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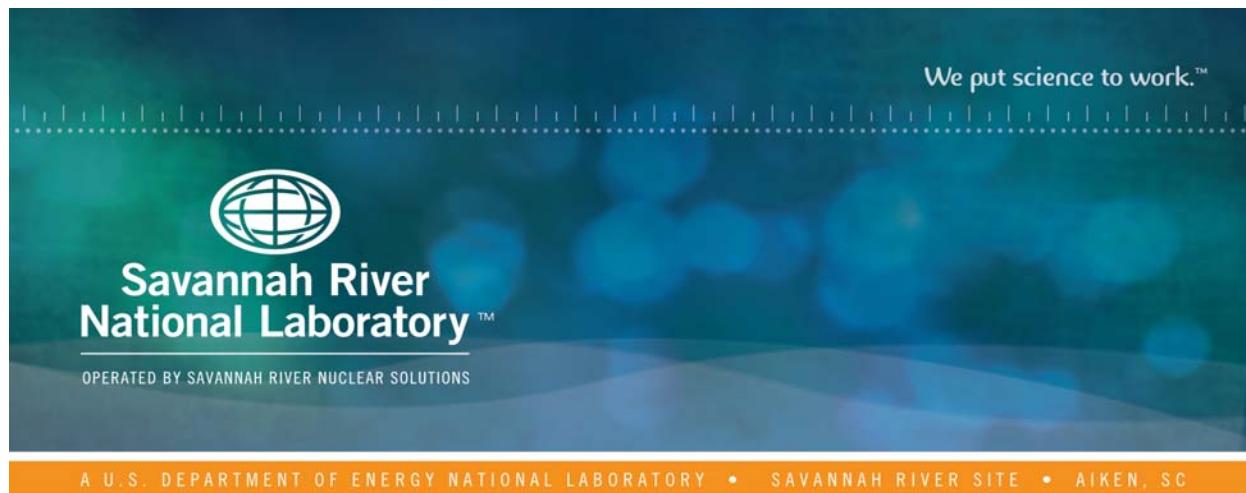
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# Solvent Hold Tank Sample Results for MCU-17-122-124 (March 2017), MCU-17- 130-132 (April 2017), MCU-17-133-135 (May 2017), and MCU-17-141-149 (June 2017): Quarterly Report

F. F. Fondeur

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September 2017

SRNL-STI-2017-00444, Revision 0



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# Solvent Hold Tank Sample Results for MCU-17-122-124 (March 2017), MCU-17-130-132 (April 2017), MCU-17-133-135 (May 2017), and MCU-17-141-149 (June 2017): Quarterly Report

F. F. Fondeur  
D. H. Jones

September 2017

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## EXECUTIVE SUMMARY

A trend summary of four Solvent Hold Tank (SHT) monthly samples; MCU-16-122-124 (March 2017), MCU-17-130-132 (April 2017), MCU-17-133-135 (May 2017), and MCU-17-141-149 (June 2017) are reported. Analyses of the June SHT sample (MCU-17-141-149) indicated that the modifier (CS-7SB) and the extractant (MaxCalix) concentrations were slightly below (4% each) their nominal recommended levels (169,000 mg/L and 46,400 mg/L respectively). The suppressor (TiDG) level has decreased since the January 2017 measurement but has remained steady in the range of 666 to 705 mg/L, well above the minimum recommended level (479 mg/L), but below the nominal level. The “flat” trends observed in the TiDG, MaxCalix, modifier, and Gamma measurement are consistent with the solvent being idle since January 10, 2017.

This analysis confirms the Isopar™ addition to the solvent on January 18, 2017. This analysis also indicates the solvent did not require further additions. Based on the current monthly sample, the levels of TiDG, Isopar™, 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.

From 20 to 190 ppm of long fatty acid (docosanoic and 3-methyltritracontane), dioctylformamide, and n-nitroso-di-n-octylamine were found in the March, May and June solvent samples by the Semi-Volatile Organic Analysis (SVOA) but further analysis with independent methods are needed to confirm these chemicals. The impurities levels were lower in the June sample and this is possibly due to the additional caustic wash the solvent received prior to sampling the June samples. No impurities were observed in the Hydrogen Nuclear Magnetic Resonance (HNMR). Another impurity observed in the samples was mercury. Based on the June SHT sample, up to  $30 \pm 6$  micrograms of mercury per mL of solvent was detected (the average of the CV-AA and XRF methods). The higher mercury concentration in the solvent (as determined in the last three monthly samples) is possibly due to the higher mercury concentration in Salt Batches 8 and 9 (Tank 49H) or sampling of previously undisturbed areas of high mercury concentration in Tank 49H.

The gamma level ( $\sim 0.18\text{E}5$  dpm/mL) measured in the March, April, May, and June SHT samples were one order of magnitude lower than the gamma levels observed in the December and January SHT samples. The gamma level is consistent with the solvent being idle (since January 10, 2017). The gamma levels observed in the March, April, May, and June SHT samples had been observed before and are consistent with previous monthly measurements where there was no process at Modular Caustic-Side Solvent Extraction (MCU).

