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Solvent Hold Tank Sample Results for MCU-15-802-803-804-805-806-807 August Monthly Sample

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-15-802-803-804-805-806-807), pulled on 08/31/2015 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-802-803-804-805-806-807 indicated a low concentration (~ 45 % of nominal) of the suppressor (TiDG) and a slightly lower than nominal concentration of the modifier (Cs-7SB) in the solvent. The extractant (MaxCalix) concentration was at its nominal value.

Based on this current monthly sample, the levels of TiDG, MaxCalix, and modifier were sufficient for continuing operation without adding a trim during that time but it is recommended that an addition of TiDG, modifier and Isopar™L should be made in the next few months.

This monthly sample's rheology, as determined by Hydrogen Nuclear Magnetic Resonance (H-NMR), is consistent with the rheology of the standard NGS solvent made in the lab (Scratch solvent 5/14/2014).

No impurities above the 1000 ppm level were found in this solvent by the Semi-Volatile Organic Analysis (SVOA). No impurities were observed in the Hydrogen Nuclear Magnetic Resonance (HNMR). In addition, up to 16.7 micrograms of mercury per gram of solvent (or 14 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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
CVAA	Cold Vapor Atomic Absorption Spectrometry
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
XRF	X-Ray Fluorescence

1.0 Introduction

In late FY13, the 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 August 31, 2015, Operations personnel pulled and delivered six samples from the SHT (MCU-15-802, MCU-15-803, MCU-15-804, MCU-15-805, MCU-15-806, and MCU-15-807) 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 are 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
20 gallons of Isopar™L added to MCU	March 6, 2015
SHT sample MCU-15-556-557-558	March 16, 2015
SHT sample MCU-15-661-662-663	April 2, 2015
10 gallons of Isopar™L added to MCU	May 6, 2015
SHT sample MCU-15-710-711-712	June 15, 2015
SHT sample MCU-15-750-751-752	June 22, 2015
SHT sample MCU-15-802-803-804-805-806-807	August 31, 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-15-802, MCU-15-803, MCU-15-804, MCU-15-805, MCU-15-806, and MCU-15-807 were composited before use. Aliquots of the composited sample were removed to perform the following analyses: Density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, cold vapor atomic adsorption spectrometry (CVAA), X-ray fluorescence (XRF), 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-15-802, MCU-15-803, MCU-15-804, MCU-15-805, MCU-15-806, and MCU-15-807 were examined and found to contain a single phase liquid with no apparent solids contamination or cloudiness. 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-15-802-803-804-805-806-807). Table 3-1 contains the results for the MCU-15-802-803-804-805-806-807 sample.

Isopar™ L and Modifier Levels

A density measurement of the sample gave a result of 0.8388 g/mL (0.04% RSD) (or 0.8345 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-802-803-804-805-806-807 at 20 °C. The calculated density (0.8345 g/mL) for MCU-15-802-803-804-805-806-807 is less than 1% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory)[i]. Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be equal to the nominal value (within analytical uncertainties).

