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# Solvent Hold Tank Sample Results for MCU-16-1247-1248-1249: August 2016 Monthly Sample

F. F. Fondeur

D. H. Jones

January 2017

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F. F. Fondeur  
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January 2017

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## EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-16-1247-1248-1249), pulled on 08/22/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-1247-1248-1249 indicated the Isopar<sup>TM</sup>L concentration is above its nominal level (101%). The extractant (MaxCalix) and the modifier (CS-7SB) are 7% and 9 % below their nominal concentrations. The suppressor (TiDG) is 63% below its nominal concentration. A summary of the concentration of the relevant solvent components is shown below.

Sample	Sampling Date	Density at 25°C (g/mL)	Isopar <sup>TM</sup> L (mg/L)	Modifier (mg/L)	MaxCalix (mg/L)	TiDG (mg/L)
MCU-16-1247-1249	8/22/2016	0.822	6.20 E5	1.54 E5	4.26 E4	5.30 E2
Baseline Solvent	Not Applicable	0.830	6.11 E5	1.69 E5	4.57 E4	1.44 E3

This analysis confirms the solvent may require the addition of TiDG, and possibly of modifier and MaxCalix to restore then to nominal levels. Based on the current monthly sample, the levels of TiDG, Isopar<sup>TM</sup>L, MaxCalix, and modifier are sufficient for continuing operation but are expected to decrease with time. Periodic characterization and trimming additions to the solvent are recommended. At the time of writing this report, A solvent trim batch containing TiDG, modifier and MaxCalix, was added to the SHT (October 2016) and expect the concentration of these components to be at their nominal values.

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). Residual concentration of oxidized oil, protein (bacteria), and silicates were found in the p-nut vials that contained MCU-16-1247, MCU-16-1248, and MCU-16-1249. These impurities are likely present in the SHT, rather than contamination in the p-nut vials. Another impurity observed in the samples was mercury. Up to  $32.9 \pm 6.6$  micrograms of mercury per gram of solvent (or 27.0 µg/mL) was detected in this sample (the average of the CV-AA and the XRF method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in Salt Batch 9 (Tank 49H) compared to previous salt batches.

The current gamma level (1.94E5 dpm/mL) confirmed that the gamma concentration has returned to previous levels (as observed in the late 2015 samples) where the process operated normally and as expected.

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( <i>tert</i> -octylbenzo-crown-6)
CSSX	Caustic-Side Solvent Extraction
CVAA	Cold Vapor Atomic Absorption Spectrometry
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
FTIR	Fourier transform infra-red spectroscopy
HNMR	Hydrogen Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
ISDP	Integrated Salt Disposition Project, NGS
MCU	Modular Caustic-Side Solvent Extraction Unit
MaxCalix	1,3- <i>alt</i> -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	<i>N,N',N''</i> -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.<sup>1</sup> On August 22 2016, Operations personnel pulled and delivered three samples from the SHT (MCU-16-1247, MCU-16-1248, and MCU-16-1249) 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<sup>2</sup> and heel solvent) was prepared in the lab (July 2016) 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 June 15, 2016, a trim addition was made to MCU that was 40.4 lbs of modifier and 0.23 lbs of TiDG in 100.54 lbs of Isopar<sup>TM</sup>L.<sup>3</sup>

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

<b>Event</b>	<b>Date</b>
SHT sample MCU-16-53-54-55	January 25, 2016
SHT sample MCU-16-270-271-272	February 21, 2016
12 gallons of Isopar <sup>TM</sup> L added to MCU	March 6, 2016
SHT sample MCU-16-348-349-350	March 30, 2016
10 gallons of Isopar <sup>TM</sup> L added to MCU	March 31, 2016
April Solvent Trim added to MCU	April 29, 2016
SHT sample MCU-16-596-597-598	April 30, 2016
SHT sample MCU-16-701-702-703	May 23, 2016
SHT sample MCU-16-710-711-712 (washed with 300 mM caustic)	May 28, 2016
20 gallons solvent trim added to MCU	June 15, 2016
SHT sample MCU-16-1247-1248-1249	June 30, 2016
SHT sample MCU-16-991-992-993	July 23, 2016
SHT sample MCU-16-1033-1034-1035 (washed with 300 mM caustic)	July 28, 2016
20 gallons of Isopar <sup>TM</sup> L added to MCU	August 21, 2016
SHT sample MCU-16-1247-1248-1249	August 22, 2016

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-16-1247, MCU-16-1248, and MCU-16-1249 were composited before use. Aliquots of the composited sample were removed to perform the following analysis: Density, SVOA, high performance liquid chromatography (HPLC), titration, gamma counting, CVAA, X-ray fluorescence (XRF), and Fourier-Transformed HNMR (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 at 25 °C<sup>2</sup>**

<b>Component</b>	<b>mg/L</b>	<b>Molar</b>
MaxCalix	~ 44,400 <sup>*</sup> to 47,800 <sup>*</sup>	~ 0.0465 to 0.050
BOBCalixC6 <sup>*</sup>	< 4,030	< 0.0035
TOA <sup>*</sup>	< 530	< 0.0015
Modifier	~ 169,000	~ 0.50
TiDG	~1440	~ 0.003
Isopar <sup>TM</sup> L	~ 607,000 <sup>*</sup> to 613,000 <sup>*</sup>	~ 73.69 to 74 wt%

