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# Solvent Hold Tank Sample Results for MCU-16-934-935-936: June 2016 Monthly Sample

F. F. Fondeur

D. H. Jones

August 2016

SRNL-STI-2016-00441, Revision 0



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D. H. Jones

August 2016

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## EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-16-934-935-936), pulled on 07/01/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-934-935-936 indicated the Isopar<sup>TM</sup>L concentration is above its nominal level (101%). The modifier (CS-7SB) and the TiDG concentrations are 8% and 29 % below their nominal concentrations. This analysis confirms the solvent may require the addition of TiDG, and possibly of modifier. 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.

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  $21.1 \pm 4$  micrograms of mercury per gram of solvent (or 17.5  $\mu\text{g/mL}$ ) was detected in this sample (as determined by the XRF method of undigested sample). 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 8 (Tank 49H).

The current gamma level (1.41E5 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   |
| 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 July 1 2016, Operations personnel pulled and delivered three samples from the SHT (MCU-16-934, MCU-16-935, and MCU-16-936) 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 (September 2015) 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>       |
|--|-------------------|
| February solvent trim added to MCU                         | February 22, 2015 |
| SHT sample MCU-15-389-390                                  | February 25, 2015 |
| SHT sample MCU-15-439-440-441                              | February 28, 2015 |
| 10 gallons of Isopar <sup>TM</sup> L added to MCU          | March 6, 2015     |
| 9 gallons of Isopar <sup>TM</sup> L added to MCU           | March 13, 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 <sup>TM</sup> 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   |
| November solvent trim added to MCU                         | November 28, 2015 |
| SHT sample MCU-15-815-816-817-818-819-820                  | November 29, 2015 |
| 14 gallons of Isopar <sup>TM</sup> L added to MCU          | December 21, 2015 |
| SHT sample MCU-15-914-915-916                              | December 22, 2015 |
| 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-16-934-935-936                              | June 30, 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-16-934, MCU-16-935, and MCU-16-936 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>**

| 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 <sup>TM</sup> 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

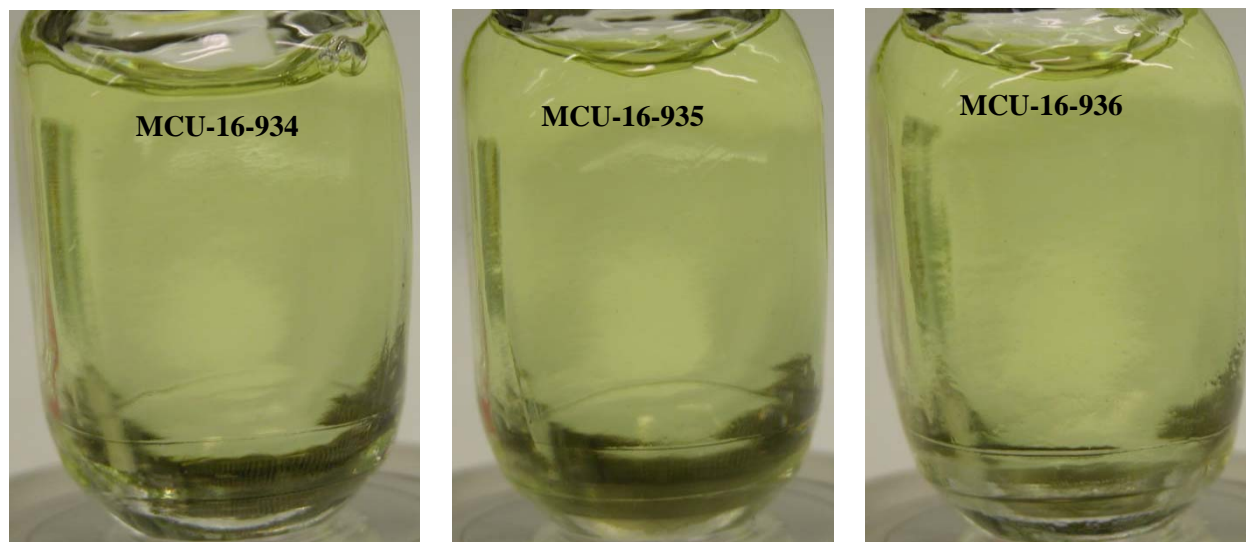
Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