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
HNMR	Hydrogen Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
ISDP	Integrated Salt Disposition Project
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 MCU implemented the Next Generation Solvent (NGS) flow sheet. Facility personnel added a non-radioactive, NGS “cocktail” containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel to implement the NGS flow sheet. The resulting “blend” solvent (“NGS Blend solvent”) is essentially NGS with residual amounts of BOBCalixC6 and trioctylamine (TOA). SHT samples are sent to Savannah River National Lab (SRNL) to examine solvent composition changes over time.<sup>1</sup> With the exception of Isopar™L which is regularly added to the SHT due to its high vapor pressure, this report shows the cumulative chemical composition data, including impurities like mercury, of four different SHT samples: MCU-17-122-123-124 (March 2017), MCU-17-130-131-132 (April 2017), MCU-17-133-134-135 (May 2017), and MCU-17-141-142-143-144-145-146-147-148-149 (9 p-nut vials) [June 2017]. A summary report for each of the SHT samples was issued earlier.<sup>2,3,4,5</sup>

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>6</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 January 18, 2017, an Isopar™L addition was made to MCU.<sup>7</sup>

**Table 2-1 Log of recent trims to the MCU solvent and SHT sampling dates**

Event	Date
20 gallons solvent trim added to MCU	November 8, 2016
11 gallons Isopar™L added to MCU	November 12, 2016
SHT sample MCU-16-1363-1364-1365	November 15, 2016
SHT sample MCU-16-122-127 (6 p-nut vials)	December 4, 2016
51 gallons solvent trim added to MCU	December 14, 2016
15 gallons Isopar™L added to MCU	December 27, 2016
SHT sample MCU-17-86-87-88	January 9, 2017
23 gallons of Isopar™L added to MCU	January 18, 2017
SHT sample MCU-17-119-120-121	February 21, 2017
SHT sample MCU-17-122-123-124	March 18, 2017
SHT sample MCU-17-130-131-132	April 18, 2017
SHT sample MCU-17-133-134-135	May 2, 2017
SHT sample MCU-17-141-142-143-144-145-146-147-148-149	June 4, 2017

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. The p-nut vials for each monthly sample (SHT) 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. Please note that the SVOA, HPLC, XRF, CV-AA, Density, titration, and FT-HNMR results for each monthly SHT sample are shown in the monthly reports.

**Table 2-2 Nominal concentrations of the relevant components in NGS Blend at 25 °C <sup>6</sup>**

Component	mg/L	Molar
MaxCalix	~ 44,400* to 47,800*	~ 0.0465 to 0.050
BOBCalixC6*	< 4,030	< 0.0035
TOA*	< 530	< 0.0015
Modifier	~ 169,000	~ 0.50
TiDG	~1440	~ 0.003
Isopar <sup>TM</sup> L	~ 607,000* to 613,000*	~ 73.05 to 73.69 wt%

