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Solvent Hold Tank Sample Results for MCU-15-389-390 and MCU-15-439-440-441: February 2015 Monthly Samples

F. F. Fondeur

K. M. L. Taylor-Pashow

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REVIEWS AND APPROVALS

AUTHORS:

F. F. Fondeur, Separations and Actinide Science Programs Date

K. M. L. Taylor-Pashow, Separations and Actinide Science Programs Date

TECHNICAL REVIEW:

T. B. Peters, Advanced Characterization and Processing Date

APPROVAL:

F. M. Pennebaker, Manager Date
Advanced Characterization and Processing

S. L. Marra, Manager Date
E&CPT Research Programs

E. A. Brass, Manager Date
MCU & Salt/Sludge Processing

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received two sets of Solvent Hold Tank (SHT) samples (MCU-15-389 and MCU-15-390 pulled on February 23, 2015 and MCU-15-439, MCU-15-440, and MCU-15-441 pulled on February 28, 2015) for analysis. The samples in each set were combined and analyzed for composition. Analysis of the composite samples MCU-15-389-390 and MCU-15-439-440-441 indicated a low concentration (~ 92 to 93 % of nominal) of the suppressor (TiDG) and slightly below nominal concentrations of the extractant (MaxCalix), but nominal levels of the modifier (CS-7SB) and of the Isopar™ L. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent on February 22, 2015. Despite that the values are below the target component levels, the current levels of TiDG and MaxCalix are sufficient for continuing operation without adding a trim at this time.

No impurities above the 1000 ppm level were found in this solvent. However, the p-nut vials that delivered the samples contained small (1 mm) droplets of oxidized modifier and amides.

The laboratory will continue to monitor the quality of the solvent in particular for any new impurity 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] The facility added trim to the solvent on February 22, 2015. On February 25, 2015, operations personnel delivered two samples from the SHT (MCU-15-389 and MCU-15-390) for analysis. Realizing that more samples were needed, operations personnel pulled and delivered another three samples (MCU-15-439, MCU-15-440, and MCU-15-441) on February 28. 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 2.23E+04 grams of modifier, 838 grams of TiDG, and 2.23E+03 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 23, 2015
SHT sample MCU-15-439-440-441	February 28, 2015

Samples shown in Table 2-1 were received in p-nut vials containing ~10 mL each (see Fig 1). Two of the p-nut vials (MCU-15-439 and MCU-15-389) contained a significant amount of secondary phase droplets attached to the bottle's interior surface. Once taken into a radioactive hood, the samples were visually inspected and analyzed for pH. MCU-15-389 and MCU-15-390 were composited. Similarly, samples MCU-15-439, MCU-15-440, and MCU-15-441 were also composited into one sample before use. Aliquots of the composited samples 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

[#] The total sum is approximately 0.842 g/mL which is more than 0.835 g/mL (standard density at 25°C)

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-15-389, MCU-15-390, MCU-15-439, MCU-15-440, and MCU-15-441 were examined and found to contain a single phase liquid with no apparent solids contamination or cloudiness. However, significant amounts of secondary phase droplets were observed on the interior walls of the MCU-15-439 and MCU-15-389 p-nut vials. All samples had a pH value of 5.5. No unusual reactions, solids, foaming, or immiscible layers were observed after compositing the samples (MCU-15-389-390 and MCU-15-439-440-441). Table 3-1 contains the results for the MCU-15-389-390 sample. Table 3-2 contains the results for the MCU-15-439-440-441 sample.

Isopar™ L and Modifier Levels

MCU-15-389-390

Density measurement of this sample gave a result of 0.839 g/mL (0.1% RSD) (or 0.836 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-389-390 at 21 °C. The temperature-adjusted density (0.836 g/mL) for MCU-15-389-390 is nearly identical to the temperature adjusted density of 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.