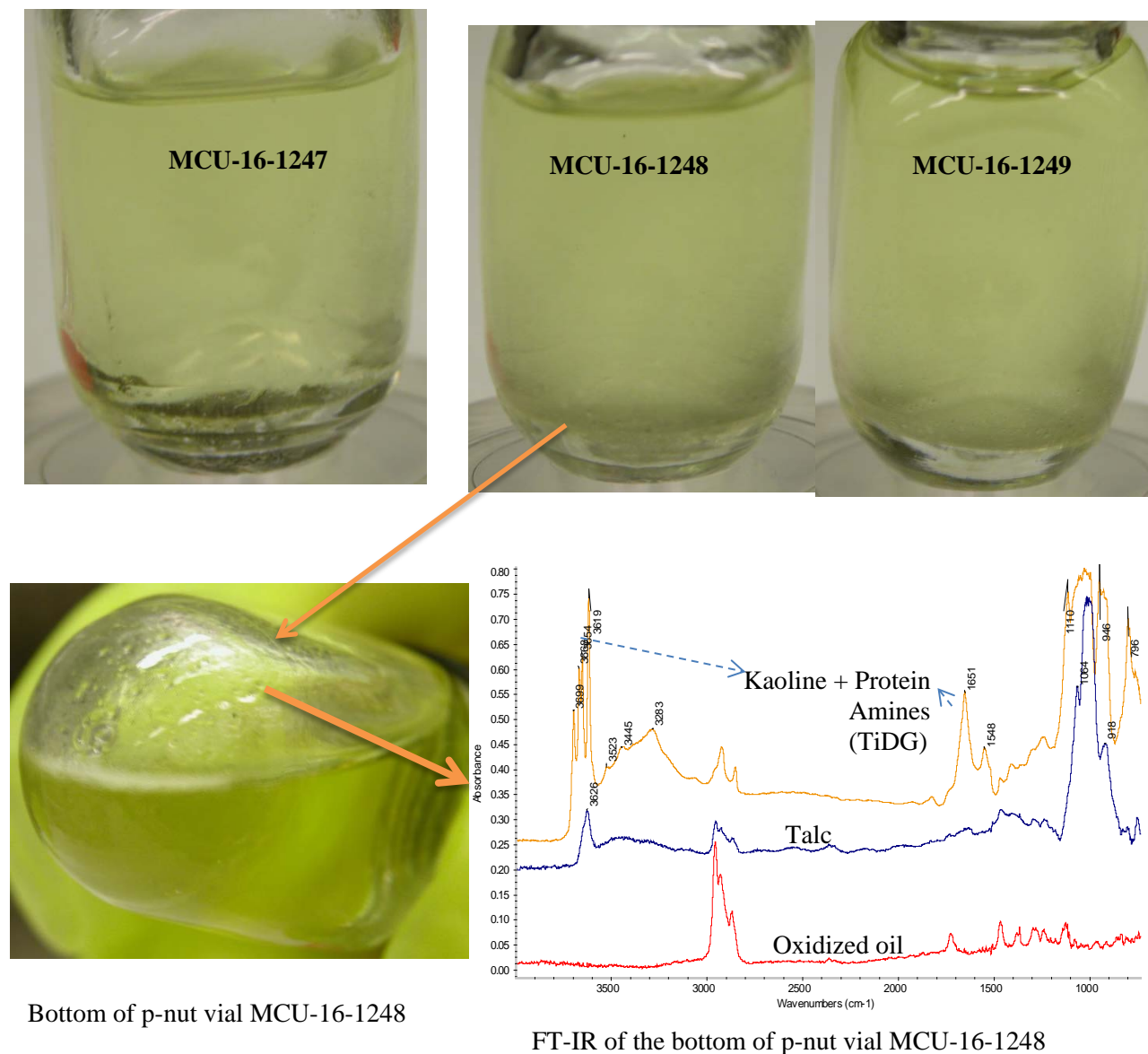
\*Values represent starting values when NGS blend was implemented. These components are no longer added to or refurbished in MCU. <sup>\*</sup> Solvent composition is closer to a pure NGS formulation. <sup>\*</sup>Solvent composition is closer to a NGS-CSSX blend formulation.

## 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

Each sample (MCU-16-1247, MCU-16-1248, and MCU-16-1249) was visually examined. No immiscible phases or floating debris or foam were observed (see Fig. 1). However, a noticeable thin film of material was observed at the walls of the p-nut vials for the three samples (Fig. 1). An FTIR analysis of these films indicated the material is a composite of magnesium silicates (some asbestos like), modifier, and oxidized oil (possibly lubricating oil from equipment upstream of MCU such as agitators). 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-16-1247-1248-1249). Table 3-1 contains the results for the MCU-16-1247-1248-1249 composite sample.