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

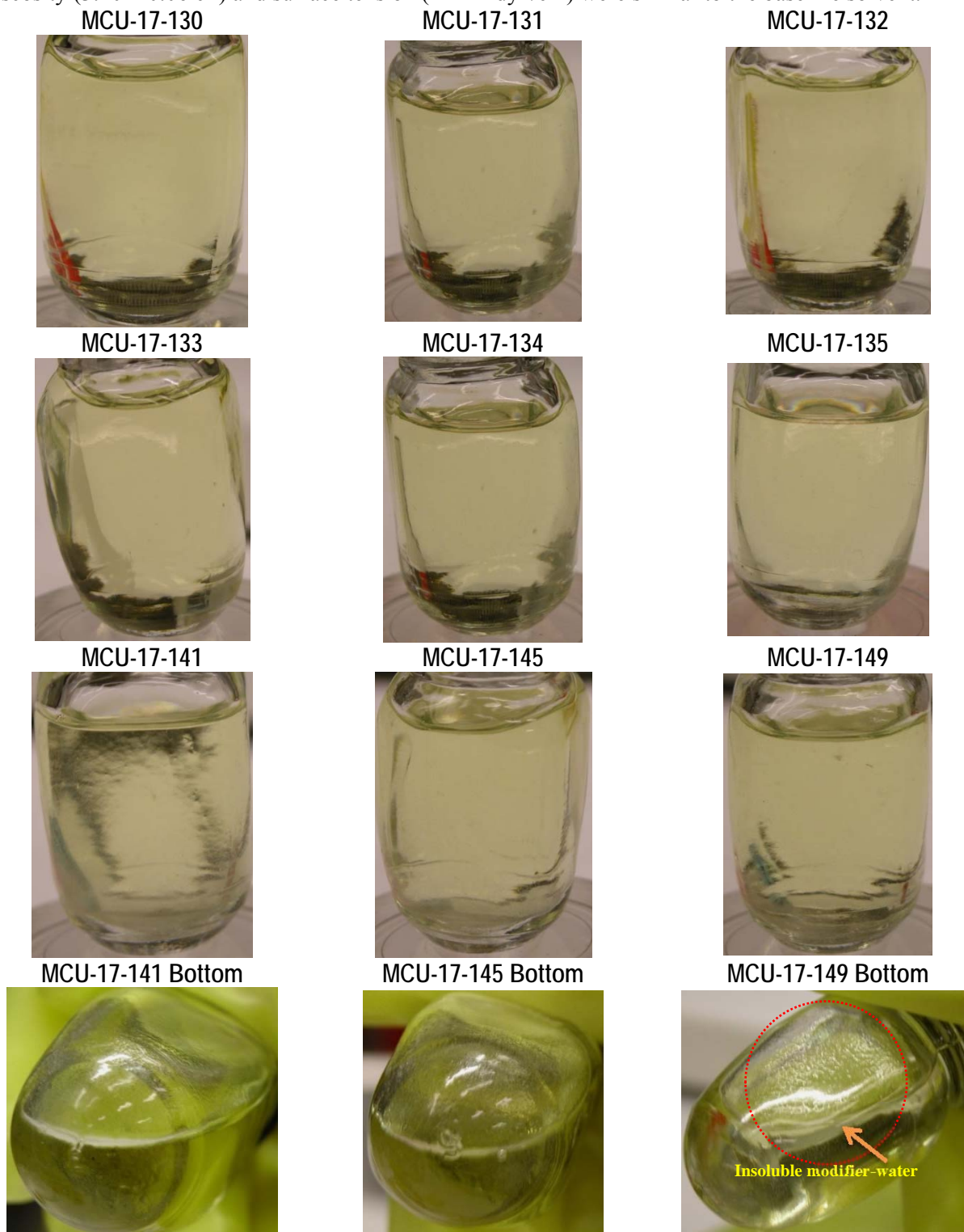
## 3.0 Results and Discussion

Each sample (and its corresponding p-nut vial) was visually examined. No immiscible phases or floating debris or foam were observed (see Fig. 1). However, a film consisting of water droplets and modifier was observed on the walls of p-nut vials MCU-17-141 through MCU-17-149 (see last set of pictures in Fig. 1). It is difficult to envision or explain the presence of this insoluble material in the June SHT sample when previous samples (April 2017 and May 2017 SHT samples) did not show this material. Perhaps, with time carried-over water in the solvent is condensing and settling and it is being collected by the sampler in the SHT. MCU suspended processing radioactive liquid waste January 10, 2017 and SHT samples collected since then should have no processing or contacted liquid waste history (for example minimal aqueous liquid carry over or minimal leached or evaporated components). However, prior to pulling the June samples, a seven hour solvent recirculation through the wash contactors where the solvent contacted a dilute caustic solution was conducted. Due to instrument malfunctions no pictures of MCU-17-122-123 (March 2017 SHT) were taken. 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 for each monthly SHT samples.

### *Modifier Levels and Density Measurements*

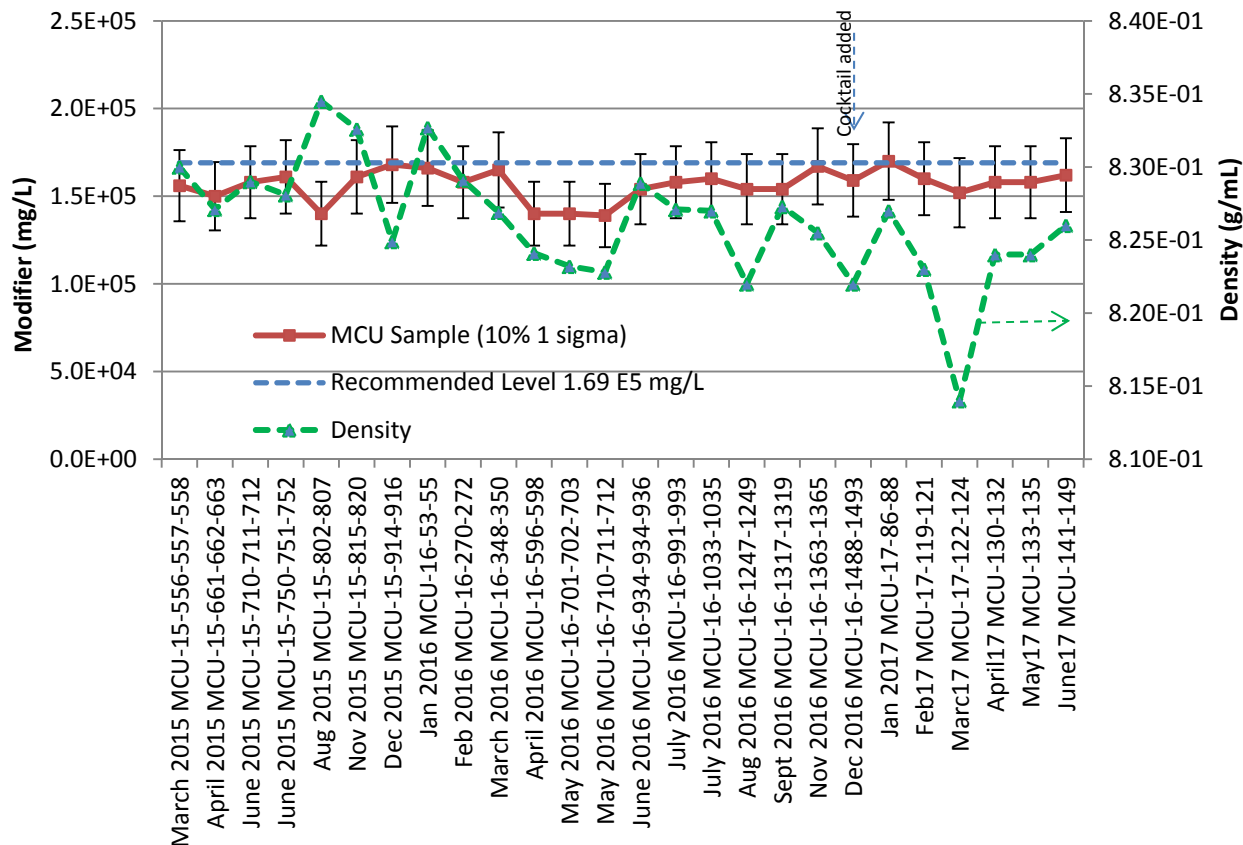