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

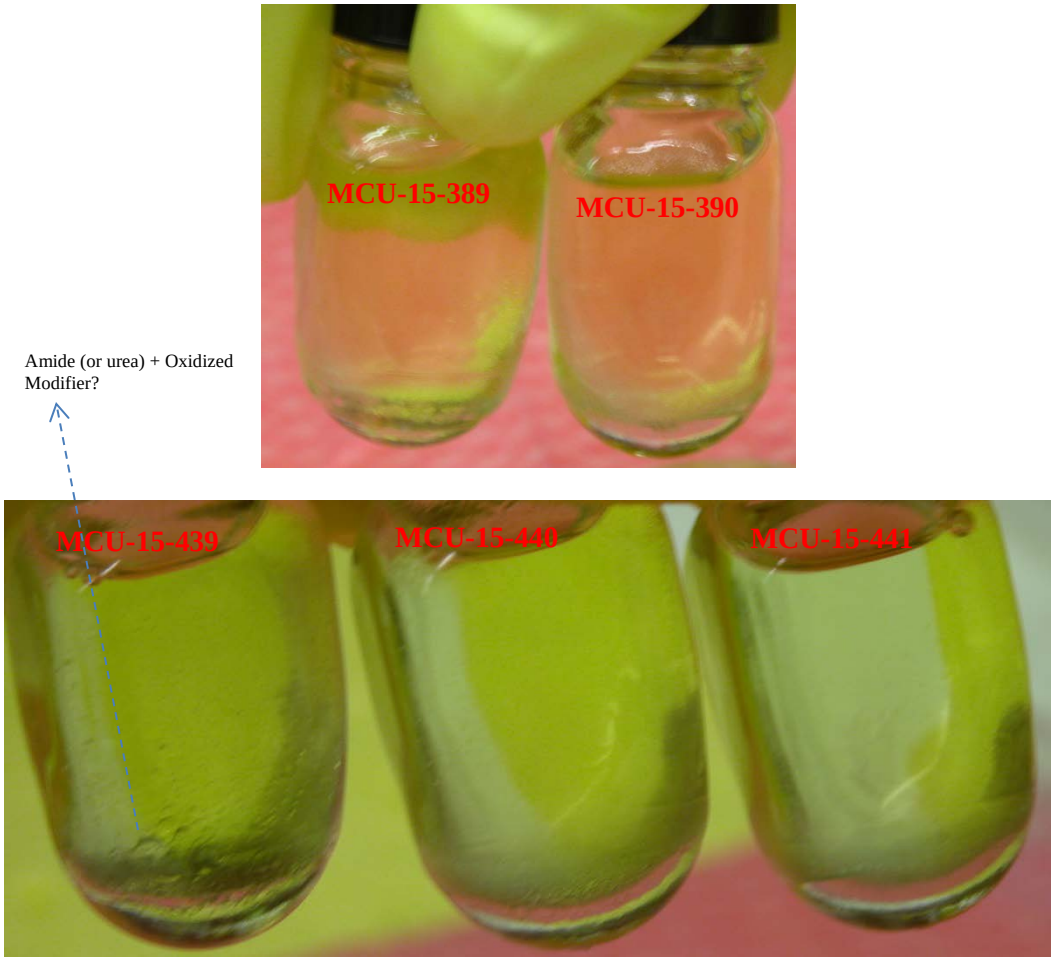

Figure 1. Typical appearance of the two vials MCU-15-389 and MCU-15-390 and the three vials MCU-15-439, MCU-15-440, and MCU-15-441

An examination of Table 3-1 shows that the Isopar™ L and the modifier concentrations are at their nominal values. This observation confirms the trim addition made to the solvent in Feb. 22, 2015. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement.

All measurements indicate the Isopar™ L level and the modifier concentration level are at their nominal value. This explains why the temperature adjusted density is similar to 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, which added up to 0.828 ± 0.020 g/mL. This value is below the measured and corrected to 25 °C mass concentration (density) of the sample (0.836 g/mL) and indicates the analytical results may be biased-low estimating the solvent's components concentrations.