**Figure 1. Typical appearance of the three MCU-16-1247, MCU-16-1248, and MCU-16-1249**

### *Isopar™ L and Modifier Levels*

Triplicate density measurements of the sample gave an arithmetic average result of 0.8247 g/mL (0.03% RSD) (or 0.8221 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula)<sup>4</sup> for MCU-16-1247-1248-1249 at 22 °C. The calculated density (0.822 g/mL) for MCU-16-1247-1248-1249 is about 1% below the calculated density for the standard sample (0.831g/mL at 25 °C for the scratch blend made in the laboratory).<sup>2,4</sup> Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be slightly above its nominal value (within analytical uncertainties) and the modifier concentration should be slightly below its nominal value.

An examination of Table 3-1 shows that the Isopar<sup>TM</sup> L concentration is above its nominal value (~ 1%) while the modifier concentration is correspondingly slightly lower (9% lower) than its nominal value. The higher Isopar<sup>TM</sup> L concentration is consistent with the Isopar<sup>TM</sup> L addition to the solvent on August 21<sup>st</sup>. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement. The last solvent trim addition to MCU was on June 15, 2016.

All measurements indicate the Isopar<sup>TM</sup> L level is slightly above its nominal value while the modifier concentration level is below its nominal value (see Fig. 2 for recent modifier concentrations from HPLC measurements). Looking at Fig. 2, the modifier level appears to trend down from the level observed right after the trim addition to the solvent on June 15, 2016. The June 2016 trim addition added five times more modifier to the solvent than the April 2016 trim addition. Thereby, the modifier level rise in the June monthly sample is more noticeable. The rising rate of the modifier level in the solvent depends if the MCU operations are continuous or intermittent. The randomness in the modifier concentration between solvent trim additions is possibly due to the process of mixing, sampling and analyzing it. The relatively lower modifier concentration and the addition of Isopar<sup>TM</sup> L explain why the measured density is slightly below the standard sample density. The trend in the modifier level correlates with the trend in the density measurements as expected (see Fig. 2). 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  $0.819 \pm 0.019$  g/mL. Their sum is consistent with the measured and temperature corrected (to 25 °C) value of 0.822 g/mL, and also with the measured and corrected to 25 °C mass concentration (density) of the standard (0.831 g/mL). With a lower modifier concentration, the solvent chemical properties are similar to that of Isopar<sup>TM</sup> L; thus, expect normal emulsification, phase separation, rheology, and phase carry-over (but increased evaporation). The current modifier concentration is well above the minimum modifier concentration below which the extractant concentration may drop due to solubility limits.

No significant impact from impurities found earlier is expected on the physical and chemical behavior of the solvent. However, a significant build-up of the micron size silicates can lead to the formation of a rag layer between the solvent and the various aqueous streams that may alter the physical-mechanical of the SHT-aqueous interface. Based on the amount of material found in the samples, there is no risk of forming a rag layer.

**Table 3-1 Sample Results for MCU-16-1247-1248-1249**

Analysis	Method	LW-AD-Proj-160412-4 (Analytical Lab. Labeling)	Result (mg/L) <sup>#</sup>	Nominal* Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar <sup>®</sup> L	FT-HNMR	NA	6.24E+05	6.13E+05	102
Isopar <sup>®</sup> L	FTIR	NA	6.22E+05		102
Isopar <sup>®</sup> L	Density	NA	6.19E+05		101
Average <sup>§</sup>	All	NA	6.20E+05	6.13E+05	101
Modifier	HPLC	LW3371	1.54E+05	1.69E+05	91
Modifier	FT-HNMR	NA	1.55E+05		92
Modifier	FTIR	NA	1.58E+05		94
Modifier	Density	NA	1.53E+05		90
Average <sup>§</sup>	All	NA	1.54E+05	1.69E+05	91
TiDG	SVOA-Titration*	LW3370	6.51E+02	1.44E+03	45
TiDG*	Titration	NA	5.15E+02	1.44E+03	36
Average <sup>§</sup>	All	NA	5.30E+02	1.44E+03	37
trioctylamine	SVOA	LW3370	1.20E+02	-	23 <sup>z</sup>
trioctylamine	Titration	NA	2.20E+02	-	42 <sup>z</sup>
Average <sup>§</sup>	All	NA	1.52E+02	-	29 <sup>z</sup>
MaxCalix	HPLC	LW3371	4.17E+04	4.57E+04 <sup>Δ</sup>	91
MaxCalix	FT-HNMR	NA	4.44E+04		97
Average <sup>§</sup>	All	NA	4.26E+04	4.57E+04	93
BOBCalixC6	HPLC	LW3371	2.06E+03	-	51 <sup>z</sup>
Average <sup>§</sup>	All	NA	2.06E+03	-	51 <sup>z</sup>
Density (g/mL)	Direct Measurement	NA	0.822	0.831	99

<sup>#</sup> Analytical uncertainty is 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, and 14% for Isopar<sup>™</sup> L. N/A = Not Applicable. Density estimations assume the combined weight percent of TiDG, MaxCalix, BOBCalixC6, and TOA to be approximately 6%. All uncertainties are 1 sigma.

