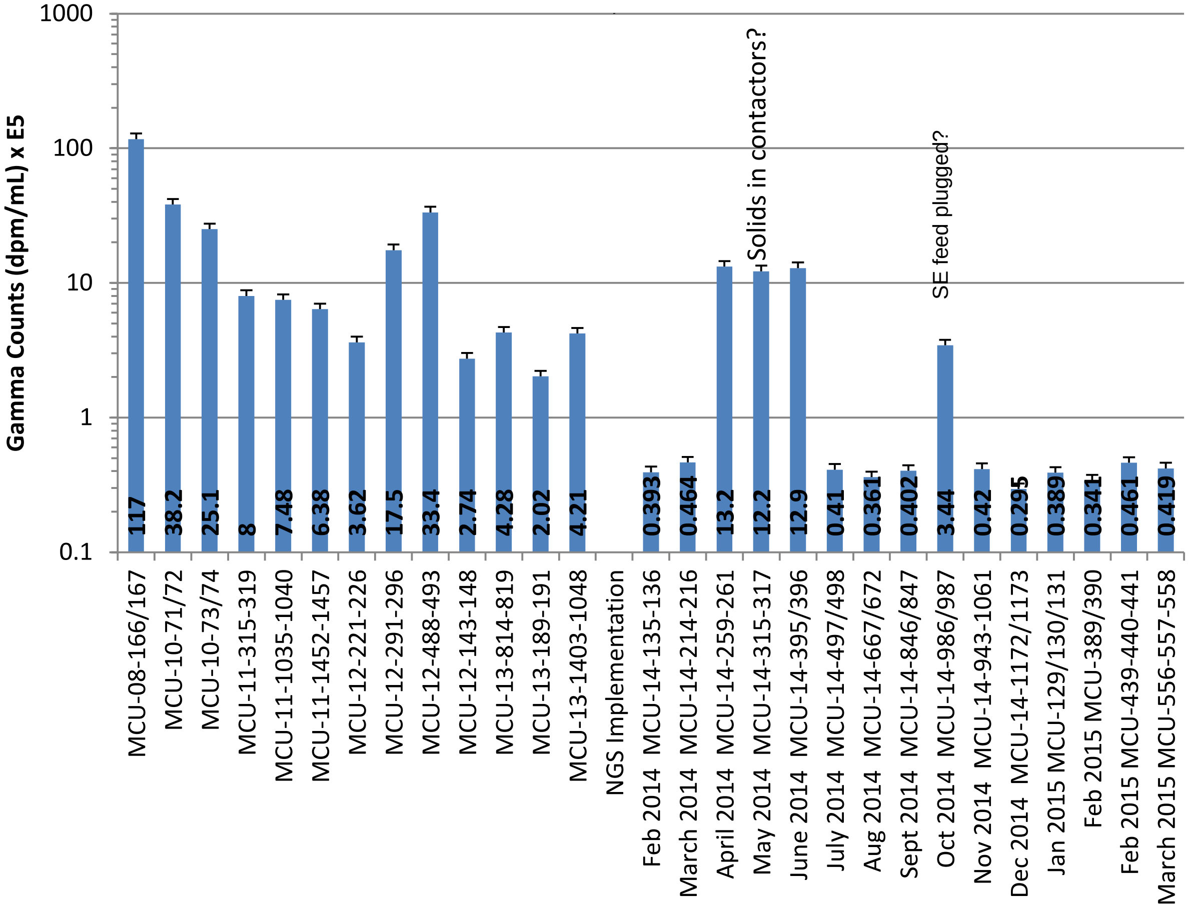

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

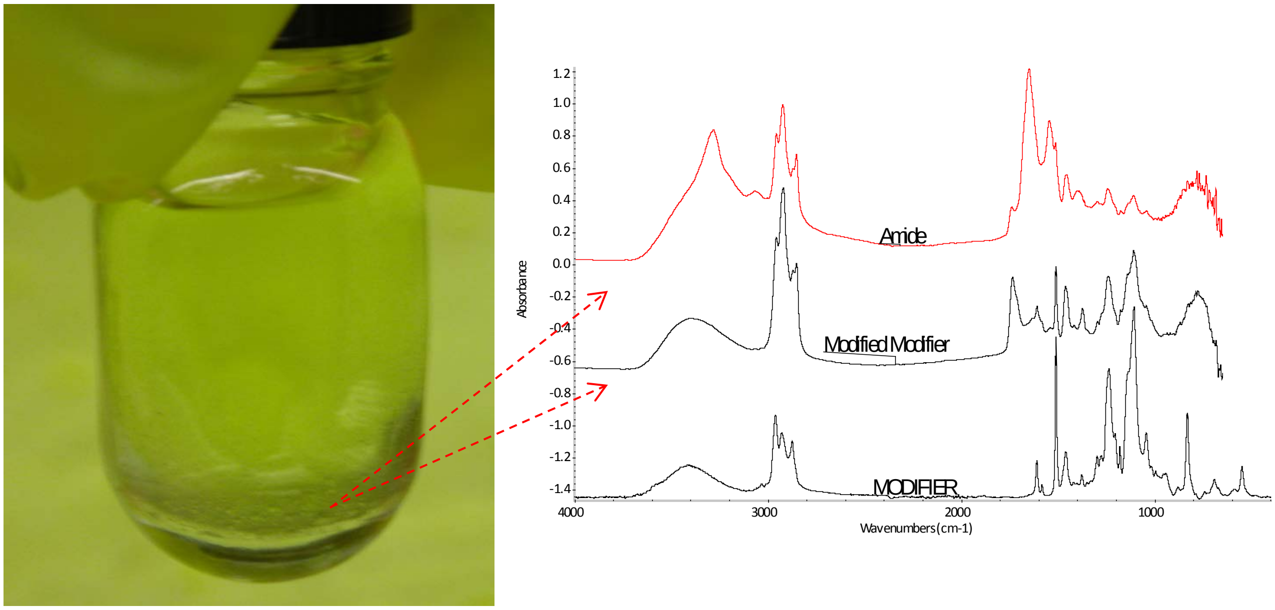

Figure 5. FTIR spectra of droplets found attached to the bottom of the vials (MCU-15-556,557,558)

4.0 Conclusions

SRNL received one set of SHT samples (MCU-15-556, MCU-15-557, and MCU-15-558), pulled on 03/16/2015 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-556-557-558 indicated a low concentration (~ 78 % of nominal) of the suppressor (TiDG) and slightly low concentration of the modifier (CS-7SB) in the solvent. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent in February 2015. Despite that the values are below the target component levels, the current level of TiDG and modifier are sufficient for continuing operation without adding a trim at this time until the next monthly sample.

No impurities above the 1000 ppm level were found in this solvent by the Semi-Volatile Organic Analysis (SVOA). However, the p-nut vials that delivered the samples contained small (1 mm) droplets of oxidized modifier and amides (as detected by the FTIR analysis). In addition, up to 21 microgram of mercury per gram of solvent (or 17.4 µg/mL) was detected in this sample.

The laboratory will continue to monitor the quality of the solvent in particular for any new impurity or degradation of the solvent components.

5.0 References

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