Table 3-1. Sample Results for MCU-15-389-390

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	5.94E+05	6.23E+05	95
Isopar® L	FTIR	NA	6.23E+05		100
Isopar® L	Density[*]	NA	6.15E+05		99
Average[$]	All	NA	6.14E+05	6.23E+05	99
Modifier	HPLC	300316025	1.68E+05	1.69E+05	99
Modifier	FT-HNMR	NA	1.49E+05		88
Modifier	FTIR	NA	1.62E+05		96
Modifier	Density[*]	NA	1.70E+05		101
Average[$]	All	NA	1.68E+05	1.69E+05	99
TiDG	Titration	NA	1.36E+03	1.44E+03	95
TiDG	FT-HNMR	NA	1.22E+03		85
Average[$]	All	NA	1.33E+03	1.44E+03	92
trioctylamine	Titration	NA	2.92E+02	5.30E+02	55
Average[$]	All	NA	2.92E+02	5.30E+02	55
MaxCalix	FT-HNMR	NA	3.83E+04	4.44E+04	86
MaxCalix	HPLC	300316025	4.30E+04		97
Average[$]	All	NA	4.10E+04	4.44E+04	92
BOBCalixC6	HPLC	300316025	3.07E+03	4.03E+03	76
Average[$]	All	NA	3.07E+03	4.03E+03	76
Density (g/mL)	Direct Measurement	NA	0.836	0.835	100

MCU-15-439-440-441

Density measurement of this sample gave a result of 0.840 g/mL (0.03% RSD) (or 0.836 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-439-440-441 at 21 °C. The temperature-adjusted density (0.836 g/mL) for MCU-15-439-440-441 is nearly identical to the temperature adjusted density of the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory).

An examination of Table 3-2 shows that the Isopar™ L concentration and the modifier concentration are at their nominal values. This confirms the trim addition to the solvent done on Feb. 22, 2015. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement.

All measurements indicate the Isopar™ L level and the modifier concentration level are at their nominal value. This explains why the temperature adjusted density is similar to the standard sample density. The sum of the "average" results in Table 3-2 added up to 0.831 ± 0.020 g/mL. This is below the measured

and corrected to 25 °C mass concentration (density) of the sample (0.836 g/mL) and indicates the analytical results may be biased-low estimating the solvent's components concentrations.

Table 3-4 Sample Results for MCU-15-439-440-441

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.44E+05	6.23E+05	103
Isopar® L	FTIR	NA	6.22E+05		100
Isopar® L	Density[*]	NA	6.14E+05		99
Average[$]	All	NA	6.15E+05	6.23E+05	99
Modifier	HPLC	300316090	1.64E+05	1.69E+05	97
Modifier	FT-HNMR	NA	1.59E+05		94
Modifier	FTIR	NA	1.63E+05		96
Modifier	Density[*]	NA	1.72E+05		102
Average[$]	All	NA	1.70E+05	1.69E+05	100
TiDG	Titration	NA	1.36E+03	1.44E+03	95
TiDG	FT-HNMR	NA	1.29E+03		90
Average[$]	All	NA	1.35E+03	1.44E+03	93
trioctylamine	Titration	NA	2.98E+02	5.30E+02	56
Average[$]	All	NA	2.98E+02	5.30E+02	56
MaxCalix	FT-HNMR	NA	3.95E+04	4.44E+04	89
MaxCalix	HPLC	300316090	4.28E+04		96
Average[$]	All	NA	4.14E+04	4.44E+04	93
BOBCalixC6	HPLC	300316090	3.06E+03	4.03E+03	76
Average[$]	All	NA	3.06E+03	4.03E+03	76
Density (g/mL)	Direct Measurement	NA	0.836	0.835	100

[#] 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.

[*] 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 TiDG concentration level (1.33E3 mg/L) for the MCU-15-389-390 is 92 % of the nominal value of 1440 mg/L confirming 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.

The TiDG concentration level in MCU-15-439-440-441 is 93% (1.35E3 mg/L) of the nominal. Again, confirming the trim addition to the 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 from the January measurement to 292 mg/L and 298 mg/L in the MCU-15-389-390 and MCU-15-439-440-441 respectively. These numbers are within analytical error. Since MCU no longer adds TOA, the drop in TOA concentration is expected. However, since TOA is an amine, personnel suspect that TiDG degradation into primary amines and urea, which have previously been identified as degradation products of the suppressor when heated may be a source.[3] The urea (carbamide) may possibly undergo further degradation to form amides.[4]

Extractant Levels

The average MaxCalix level in the MCU-15-389-390 sample is 4.10 E4 mg/L (±13%) which is 8% below the nominal concentration but it is within the 95% confidence level of the analytical measurement (see Figure 3). The measured MaxCalix concentration level in MCU-15-439-440-441 is 4.14E4 mg/L which is 7% below the recommended nominal level but within the analytical uncertainty. The BOBCalixC6 concentration levels in MCU-15-389-390 and MCU-15-439-440-441 are 3.07E3 and 3.06E3 mg/L respectively.