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

<sup>§</sup> Reported value for a MCU component is the weighted average of the values reported by the techniques that measured that component.

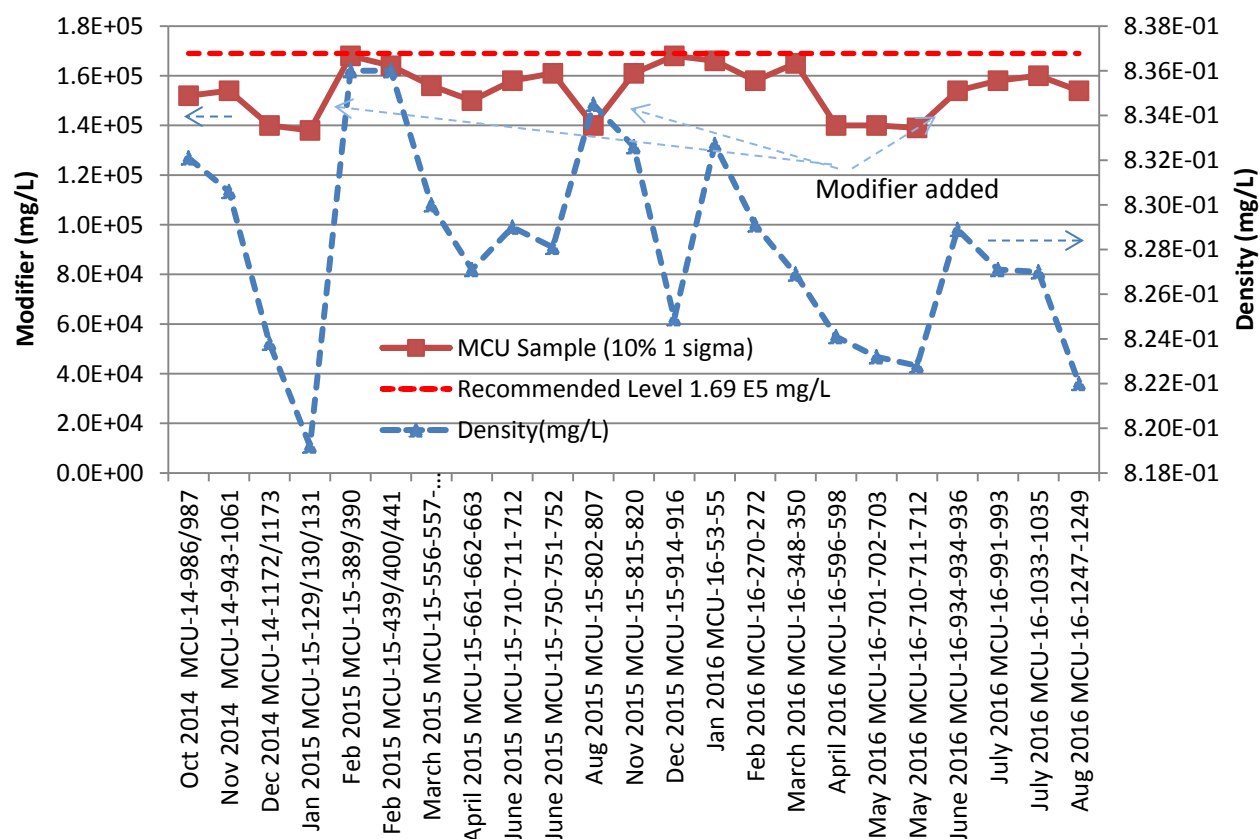
$$x = \frac{\sum_1^i \left( \frac{x_i}{\delta_i^2} \right)}{\sum_1^i \left( \frac{1}{\delta_i^2} \right)}; \quad x_i \text{ stands for the concentration obtained at a given method and } \delta_i \text{ is the corresponding uncertainty.}$$

<sup>Δ</sup> No TiDG value was estimated by FT-HNMR due to an aged (questionable) standard.

<sup>z</sup> Trioctylamine obtained from the SVOA method was subtracted from the measured total base in the titration method to obtain a calculated TiDG concentration.

<sup>z</sup> Percent are relative to the initial TOA concentration of 530 mg/L and BOBCalixC6 concentration of 4030 mg/L in 2008.