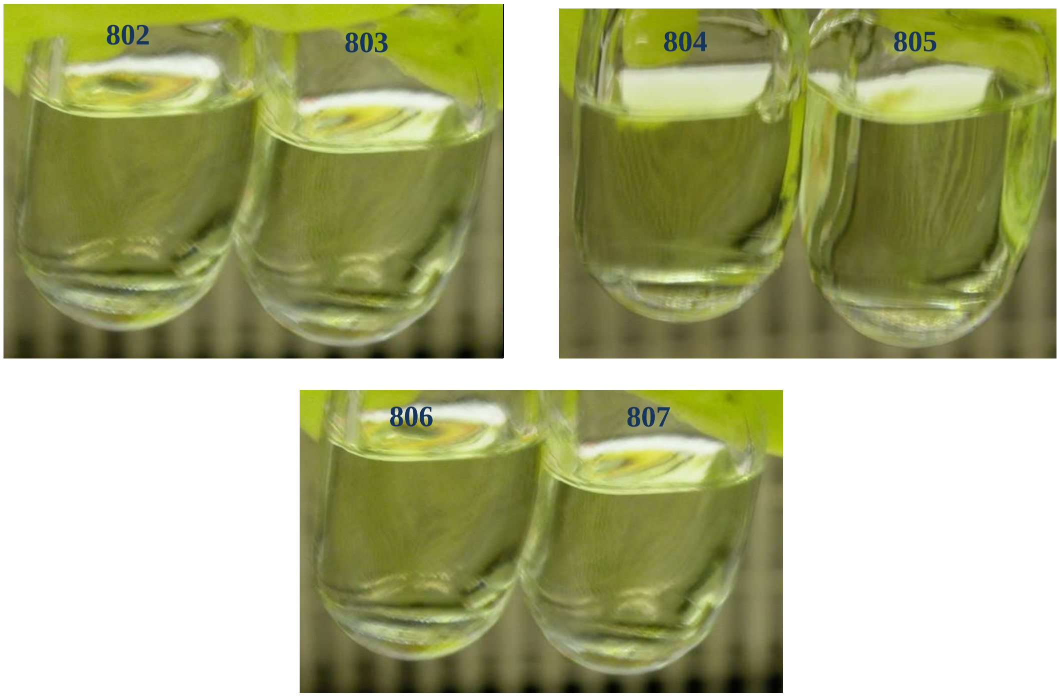


Figure 1. Typical appearance of the six vials MCU-15-802, MCU-15-803, MCU-15-804, MCU-15-805, MCU-15-806, and MCU-15-807

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 (3% lower) than its nominal value. The large deviation observed in the HPLC data (for the modifier) is possibly due to sample handling errors. 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 is at nominal value while the modifier concentration level is below its nominal value (see Fig. 2 for recent modifier concentration from HPLC measurements). The modifier level appears to trend up and down possibly reflecting randomness in the process of mixing, sampling and analyzing it. The relatively lower modifier concentration 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 0.830 ± 0.019 g/mL. Their sum is consistent with the measured and temperature corrected (to 25 ºC) value of 0.834 g/mL, but it is below the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL).

Table 3-1 Sample Results for MCU-15-802-803-804-805-806-807

Analysis	**Method**	**LIMS #**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar® L	FTIR	NA	6.27E+05	6.23E+05	101
Isopar® L	FT-HNMR	NA	6.33E+05		102
Isopar® L	Density[*]	NA	6.17E+05		99
Average[$]	All	NA	6.18E+05	6.23E+05	99
Modifier	HPLC	300319064	1.40E+05	1.69E+05	83
Modifier	FT-HNMR	NA	1.59E+05		94
Modifier	FTIR	NA	1.58E+05		94
Modifier	Density[*]	NA	1.67E+05		99
Average[$]	All	NA	1.63E+05	1.69E+05	97
TiDG[♠]	Titration	NA	6.42E+02	1.44E+03	45
Average[$]	All	NA	6.42E+02	1.44E+03	45
trioctylamine	Titration	NA	3.11E+02	5.30E+02	59
Average[$]	All	NA	3.11E+02	5.30E+02	59
MaxCalix	FT-HNMR	NA	4.71E+04	4.44E+04	106
MaxCalix	HPLC	300319064	4.37E+04		98
Average[$]	All	NA	4.49E+04	4.44E+04	101
BOBCalixC6	HPLC	300319064	3.13E+03	4.03E+03	78
Average[$]	All	NA	3.13E+03	4.03E+03	78
Density (g/mL)	Direct Measurement	NA	0.8345	0.835	100

[#] Analytical uncertainty is 10% for HPLC. Titration method uncertainty is 10% for TiDG and 20% 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 combined weight percent of TiDG, MaxCalix, BOBCalixC6, and TOA to be approximately 6%.

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

[$] $x = \frac{\Sigma_1^i\left(x_i/\delta_i^2\right)}{\Sigma_1^i\left(1/\delta_i^2\right)}$; x_i stands for the concentration obtained at a given method and δ_i is the corresponding uncertainty.

[♠] No TiDG value was estimated by FTHNMR due to an aged (questionable) standard.