Since MCU stopped processing aqueous liquid waste in January 2017, the chemical composition of the SHT is not expected to change with time (leaching, evaporation, chemical decomposition and/or reaction, and radiation damage rates are minimal). Based on the June sample, triplicate density measurements (by gravimetric and vibrating a filled tube method) gave an arithmetic averages slightly less than 1% lower than the baseline solvent at 25 °C when corrected for temperature using the CSSX temperature correction formula<sup>6</sup> (see Fig. 2) but the measurement error intervals include the baseline solvent density value (The calculated density for the baseline solvent is 0.830 g/mL at 25 °C); therefore, it cannot be concluded that the measurements are different from the baseline sample measurement.<sup>2,4</sup> However, an independent method (HNMR) has also reported that the Isopar<sup>TM</sup>L level in the June sample is higher (3%) than the baseline solvent. Therefore, the calculated Isopar<sup>TM</sup>L level in the June sample is 1% higher than the baseline solvent. Similarly, the calculated modifier level is 4% below the recommended modifier level (1.69E05 mg/L). Figure 2 shows the monthly modifier level and density of the SHT samples. The recommended modifier level (1.69E05 mg/L) in Fig. 2 is well within the error intervals of the three MCU samples reported in this report. Both the density data and the modifier concentration correlate with each other as expected; the solvent density is a concentration-weighted linear combination of the modifier and