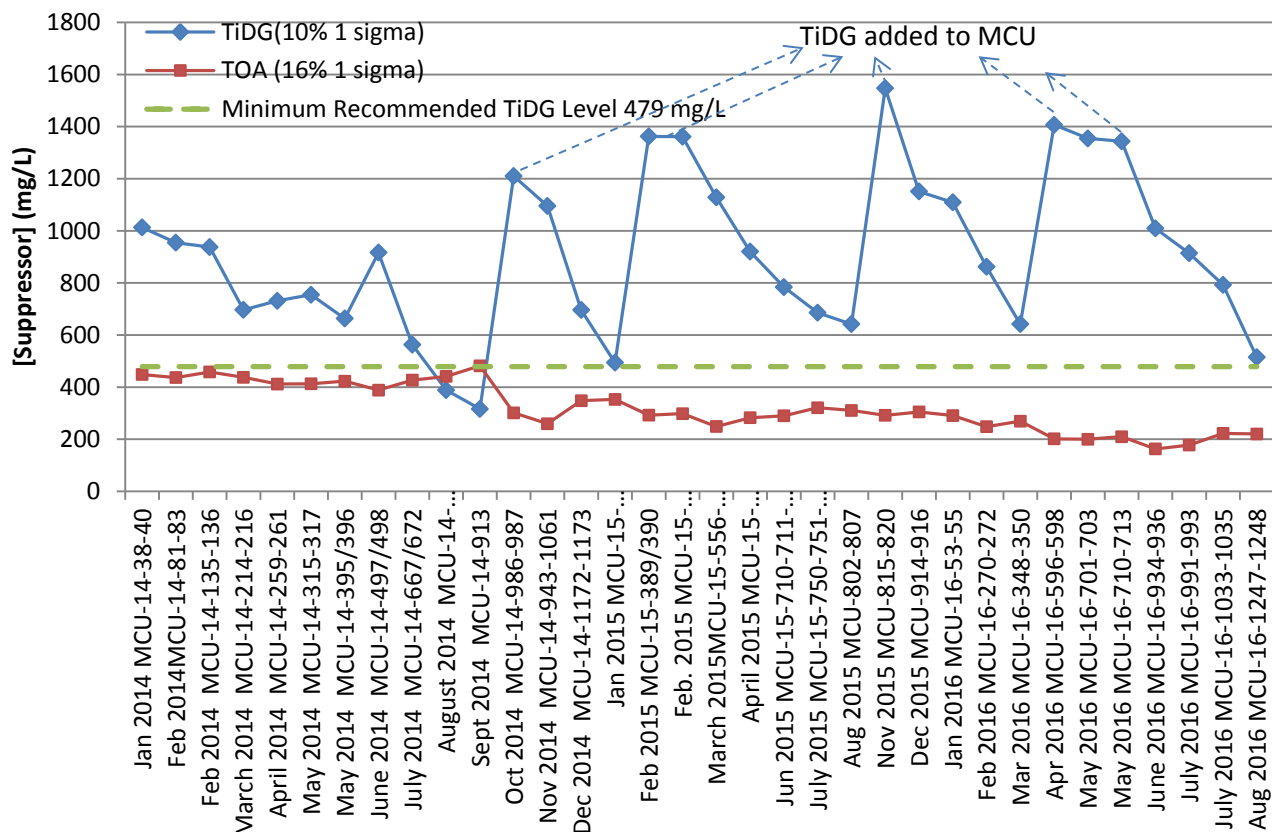
<sup>Δ</sup> Value shown is the difference between 47,765 mg/L (50 mM MaxCalix) and the current BOBCalixC6 concentration (2,060 mg/L in this case).



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

### *Suppressors Levels*

The average TiDG concentration level ( $5.30 \pm 5.3 \text{ E2 mg/L}$ ) is at 37 % of its nominal value of 1440 mg/L confirming the continued depletion of the trim addition to the solvent done in April 29, 2016 (a noticeable spike in the TiDG concentration level was observed in Fig. 3 in the April 2016 SHT monthly sample). Fig.3 also confirmed the lesser amount of TiDG that was added to the solvent in the June 2016 trim relative to the April solvent trim. The much lower TiDG level in the August monthly sample (compared to the July monthly sample) is due to the higher processing rate of salt solution in June at MCU. The suppressor concentration is at its minimum recommended operating level (479 mg/L) and thus, it is recommended that the solvent receives a TiDG addition. The TOA concentration appears to remain steady and it is currently at  $152 \pm 31 \text{ mg/L}$ . Since MCU no longer adds TOA, a drop in TOA concentration is expected with time. However, a detectable and steady TOA concentration persists with time, perhaps due to TiDG degradation into primary amines, which have previously been identified as degradation products of the suppressor when heated (3 °C, 25 °C and 36 °C).<sup>5</sup> The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.<sup>6</sup>