## 3.0 Results and Discussion

Each sample (MCU-16-934, MCU-16-935, and MCU-16-936) was visually examined. No immiscible phases or debris or foam were observed. 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-16-934-935-936). Table 3-1 contains the results for the MCU-16-934-935-936 composite sample.

### *Isopar<sup>TM</sup> L and Modifier Levels*

Triplicate density measurements of the sample gave an arithmetic average result of 0.8318 g/mL (0.03% RSD) (or 0.8289 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula)<sup>4</sup> for MCU-16-934-935-936 at 21.5 °C. The calculated density (0.829 g/mL) for MCU-16-934-935-936 is about 1% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory).<sup>2</sup> Using the density as a starting point, we know that the concentration level of the Isopar<sup>TM</sup>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.



**Figure 1. Typical appearance of the three MCU-16-934, MCU-16-935, and MCU-16-936**

An examination of Table 3-1 shows that the Isopar™ L concentration is above its nominal value (~ 1%) while the modifier concentration is correspondingly slightly lower (8% lower) than its nominal value. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement. The last solvent trim addition to MCU was on June 15, 2016.

All measurements indicate the Isopar™ 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 up as a result of the trim addition made on June 15, 2016. The rise in modifier concentration was slower than that observed after the February and December 2015 solvent trim additions. 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 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  $0.827 \pm 0.019$  g/mL. Their sum is consistent with the measured and temperature corrected (to 25 °C) value of 0.829 g/mL, and also with the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL). With a lower modifier concentration, the solvent chemical properties are similar to that of Isopar™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.

**Table 3-1 Sample Results for MCU-16-934-935-936**

| Analysis              | Method             | LW-AD-Proj-160412-4 | Result (mg/L) <sup>#</sup> | Nominal* Result (mg/L) | % of (Result ÷ Nominal Result) |
|-----------------------|--------------------|---------------------|----------------------------|------------------------|--------------------------------|
| Isopar <sup>®</sup> L | FT-HNMR            | NA                  | 6.30E+05                   | 6.23E+05               | 101                            |
| Isopar <sup>®</sup> L | FT-IR              | NA                  | 6.30E+05                   |                        | 101                            |
| Isopar <sup>®</sup> L | Density            | NA                  | 6.26E+05                   |                        | 100                            |
| Average <sup>§</sup>  | All                | NA                  | 6.26E+05                   | 6.23E+05               | 101                            |
| Modifier              | HPLC               | LW2079              | 1.54E+05                   | 1.69E+05               | 91                             |
| Modifier              | FT-HNMR            | NA                  | 1.55E+05                   |                        | 92                             |
| Modifier              | FT-IR              | NA                  | 1.54E+05                   |                        | 91                             |
| Modifier              | Density            | NA                  | 1.55E+05                   |                        | 92                             |
| Average <sup>§</sup>  | All                | NA                  | 1.55E+05                   | 1.69E+05               | 92                             |
| TiDG                  | SVOA-Titration*    | NA                  | 1.02E+03                   | 1.44E+03               | 71                             |
| TiDG*                 | Titration          | NA                  | 1.01E+03                   | 1.44E+03               | 70                             |
| Average <sup>§</sup>  | All                | NA                  | 1.02E+03                   | 1.44E+03               | 71                             |
| trioctylamine         | SVOA               | LW2078              | 1.60E+03                   | 5.30E+02               | 30                             |
| trioctylamine         | Titration          | NA                  | 1.63E+02                   | 5.30E+02               | 31                             |
| Average <sup>§</sup>  | All                | NA                  | 1.62E+02                   | 5.30E+02               | 31                             |
| MaxCalix              | HPLC               | LW2079              | 4.21E+04                   | 4.44E+04               | 95                             |
| MaxCalix              | FT-HNMR            | NA                  | 4.29E+04                   |                        | 97                             |
| Average <sup>§</sup>  | All                | NA                  | 4.24E+04                   | 4.44E+04               | 95                             |
| BOBCalixC6            | HPLC               | LW2079              | 1.40E+03                   | 4.03E+03               | 35                             |
| Average <sup>§</sup>  | All                | NA                  | 1.40E+03                   | 4.03E+03               | 35                             |
| Density (g/mL)        | Direct Measurement | NA                  | 0.8289                     | 0.835                  | 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.