Isopar™ pure densities. Other physical measurements of the May and June SHT samples such as viscosity ( $3.20 \pm 0.06$  cP) and surface tension ( $21 \pm 2$  dyn/cm) were similar to the baseline solvent.



**Figure 1** A picture of sample MCU-17-130-132 (top), MCU-17-133-135 (middle) and MCU-17-141-145-149 (bottom). A picture of MCU-17-133-135 was not available due to equipment malfunction

All measurements indicate (based on the June sample) the Isopar<sup>TM</sup>L level is 1% above its nominal value while the modifier concentration level is 4% below its nominal value (see Fig. 2 for recent modifier concentrations from HPLC measurements). Looking at Fig. 2, the modifier level appears to return to its nominal level observed right after the trim addition to the solvent on December 14, 2016. The trend in the modifier level correlates with the trend in the density measurements as expected (see Fig. 2).<sup>8</sup>

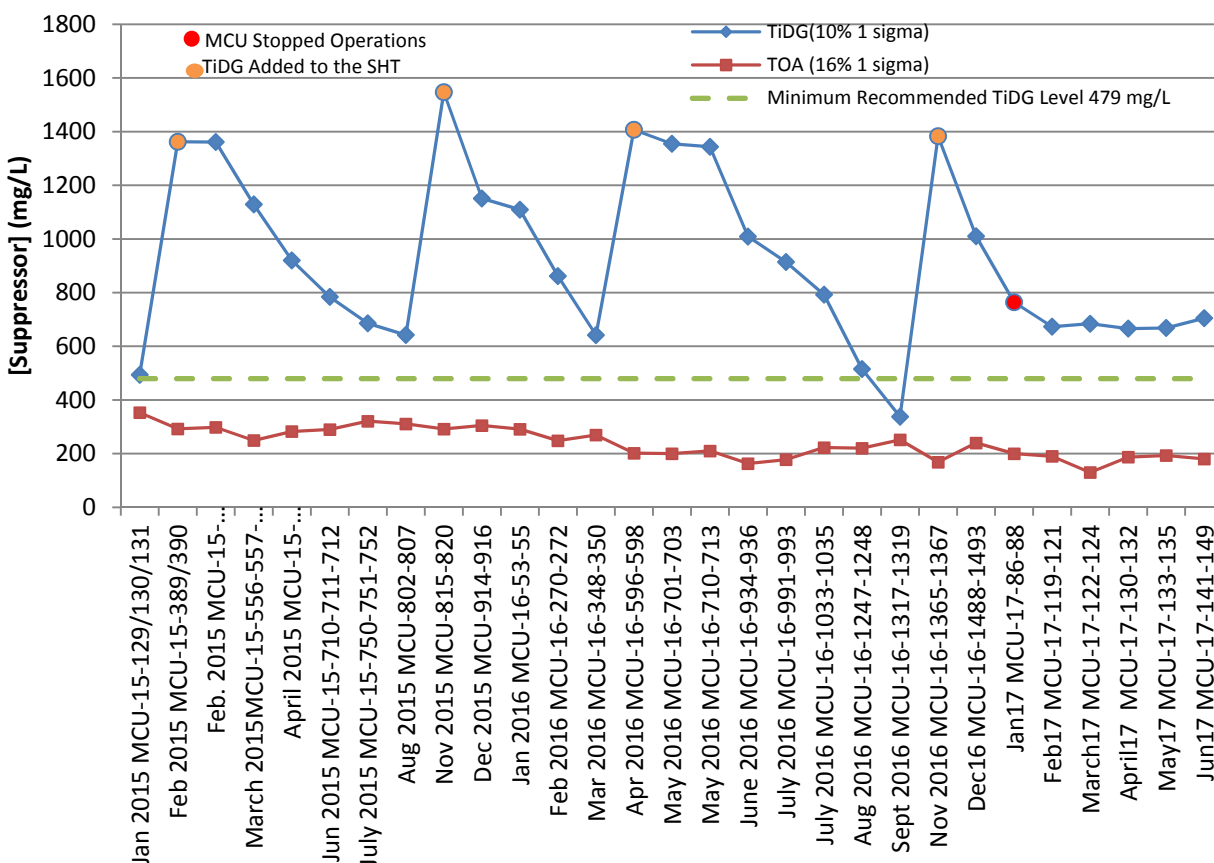


**Figure 2. Modifier level in the solvent as measured by HPLC (one sigma is 10%).**

### Suppressors Levels

The average TiDG concentration levels for MCU-16-122-127, MCU-17-130-132, MCU-17-133-135, and MCU-17-141-149 are shown in Figure 3. As can be seen in Fig. 3, the TiDG level has remained steady between 666 and 705 mg/L since MCU suspended operations in January 10, 2017. Part of that trend is essentially “flat” after MCU stopped processing any aqueous solution. Thus, the “flat” trend reflects the TiDG degradation under radiolysis and caustic solution conditions alone (without mass transfer losses to any aqueous solutions or thermal degradation). Since the solvent has been reading approximately 2E4 dpm/mL gamma since the February sample, it appears that there is insufficient total gamma energy (and/or dose rate) to cause any systematic change in the TiDG concentration. Based on the June SHT sample suppressor concentration ( $705 \pm 71$  mg/L) is above its minimum recommended operating level (479 mg/L), but below the nominal level. The TOA concentration appears to remain steady and it is currently (based on the June sample) at  $182 \pm 28$  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 slower than expected degradation rate (or slower transfer rate to aqueous streams during operation) or the degradation of TiDG into primary amines, which have previously been identified

as degradation products of the suppressor when heated (3 °C, 25 °C and 36 °C).<sup>9</sup> The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.<sup>10</sup>



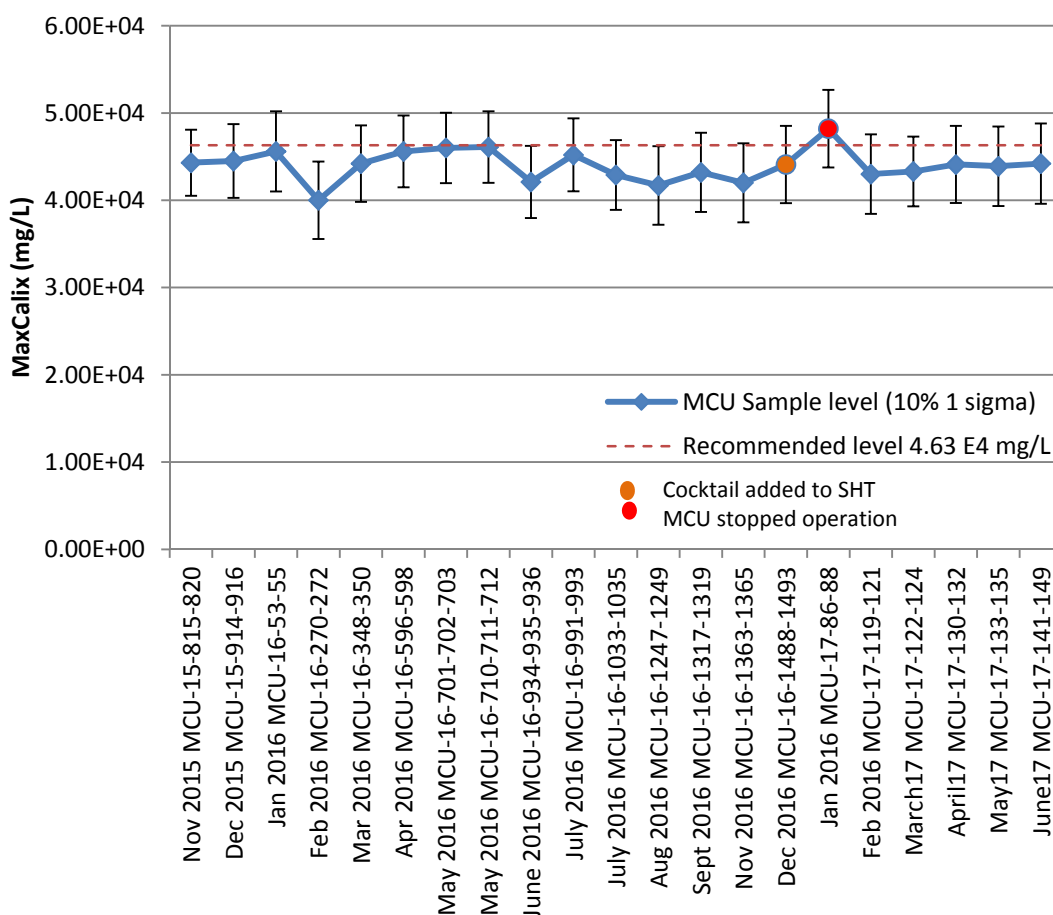
**Figure 3. Suppressor concentration as measured by titration in the SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.**