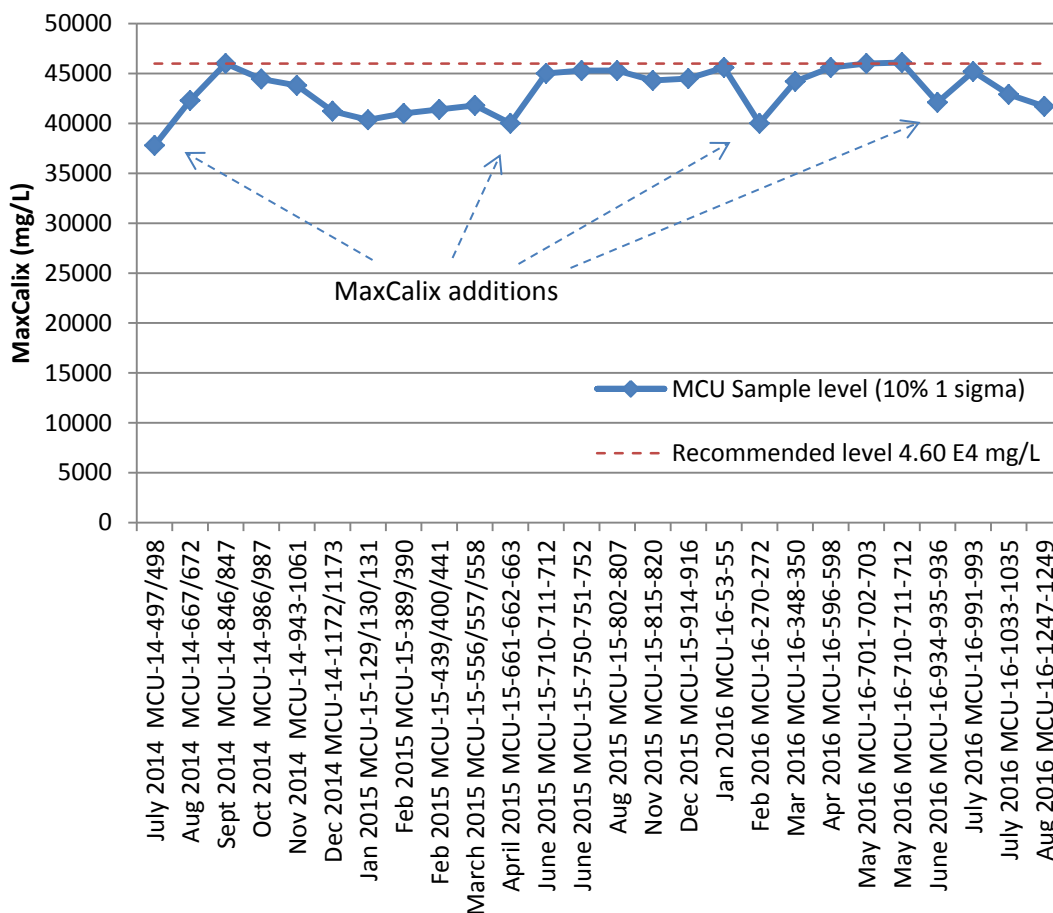
**Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.**

### Extractant Levels

The average calculated MaxCalix level is 4.26E4 mg/L ( $\pm 10\%$ ) and it is at 7% below its nominal value. Note the current recommended value is the difference between 47,765 mg/L (50 mM MaxCalix) and the current BOBCalixC6 concentration in the SHT. The sudden drop in the MaxCalix concentration seen in Fig. 4 is within the uncertainty range for this measurement. However, the observed downward trend in the MaxCalix concentration is probably due to systemic removal mechanisms beyond analytical variance or possibly from reaching solubility limit. The current downward trend in the MaxCalix level has been previously observed after a solvent trim addition (see Fig. 4). Further inquiries may be required (for example, if the MaxCalix loss rate correlates with a differences in salt batch or processing higher flow rate of salt batch) to determine the loss of MaxCalix after each solvent trim.

The residual concentration of BOBCalixC6 level is currently at 51% of the level measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). This level is higher than level observed in the July samples. Since no BOBCalixC6 is added to the SHT, the variable trend in BOBCalixC6 concentration with time is more reflective of the analytical uncertainty. Given that no BOBCalixC6 is added to the solvent, the level is expected to decrease with time.