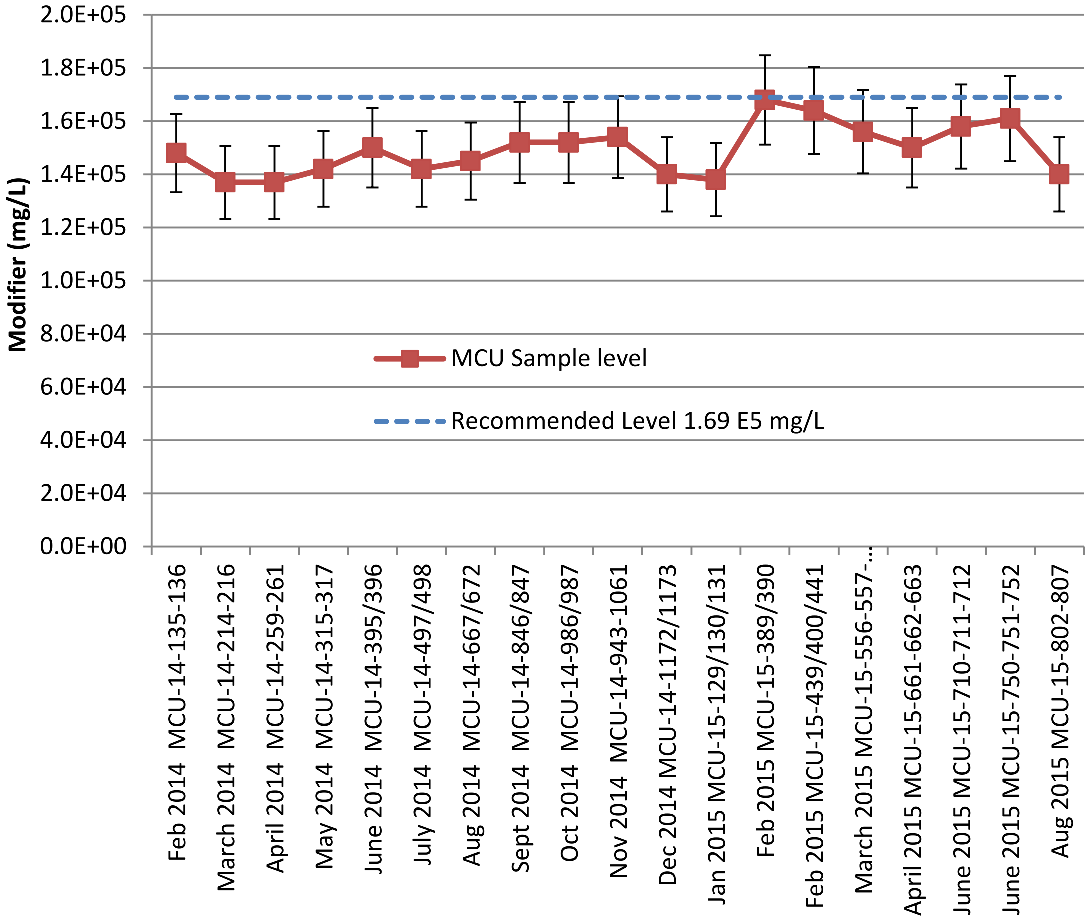


Figure 2. Modifier level in the solvent as measured by HPLC (one sigma is 10%).

Suppressors Levels

The average TiDG concentration level (6.42 ± 0.6E2 mg/L) is at 45% 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 (479 mg/L) and thus, the solvent did not require a TiDG addition at the time sample MCU-15-802-803-804-805-806-807 was collected. Inferring from past TiDG concentration level trends and in the absence of new additions or new removal mechanisms, the TiDG concentration is expected to drop as shown in Fig. 3. This drop is due to the combined effect of auto-decomposition and phase transfer to the aqueous phases (salt solution and boric acid). The TOA concentration appears to have remained steady 311 ± 62 mg/L (in the previous month the TOA level was at 321 mg/L). These numbers are within analytical error. In addition, looking at the slope of the TOA concentration data, it appears to trend upwards with time. The upward trend appears to correlate with the disappearance of TiDG (or the disappearance of Isopar™ L) concentration. This correlation is believed to be due to the combined effects of titration of TiDG's decomposition products and to the evaporation of Isopar™ L. Since MCU no longer adds TOA, a drop in TOA concentration is expected. However, a closer inspection of Fig. 3 reveals the TOA level increasing in the last three MCU samples. The rise is perhaps due to TiDG degradation into primary amines, which have previously been identified as degradation products of the suppressor (TiDG) when heated.[3] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.[4]

Extractant Levels

The average MaxCalix level is 4.49 E4 mg/L (±13%) which is 1% above the nominal concentration and it is within the 95% confidence level of the analytical measurement as shown in Figure 4. The residual concentration of BOBCalixC6 level is currently at 78% of the level measured when the NGS was implemented in late FY13.