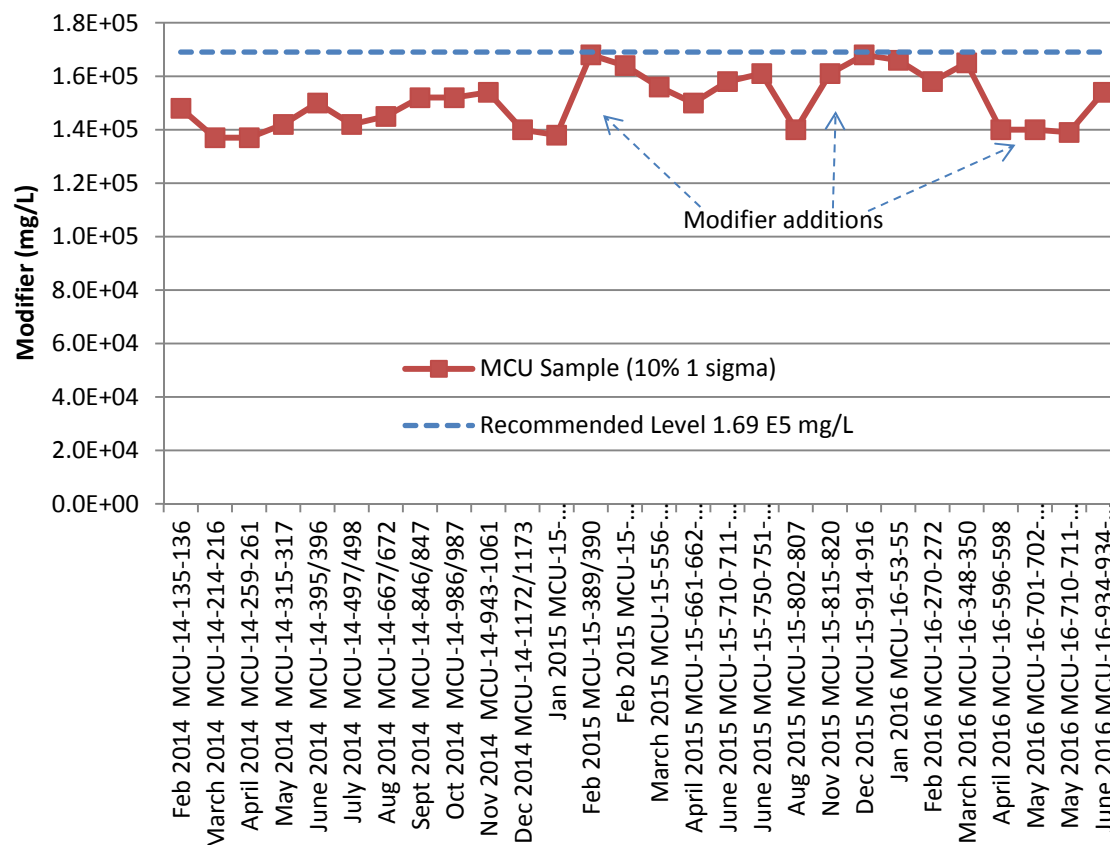
\* Nominal value is the expected value for freshly prepared blended solvent with a target density of 0.8352 g/mL at 25 °C.