### Extractant Levels

The calculated MaxCalix levels ranged from 4.33E4 to 4.46E4 mg/L in the last four SHT samples. That level of MaxCalix has been previously observed (see Fig. 4). Their error intervals include the recommended value (4.63E4 mg/L). Note the current recommended value is the difference between 47,800 mg/L (50 mM MaxCalix) and the current BOBCalixC6 concentration in the SHT (1.42E3 mg/L in the February sample). The “flat” trend in the MaxCalix level began after MCU stopped operations in January 2017. The recent variations in the MaxCalix concentration seen in Fig. 4 (a concentration spike in the January SHT sample) is within the uncertainty range for this measurement despite the addition of MaxCalix to the solvent on December 14, 2016. The uncertainty is possibly due to the aggregate of analytical, sampling, and process variances.

The residual concentration of BOBCalixC6 level is (based on the June sample) at 35% of the level measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). This level is approximately the same level observed in previous samples. Since no

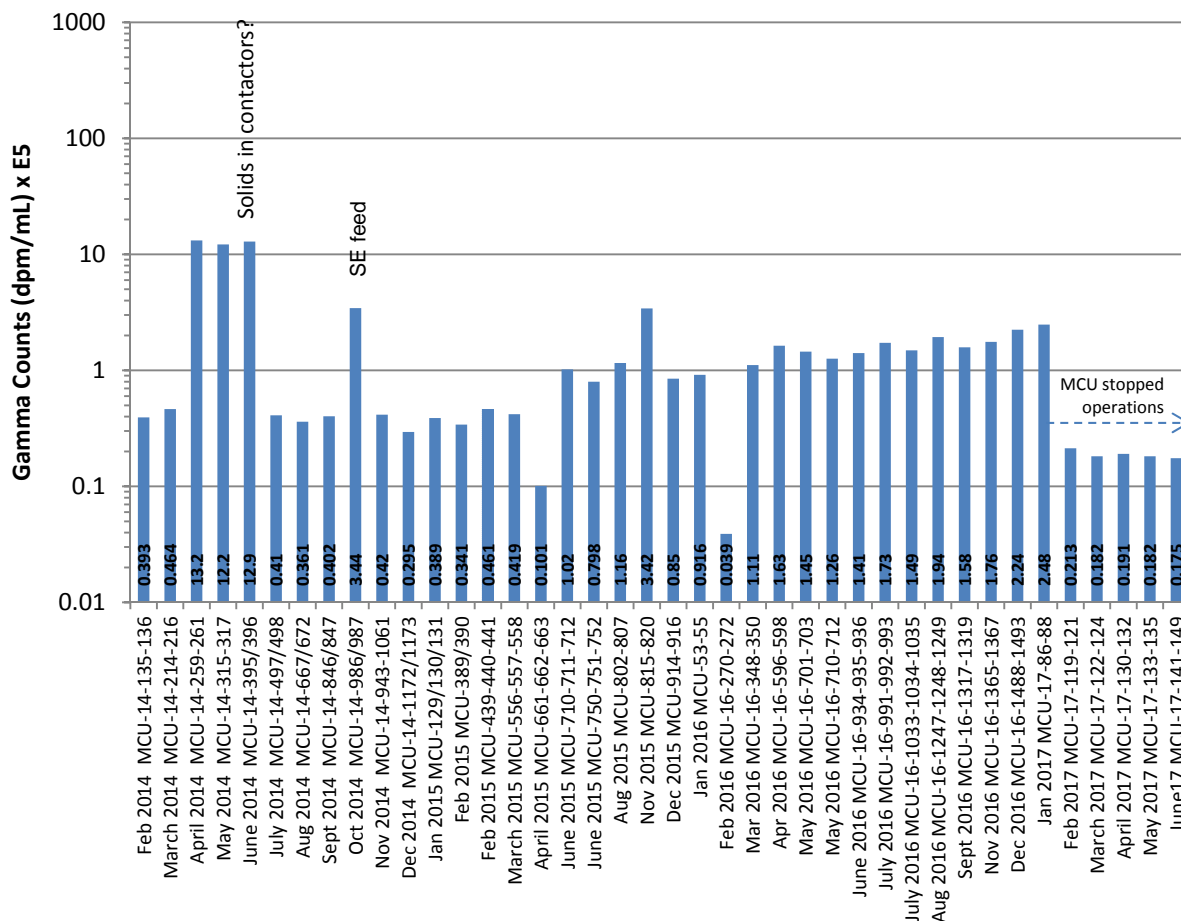
BOBCalixC6 is added to the SHT, the variable trend in BOBCalixC6 concentration with time is more reflective of the analytical uncertainty. Given that no BOBCalixC6 is added to the solvent, the level is expected to decrease with time.