Gamma Level

The gamma measurements of MCU-15-389-390 and MCU-15-439-440-441 are 3.41E4 and 4.61E4 dpm/mL (±5%) respectively. These levels are 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, large concentrations of droplets were observed on the wall of two of the p-nut vials (MCU-15-439 and MCU-15-389). 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 the presence of amides and oxidized material possibly modifier (or oxidized aliphatic lubricant). Personnel conducted a closer look at the HNMR and FTIR data of the MCU-15-389-390 and MCU-15-439-440-441 samples. The spectroscopy data shows (Fig. 5) shows the possible presence of amides or aromatics containing amides in the FT-HNMR and the presence of a carbonyl in the FTIR of the MCU-15-389-390 sample. Possible sources of amides 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.

Recommendation

The current analysis indicates low modifier and TiDG levels in this solvent relative to the standard. The 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.

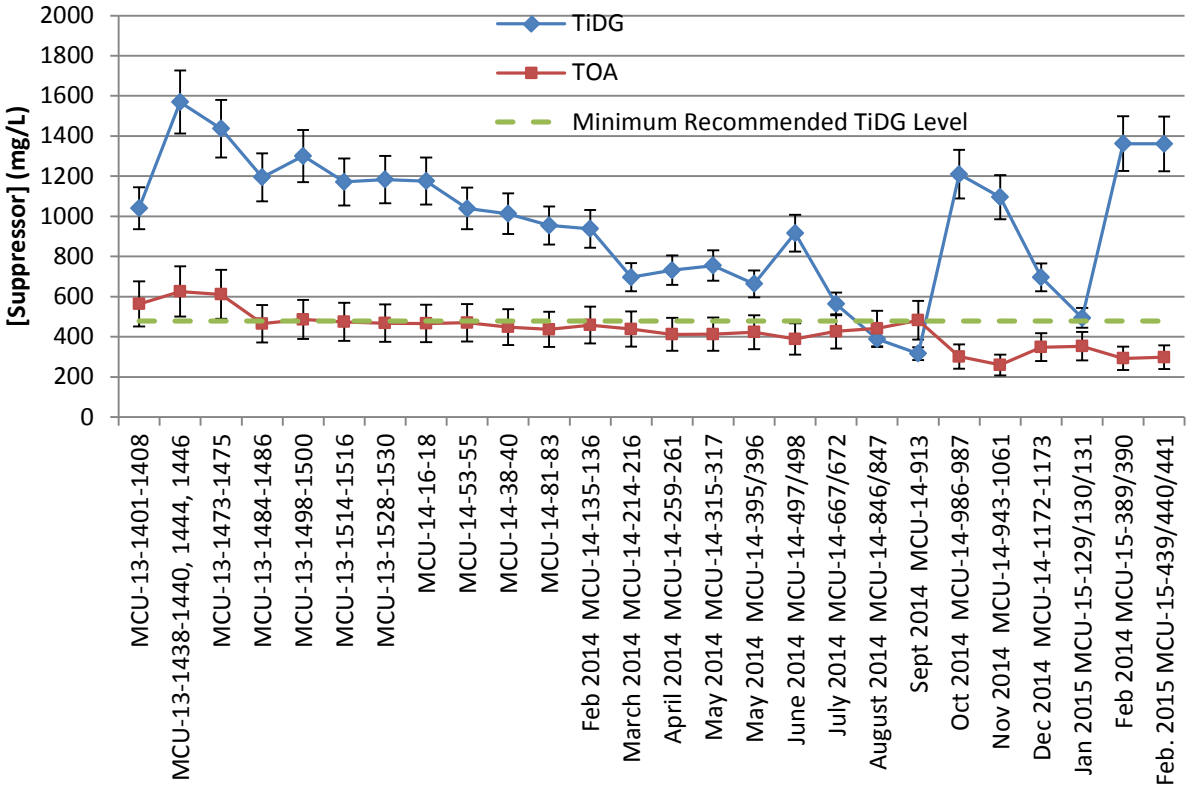

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 480 mg/L for TiDG.