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

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

\* No TiDG value was estimated by FT-HNMR due to an aged (questionable) standard.

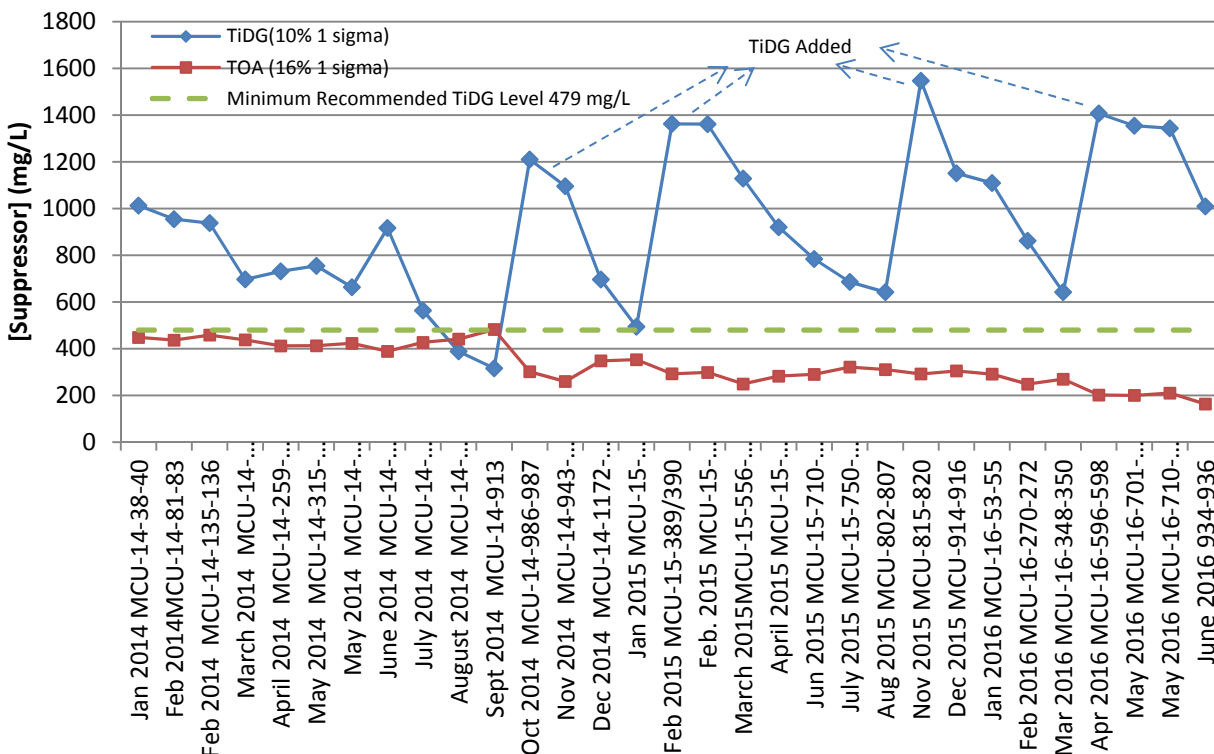
\* Trioctylamine obtained from the SVOA method was subtracted from the measured total base in the titration method to obtain a calculated TiDG concentration.