Gamma Level

The gamma measurement of MCU-15-802-803-804-805-806-807 is 1.16E+05 dpm/mL (±5%). This level of activity appears to indicate an upward trend in the data (see Fig. 5) and in recent past, an apparent correlation was observed between poor extraction and/or stripping performance of the solvent and relatively high gamma activity levels in the solvent.

Impurities

No impurities were seen at the 1000 ppm level or higher as indicated by the SVOA method. No impurities were observed in the FTIR or in the HNMR spectrum of this sample.

A few mL of the blended solvent were digested and analyzed for mercury (by the cold vapor method and the XRF method). The total mercury level in the solvent measured 16.7 $\mu g/g_{solvent}$ (20% st.dev.) or 14 $\mu g/mL_{solvent}$ as determined by the CV-AA method (the XRF results are still under further review). This is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm)[5] implying that other solubility-enhancing mechanisms are at play (for example extraction by an extractant or sorption on trapped solids) or a more soluble form of mercury is present (organo-mercury like ethyl or dimethyl mercury). Organo-mercury compounds were recently detected in Tank 22H.[6] For 200 gallons of solvent (757.1 L) and assuming a density of 0.834 g/mL, the solvent could contain a total of 10.6 ± 2 g of mercury. See Figure 6 for a comparison of recent SHT mercury concentrations.

Microrheology (self-diffusivity)

Approximately 1.5 mL of MCU-15-802-803-804-805-806-807 was analyzed in the NMR by imposing spatial field gradients across the sample. The hydrogen signal (above the instrument noise) from each component of the SHT sample was monitored. The data from this experiment provided the self-diffusivity of each component.[7] Figure 7 shows the measured self-diffusivity of Isopar™L, modifier and MaxCalix in MCU-15-802-803-804-805-806-807 and in the standard (scratch May 2014). As can be seen from Fig. 7, the self-diffusivity of Isopar™L is higher than that of the modifier and MaxCalix moves the slowest in the solvent (see two-dimensional plot in Fig. 7) as expected. When comparing the two solvents (MCU-15-802-803-804-805-806-807 and Scratch), the self-diffusivity of each component is the same. This implies that both solvents have the same viscosity and moreover, there is no significant chemical change or impurities in MCU-15-802-803-804-805-806-807 relative to the scratch.

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 made to the solvent. However, the current TiDG level is below the recommended operating level (958 mg/$L_{solvent}$) but 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. However, to remain two-sigma above the minimum recommended level, it is recommended that TiDG, modifier and appropriate amounts of Isopar™L be added to restore the components to nominal levels. Similarly, the modifier level (1.54E5 mg/L) is well above the minimum modifier level at which the MaxCalix becomes insoluble in the solvent.