**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 measurements for the March, April, May, and June samples are in Fig. 5 in relation to past gamma measurements. The gamma measurements for the March, April, May, and June samples were one order of magnitude lower than the January measurement. This low gamma level has been previously observed before but this time is probably due to MCU not processing salt solutions since January 2017. It is possible that the solvent sitting idle since January, that any radioactive aqueous solution carried-over has physically separated from the solvent. Thereby, reducing the total emitted energy level of the solvent.



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

### Impurities

Long fatty acid such as docosanoic acid (from 160 to 370 ppm) and 3-methyltritracontane (from 28 to 100 ppm) and n-nitroso-di-n-octylamine (from 46 to 150 ppm but not observed in the March sample) were observed in the March, April, May and June SHT samples as indicated by the SVOA method ( $\pm 20\%$  uncertainty) shown in Table 3-1. The aliphatic organic acid if neutralized could complex the cesium but it is believed that it will complex with the suppressor first and expect not interferences on the cesium mass transfer during stripping. The presence of the organic nitroso is a bit perplexing since from known chemistry it requires acidic conditions ( $\text{pH} < 5$ ) to form the nitroso ion (from nitrites) which can readily oxidize secondary amines (as found in the TiDG and TOA) or oxidation by strong oxidizer like peroxides (which are present in very small concentration). The nitroso observed appears to originate from degradation of TOA but further analysis is needed. Since the pH of the solvent is approximately 5.5 (paper strip), there may be sufficient nitrous acid and nitrous ions generated from solvent carry over of nitrites to react with TOA and generate N-nitrosodioctyl amine at levels that the GC-MS can detect but further testing and analysis is required to verify this hypothesis. The dioctylformamide is likely the reaction between the docosanoic acid and an amine from the breakdown of the TOA (this reaction could have possibly occurred in the oven of the GC-MS) but more evidence is needed. No impurities were observed in the HNMR spectrum and this indicates that further analysis is needed to confirm these impurities.



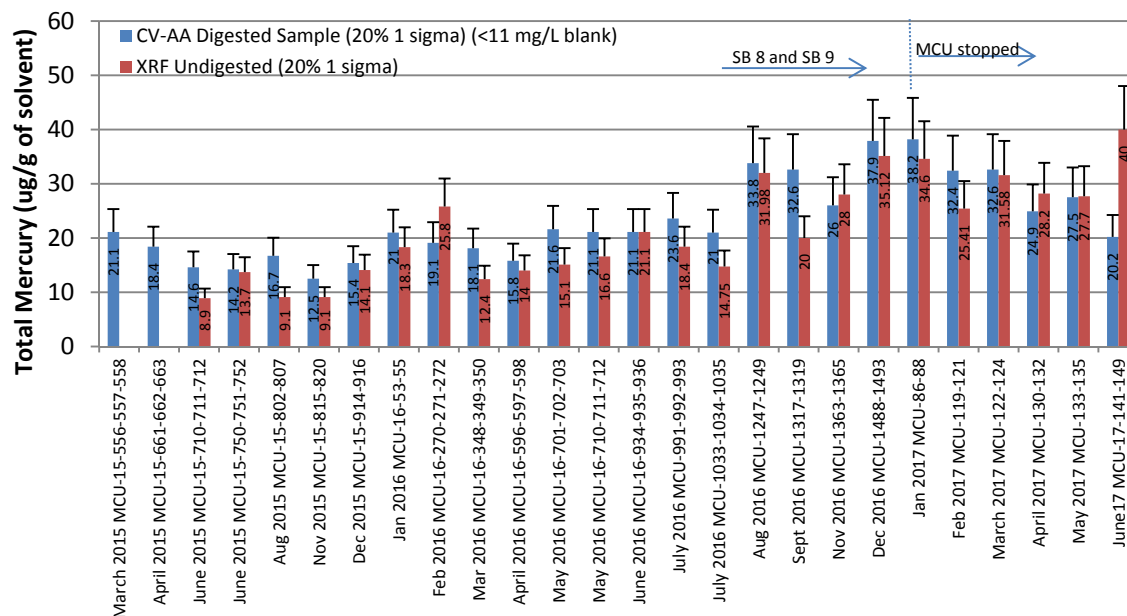
**Table 3-1. GC-MS results of impurities observed in the March through June SHT 2017 samples**

Chemical	March	April	May	June
Docosanoic acid	370	190	160	260
3-Methyltrtriacontane	100	28	31	32
N-Nitrosodioctylamine	ND	150	48	46
N N-Dioctylformamide	28	ND	ND	ND

ND = Not detected. All numbers are given in mg/L (as measured by GC-MS) with an one sigma of 20%

A few mL of each sample was analyzed by XRF and then digested and analyzed for total mercury by the CVAA method. The average mercury concentrations in the March, April, May, and June 2017 SHT samples were  $32 \pm 6$  mg/L,  $26 \pm 5$  mg/L,  $28 \pm 6$  mg/L, and  $30 \pm 6$  mg/L respectively. These levels are consistently lower than the levels observed on December 2016. A second June SHT is being analyzed by XRF given the large result reported (40 mg/L).