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

### *Suppressors Levels*

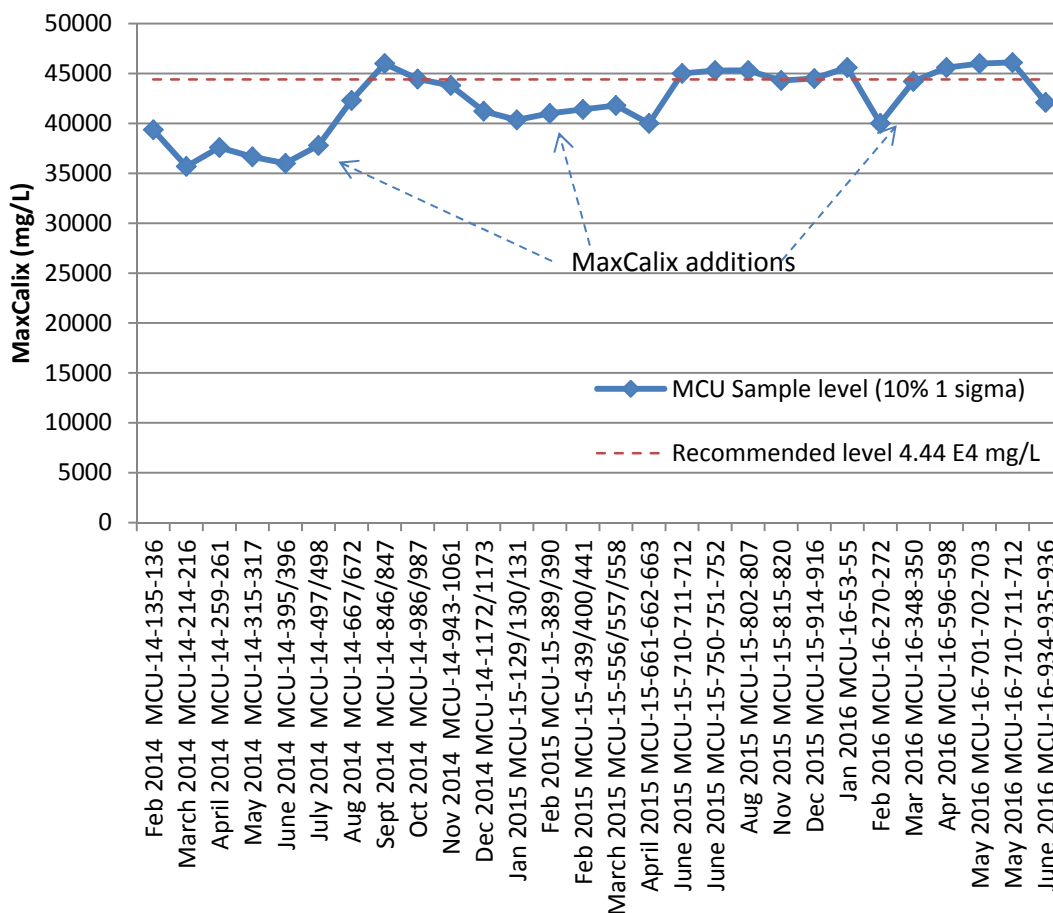
The average TiDG concentration level ( $1.02 \pm 1.54 \text{ E3 mg/L}$ ) is at 71 % of its nominal value of 1440 mg/L confirming the continued depletion of the trim addition to the solvent done in April 29, 2016 (a noticeable spike in the TiDG concentration level was observed in Fig. 3 in the April 2016 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 June monthly sample (compared to the May monthly sample) is due to the higher processing rate of salt solution in June at MCU. 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-16-934-935-936 was collected. Inferring from past TiDG concentration level trends (see Fig. 3) and in the absence of new additions or new removal mechanisms (and assuming continuous steady operation), the TiDG concentration is expected to drop and reach the minimum recommended level sometime in August 2016. This drop is due to the combined effect of a chemical decomposition (reaction with caustic water) and phase transfer to the aqueous phases (salt solution and boric acid). The TOA concentration appears to trend downwards and it is currently at  $163 \pm 33 \text{ mg/L}$  (in the previous sample the TOA level was at 210 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 4.24E4 mg/L ( $\pm 10\%$ ) and it is at its nominal value. The sudden drop in the MaxCalix concentration is probably due to analytical variance and not that the solubility limit was reached (see Figure 4). However, if another “sudden” drop in the MaxCalix level is observed after a solvent trim addition, further inquiry 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). The current MaxCalix concentration level is consistent with its historical trend (Fig. 4). The residual concentration of BOBCalixC6 level is currently at 35% of the level measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). Since no BOBCalixC6 is added to the SHT, the BOBCalixC6 level is expected to decrease with time.