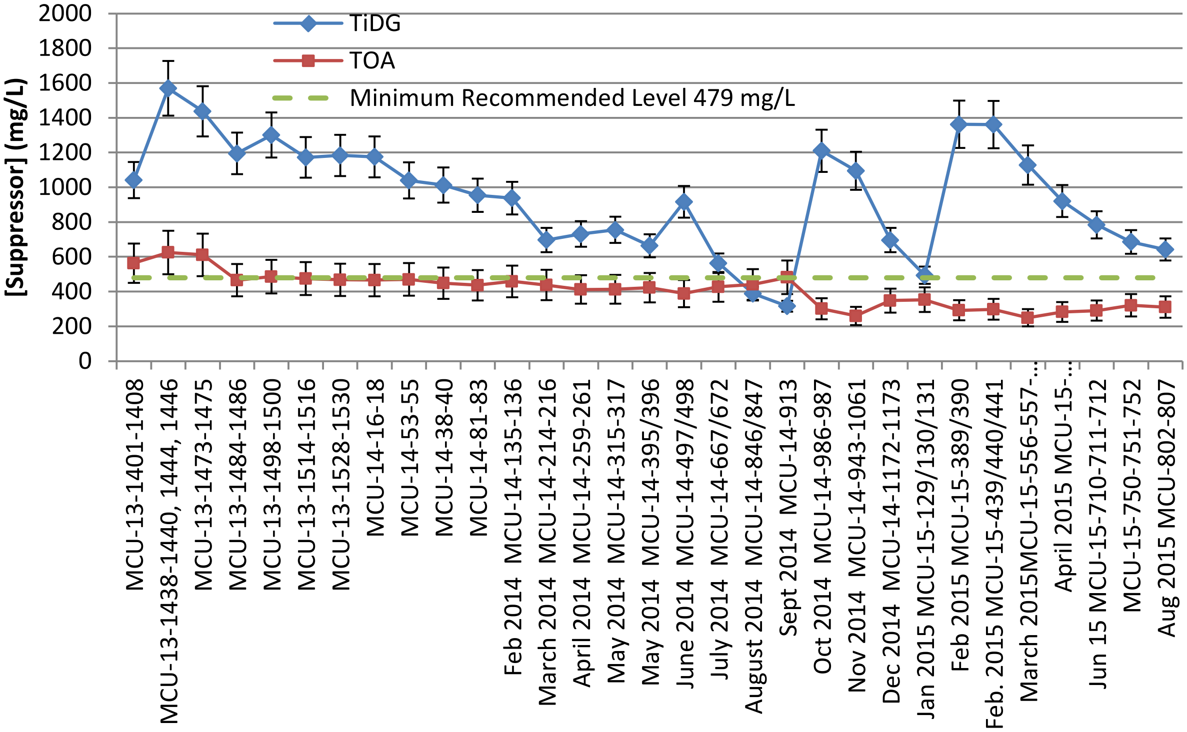


Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 479 mg/L for TiDG.