The level of mercury observed in the March, April, May, and June samples are significantly higher than the solubility of metallic Hg in dodecane ( $\sim 3$  ppm)<sup>11</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>12</sup> Based on the June SHT sample CV-AA mercury measurements, for 200 gallons of solvent (757.1 L), the solvent could contain up to  $23 \pm 4$  g of mercury (based on the June SHT sample measurement). A comparison of these measurements with previous months (especially 2016 samples) confirms a higher mercury concentration in the solvent (data is shown in Fig. 6). This may be consistent with the higher levels of total mercury ( $\sim 109$  ppm) observed in Tank 50H in the third and fourth quarters surveillance samples.<sup>13</sup> 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 downward trend observed in Fig. 6 since the January 2017 SHT sample might be due to the fact that the SHT solvent has not contacted any radioactive aqueous waste since January 10, 2017.



**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 June SHT sample analysis indicates the solvent was at 96% of its nominal modifier level and 49% of its suppressor (TiDG) nominal level, but it had slightly higher concentration of Isopar<sup>TM</sup>L (101%) relative to the standard. The MaxCalix concentration was at 96% of its nominal level. The TiDG, MaxCalix, modifier, and Isopar<sup>TM</sup>L amounts are expected to trend downward with time but at different rates. Based on the June sample, the solvent did not require any further trim addition. Long fatty acid and N-nitrosodiocetylamine were detected in these samples. Nitrosoamine has been observed in supernate samples.

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 component concentrations in the solvent.

### **4.0 Conclusions**

A trend summary of four SHT monthly samples; MCU-16-122-124 (March 2017), MCU-17-130-132 (April 2017), MCU-17-133-135 (May 2017), and MCU-17-141-149 (June 2017) are reported. Analyses of the June SHT sample (MCU-17-141-149) indicated that the modifier (CS-7SB) and the extractant (MaxCalix) concentrations were slightly below (4% each) their nominal recommended levels (169,000 mg/L and 46,400 mg/L respectively). The suppressor (TiDG) level has decreased since the January 2017 measurement but has remained steady in the range of 666 to 705 mg/L, well above the minimum recommended level (479 mg/L), but below the nominal level. The “flat” trends observed in the TiDG, MaxCalix, modifier, and Gamma measurement are consistent with the solvent being idle since January 10, 2017.

This analysis confirms the Isopar<sup>TM</sup> addition to the solvent on January 18, 2017. This analysis also indicates the solvent did not require further additions. 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.

From 20 to 190 ppm of long fatty acid (docosanoic and 3-methyltritracontane), dioctylformamide, and n-nitroso-di-n-octylamine were found in the March, May and June solvent samples by the SVOA but further analysis with independent methods are needed to confirm these chemicals. The impurities levels were lower in the June sample and this is possibly due to the additional caustic wash the solvent received prior to sampling the June samples. No impurities were observed in the HNMR. Another impurity observed in the samples was mercury. Based on the June SHT sample, up to  $30 \pm 6$  micrograms of mercury per mL of solvent was detected (the average of the CV-AA and XRF methods). The higher mercury concentration in the solvent (as determined in the last three monthly samples) is possibly due to the higher mercury concentration in Salt Batches 8 and 9 (Tank 49H) or sampling of previously undisturbed areas of high mercury concentration in Tank 49H.

The gamma level ( $\sim 0.18\text{E}5$  dpm/mL) measured in the March, April, May, and June SHT samples were one order of magnitude lower than the gamma levels observed in the December and January SHT samples. The gamma level is consistent with the solvent being idle (since January 10, 2017). The gamma levels observed in the March, April, May, and June SHT samples had been observed before and are consistent with previous monthly measurements where there was no process at Modular Caustic-Side Solvent Extraction (MCU).

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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- <sup>1</sup> W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.
- <sup>2</sup> F. Fondeur, “Solvent Hold Tank Sample Results for MCU-17-122/123/124: March 2017 Monthly Sample”, SRNL-L3100-2017-00046, Rev. 0, May 2017.
- <sup>3</sup> F. F. Fondeur, “Solvent Hold Tank Sample Results for MCU-17-130/131/132: April 2017 Monthly Sample” SRNL-L3100-2017-00063, Rev. 0, May 2017.
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**Distribution:**

A. P. Fellingner, 773-43A  
T. B. Brown, 773-A  
M. E. Cercy, 773-42A  
D. A. Crowley, 773-43A  
D. E. Dooley, 773-A  
S. D. Fink, 773-A  
C. C. Herman, 773-A  
E. N. Hoffman, 999-W  
B. B. Looney, 773-42A  
F. M. Pennebaker, 773-42A  
G. N. Smoland, 773-42A  
A. L. Washington, 773-42A  
W. R. Wilmarth, 773-A  
B. J. Wiedenman, 773-42A  
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E. A. Brass, 241-121H  
J. P. Schwenker, 704-56H  
A. G. Garrison, 241-121H  
V. X. Jain, 766-H  
C. M. Santos, 241-152H  
P. E. Fogelman, 241-121H  
K. M. Marra, 241-120H  
B. A. Gifford, 704-56H  
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C. A. Nash, 773-42A  
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