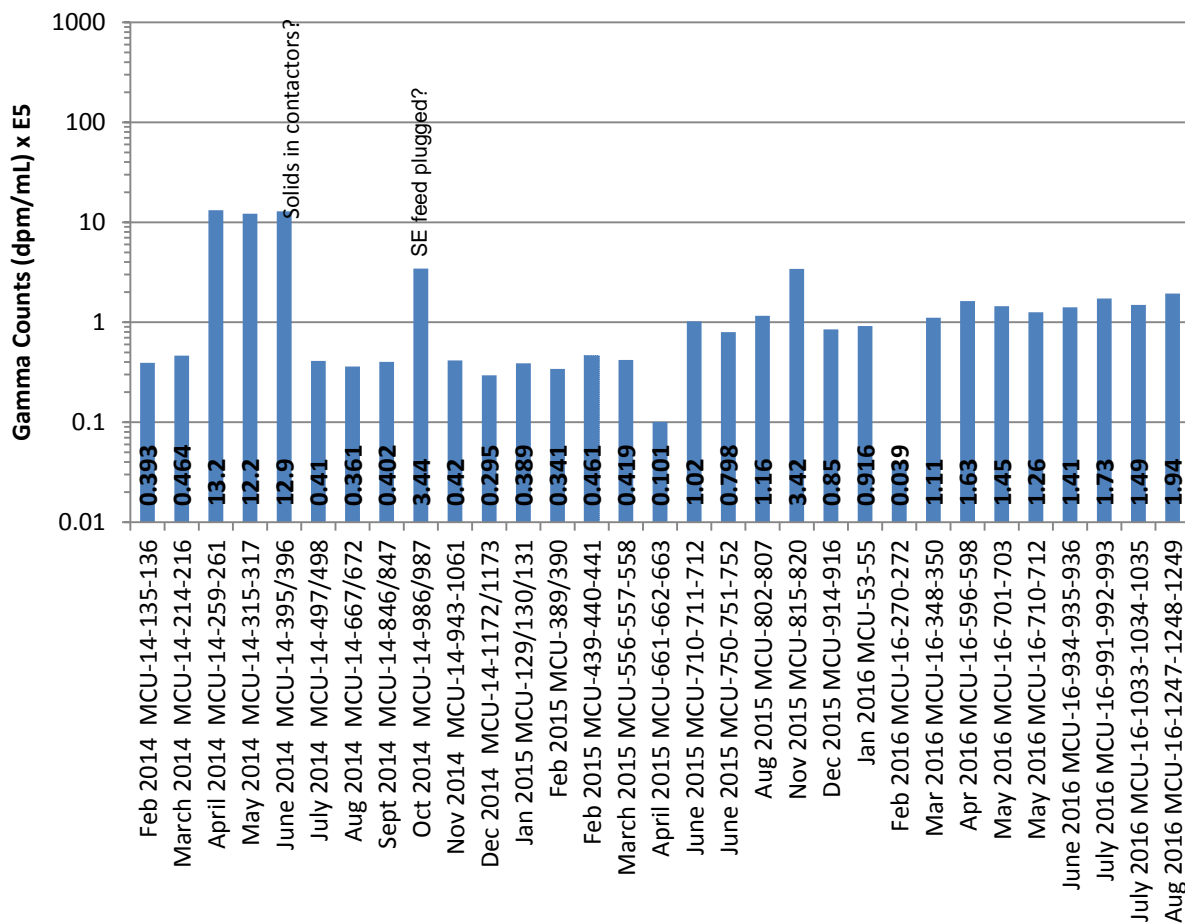




**Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (46,000 mg/L is the nominal concentration).**

#### *Gamma Level*

The gamma measurement of MCU-16-1247-1248-1249 is  $1.94\text{E}5$  dpm/mL ( $\pm 5\%$ ). This level of activity is consistent with the previous gamma levels when the process was operating normally in late 2015 and in early 2016 (the low Gamma counts from the February 2016 sample is unclear at this point). It confirms the steady state trend level observed since June 2015 (see Fig. 5).



**Figure 5. The gamma count of selected SHT samples. One sigma is 5%.**

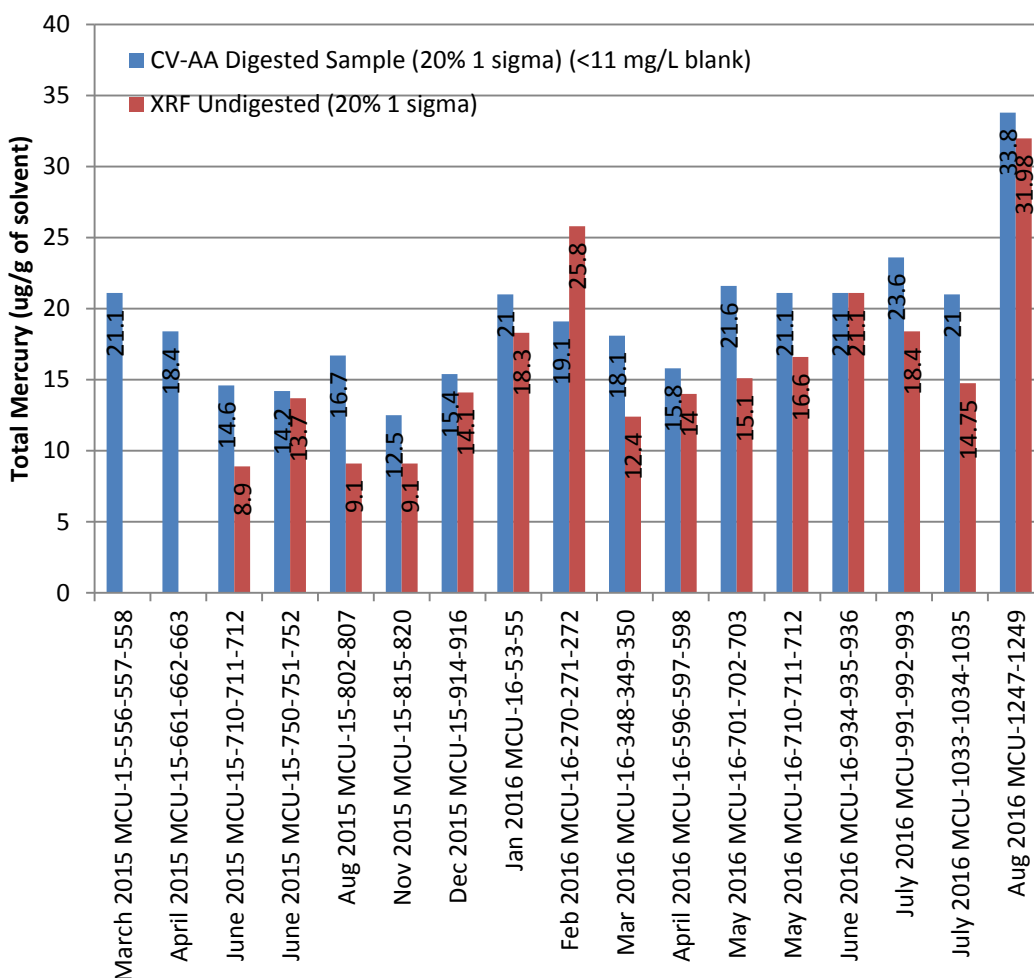
### Impurities

No impurities were seen at the 1000 ppm level or higher as indicated by the SVOA method ( $\pm 20\%$  uncertainty). No impurities were observed in the HNMR spectrum.