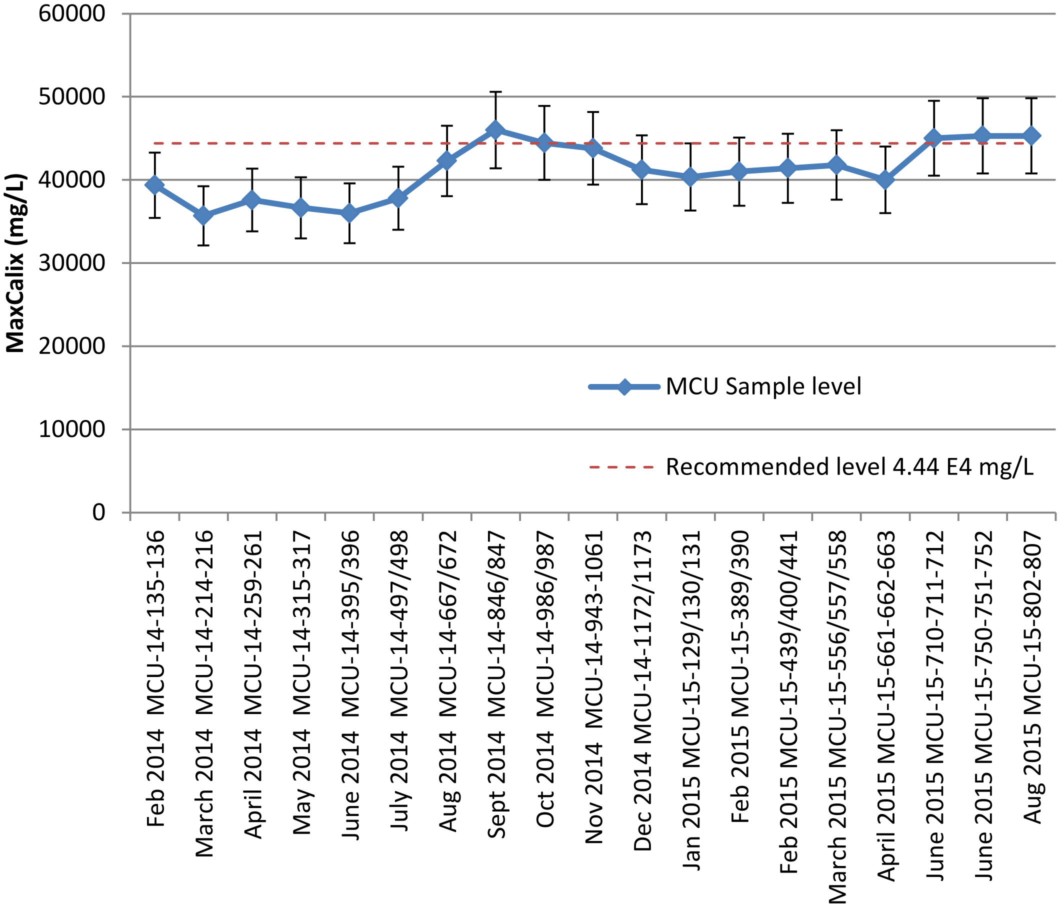


Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

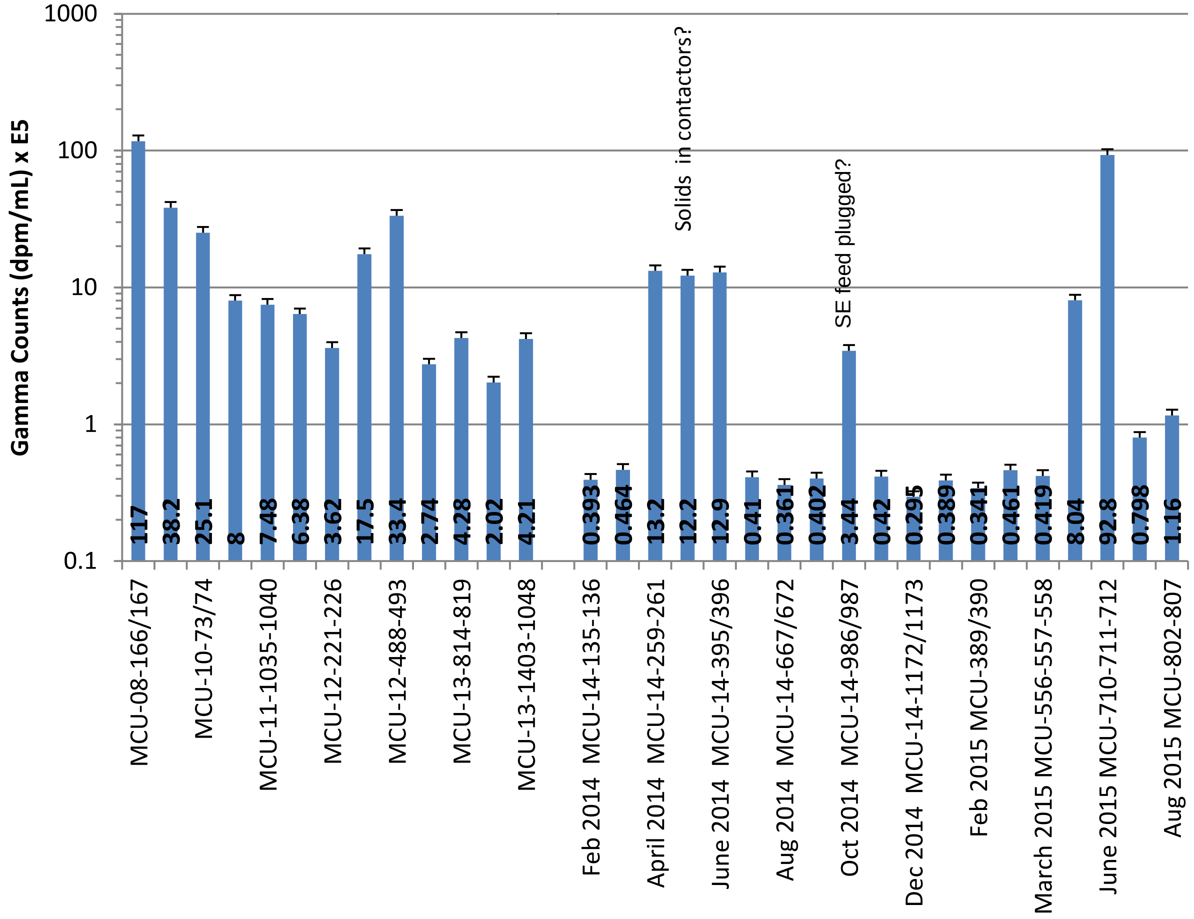


Figure 5. The gamma count of selected SHT samples. One standard deviation is 5%.