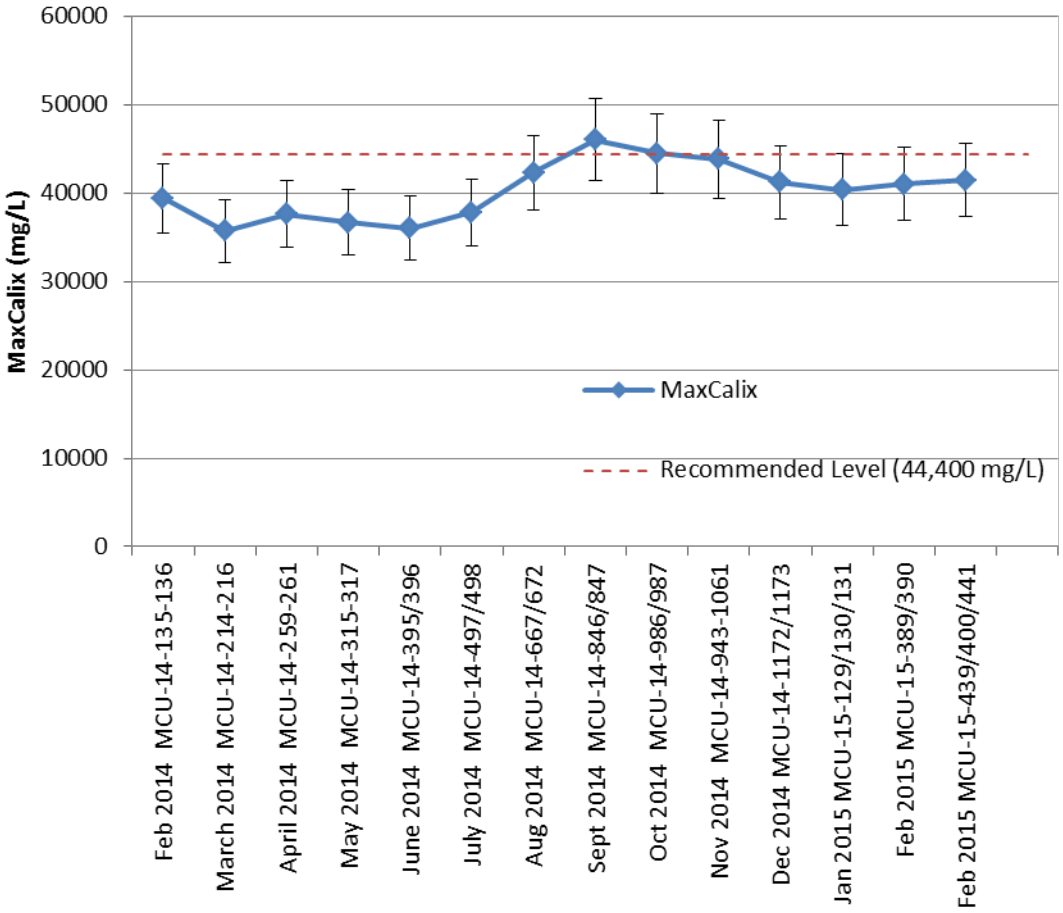

Figure 3. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

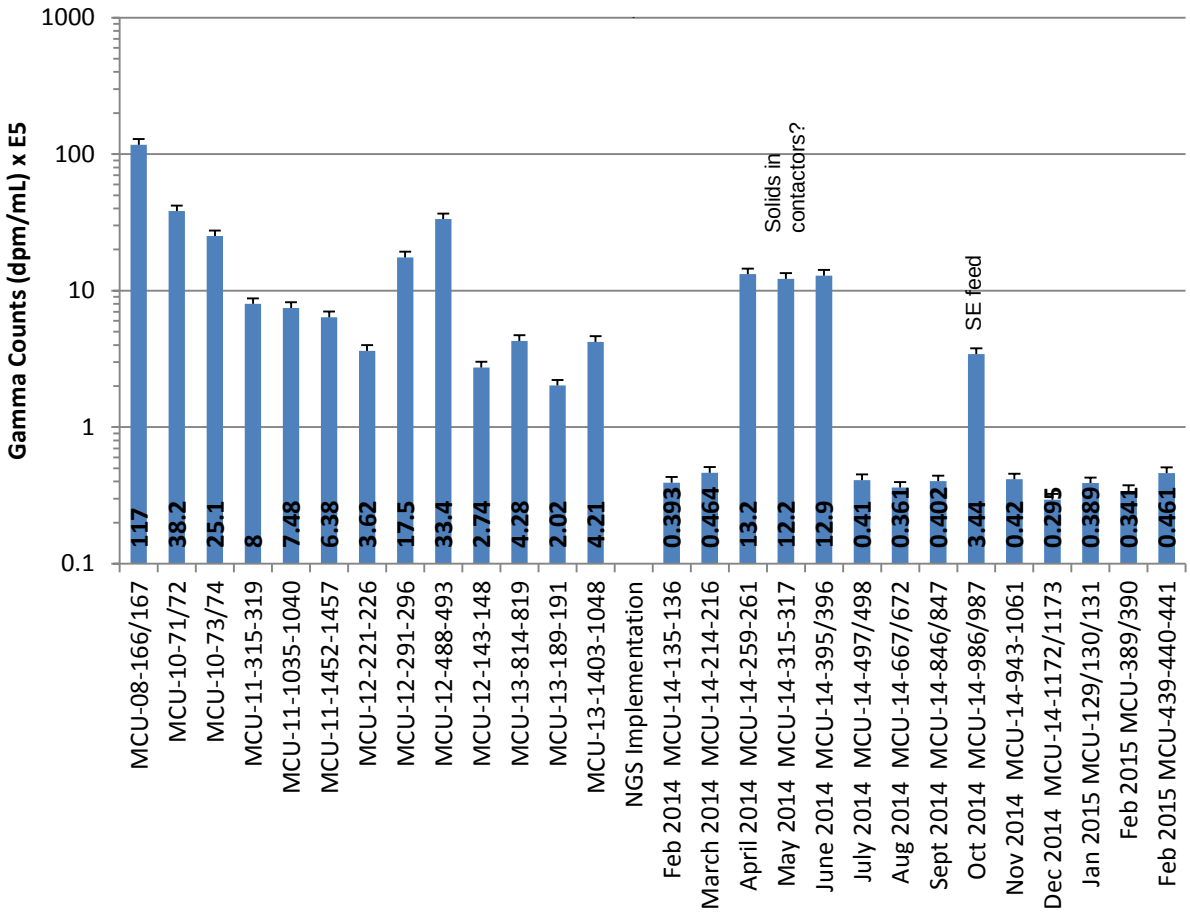

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

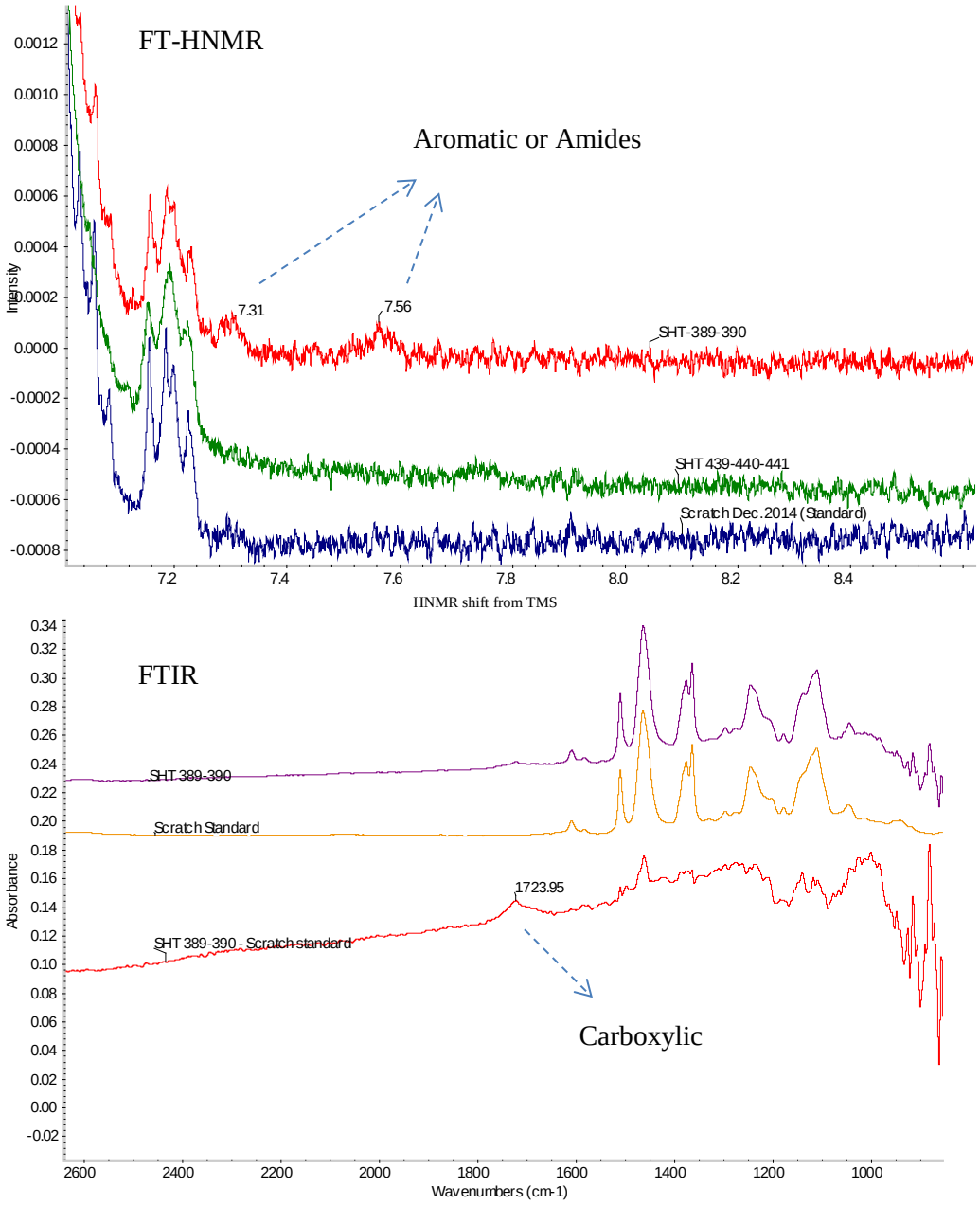

Figure 5. FTHNMR and FTIR of the impurity found in MCU-15-389-390

4.0 Conclusions

SRNL received two sets of SHT samples (MCU-15-389 and MCU-15-390 pulled on February 23, 2015 and MCU-15-439, MCU-15-440, and MCU-15-441 pulled on February 28, 2015) for analysis. The samples in each set were combined and analyzed for composition. Analysis of the composite samples MCU-15-389-390 and MCU-15-439-440-441 indicated a low concentration (~ 92 to 93 % of nominal) of the suppressor (TiDG) and a slightly below the nominal concentration of the extractant (MaxCalix), but nominal levels of the modifier (CS-7SB) and of the Isopar™ L. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent on February 22, 2015. Despite that the values are below target component levels, the current levels of TiDG and MaxCalix 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. However, two p-nut vials out of the five that delivered the samples contained small (1 mm) droplets of oxidized modifier and amides.

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

[1] W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.

[2] T. B. Peters and M. R. Williams, "Results of Analysis of NGS Concentrate Drum Samples" SRNL-STI-2013-00521, September 2013.

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[4] March, J. *Advanced Organic Chemistry*; John Wiley & Sons: New York, 1992; pp. 416–425

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