A few mL of MCU-16-1247-1248-1249 was digested and analyzed for total mercury by the CVAA method. The CV-AA method detected  $33.8 \pm 6.8 \text{ ug/g}_{\text{solvent}}$  of mercury (or  $27.8 \text{ ug/mL}_{\text{solvent}}$  at  $25^\circ\text{C}$ ). The XRF method also detected a concentration of  $32.0 \pm 6.4 \text{ ug/g}_{\text{solvent}}$  of mercury (or  $26.3 \text{ ug/mL}_{\text{solvent}}$  at  $25^\circ\text{C}$ ) of the undigested MCU-16-1247-1248-1249 sample. The average of both methods is  $32.9 \pm 6.6 \text{ ug/g}_{\text{solvent}}$  of mercury.

The differences between the CVAA and XRF results are within their analytical uncertainties. Regardless of which result is true, this level of mercury is significantly higher than the solubility of metallic Hg in dodecane ( $\sim 3 \text{ ppm}$ )<sup>7</sup> 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.<sup>8</sup> For 200 gallons of solvent (757.1 L) and assuming a density of  $0.822 \text{ g/mL}$ , the solvent could contain a total of  $20 \pm 4 \text{ g}$  of mercury (based on the CV-AA data). A comparison of this measurement with previous month confirms a positive trend in the mercury concentration in the solvent

(data is shown in Fig. 6). Please note all the XRF data since November were renormalized and compensated for solvent density variation in this report. Thus, these values differ (slightly lower values) from previous reports. The positive trend in Fig. 6 might be due to a higher mercury concentration in Salt Batch 9 (Tank 49H).



**Figure 6. Total mercury in recent SHT samples. One sigma is 20%. CVAA = Cold Vapor Atomic Absorption Spectrometry. XRF =X-ray Fluorescence (20% one sigma).**

### Recommendations

The current analysis indicates the solvent has lower modifier (91% of its nominal concentration) and TiDG (37% of its nominal concentration) levels, but it has slightly higher levels of Isopar™ (101%) relative to the standard. The MaxCalix concentration has dropped after the June solvent trim addition and it is currently at 96% of its nominal level. The TiDG, MaxCalix, modifier, and Isopar™ levels are expected to trend downward with time. Based on the August sample, it is recommended that a solvent trim should be added to the solvent to restore the relevant components to their nominal levels.

Furthermore, it is advisable to conduct tests that measure the rate of modifier dispersion from a trim addition to spent NGS solvent in the laboratory that may shed light into the observed modifier behavior in the solvent. In order to remain two-sigma above the minimum recommended level, it is recommended to continue the periodic surveillance of the solvent and to make trim additions as needed.

The temperature dependence of the current gravimetric density equation for solvent composition (originally obtained from CSSX solvent) needs reverification with the current NGS-CSSX solvent to improve the formula accuracy in extracting the components concentration in the solvent.

#### 4.0 Conclusions

SRNL received one set of SHT samples (MCU-16-1247-1248-1249), pulled on 08/22/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-1247-1248-1249 indicated the Isopar<sup>TM</sup>L concentration is above its nominal level (101%). The modifier (CS-7SB) and the TiDG concentrations are 9% and 63 % below their nominal concentrations. The extractant (MaxCalix) was found to be 7% below its nominal level but at a sufficient level for continuing operations. This analysis confirms the solvent may require a solvent trim. Based on the current monthly sample, the levels of TiDG, Isopar<sup>TM</sup>L, MaxCalix, and modifier are sufficient for continuing operation but are expected to decrease with time. It is recommended to continue with the periodic characterization and trimming additions to the solvent. A solvent trim batch, containing TiDG, modifier, and MaxCalix has been prepared by SRNL and will be added to the SHT upon exiting the current outage.

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). Residual concentration of oxidized oil, protein (bacteria), and silicates were found in the p-nut vials that contained MCU-16-1247, MCU-16-1248, and MCU-16-1249. These impurities are likely present in the SHT, rather than contamination in the p-nut vials. Another impurity observed in the samples was mercury. Up to  $32.9 \pm 6.6$  micrograms of mercury per gram of solvent (or 27.0  $\mu\text{g/mL}$ ) was detected in this sample (the average of the CV-AA and the XRF method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in Salt Batch 9 (Tank 49H) compared to previous salt batches.

The current gamma level (1.94E5 dpm/mL) confirmed that the gamma concentration has returned to previous levels (as observed in the late 2015 samples) where the process operated normally and as expected.

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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