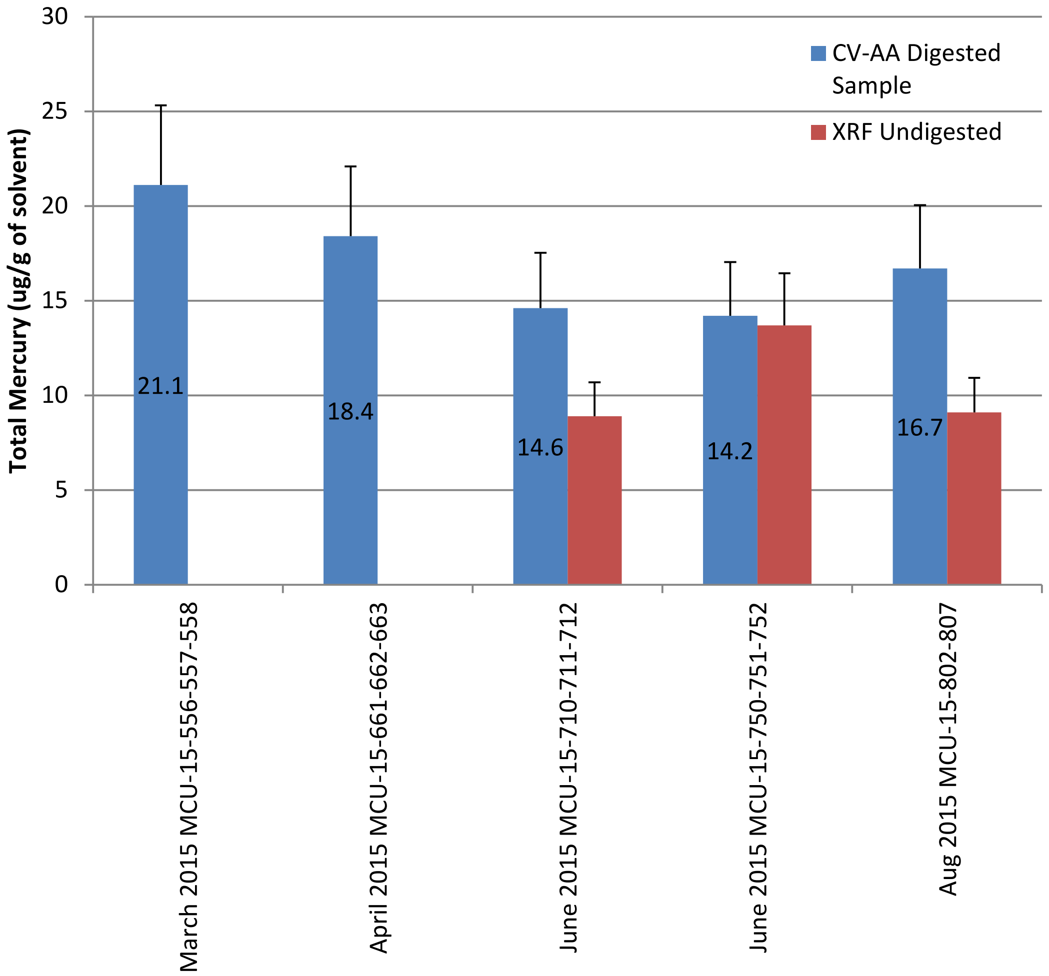
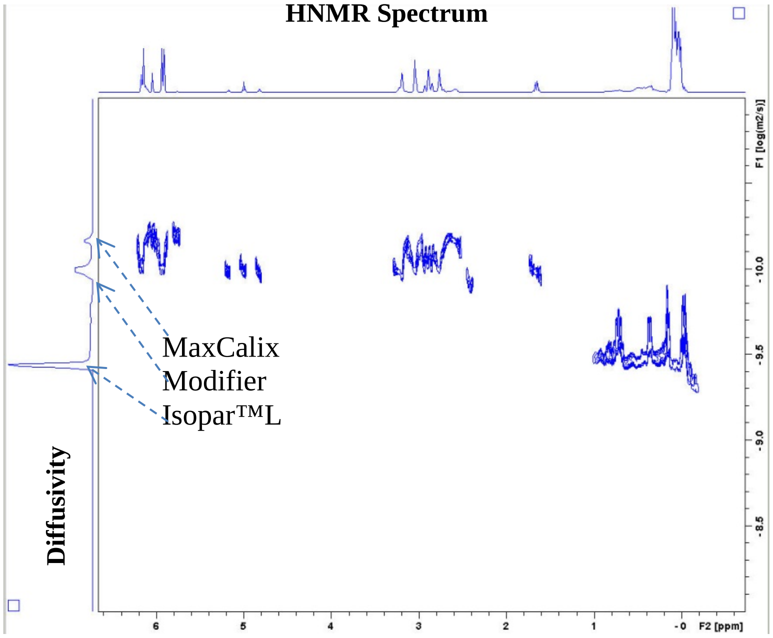
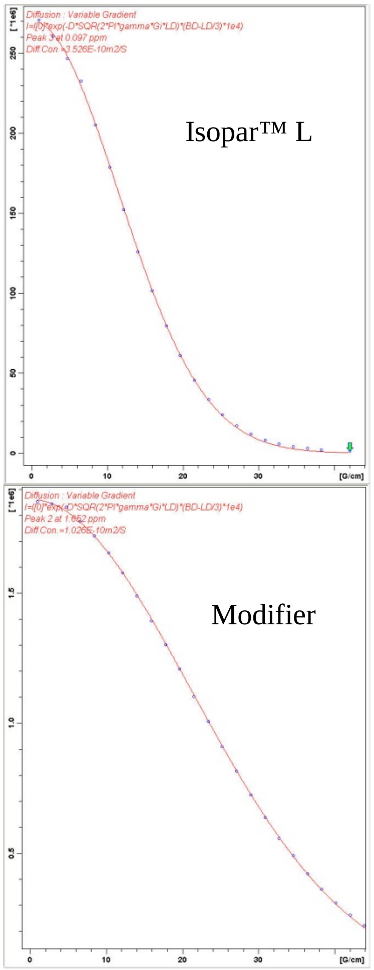


Figure 6. Total mercury in recent SHT samples. One standard deviation is 20%. XRF =X-ray Fluorescence, CVAA = Cold Vapor Atomic Absorption Spectrometry.



Each peak area was plotted against the value of the applied magnetic field gradient (see right figure) and then fitted with a single exponential decay (see Ref. 7) to yield the diffusivity (see table below).



Self-diffusivity of the solvent components (m^2/s)

Component	**MCU-15-802-807**	**Scratch May 2014**
MaxCalix	6.545 E-11	6.691 E-11
Modifier	1.006 E-10	1.026 E-10
Isopar™L	3.368 E-10	3.526 E-10

Figure 7. The self-diffusivity of Isopar™ L, modifier and MaxCalix in MCU-15-802-803-804-805-806-807 and in Scratch May 2014 standard (for comparison).

4.0 Conclusions

SRNL received one set of SHT samples (MCU-15-802, MCU-15-803, MCU-15-804, MCU-15-805, MCU-15-806, and MCU-15-807), pulled on 08/31/2015 for analysis. The samples were inspected, combined, and analyzed for composition. Chemical analysis of the composite sample MCU-15-802-803-804-805-806-807 indicated a low concentration (~ 45 % of nominal) of the suppressor (TiDG) and a slightly lower concentration of the modifier (CS-7SB). The extractant concentration level (MaxCalix) is at its nominal value.

Based on this current monthly sample, the levels of TiDG, MaxCalix, and modifier are sufficient for continuing operation without adding a trim at this time but it is recommended that an addition of TiDG, modifier and Isopar™L should be made in the near future.

This monthly sample's rheology is consistent with the standard solvent rheology.

No impurities above the 1000 ppm level were found in this solvent by the Semi-Volatile Organic Analysis (SVOA). No impurities were observed in the Hydrogen Nuclear Magnetic Resonance (HNMR). However, up to 16.7 ± 3.3 micrograms of mercury per gram of solvent (or 14 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.

5.0 References

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