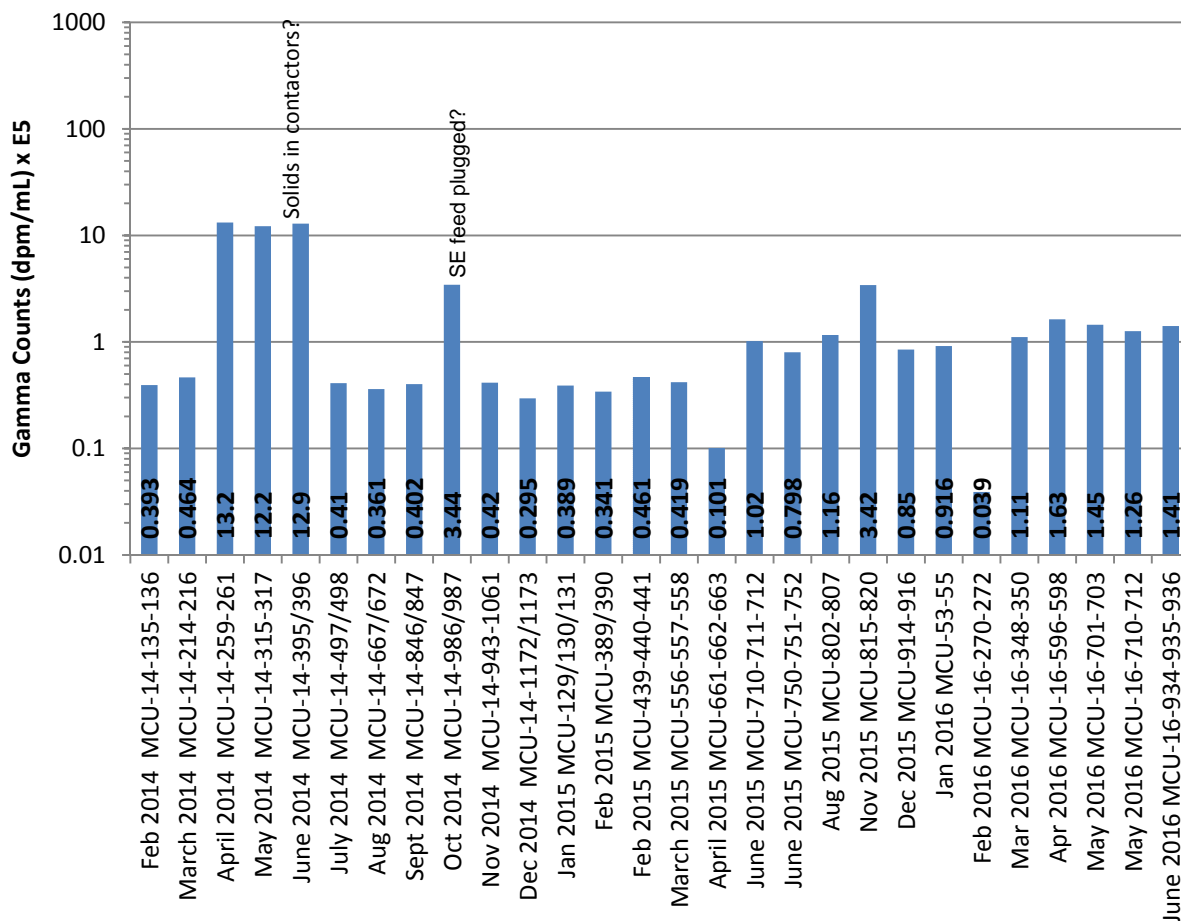


**Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).**

#### *Gamma Level*

The gamma measurement of MCU-16-934-935-936 is 1.41E5 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%.**

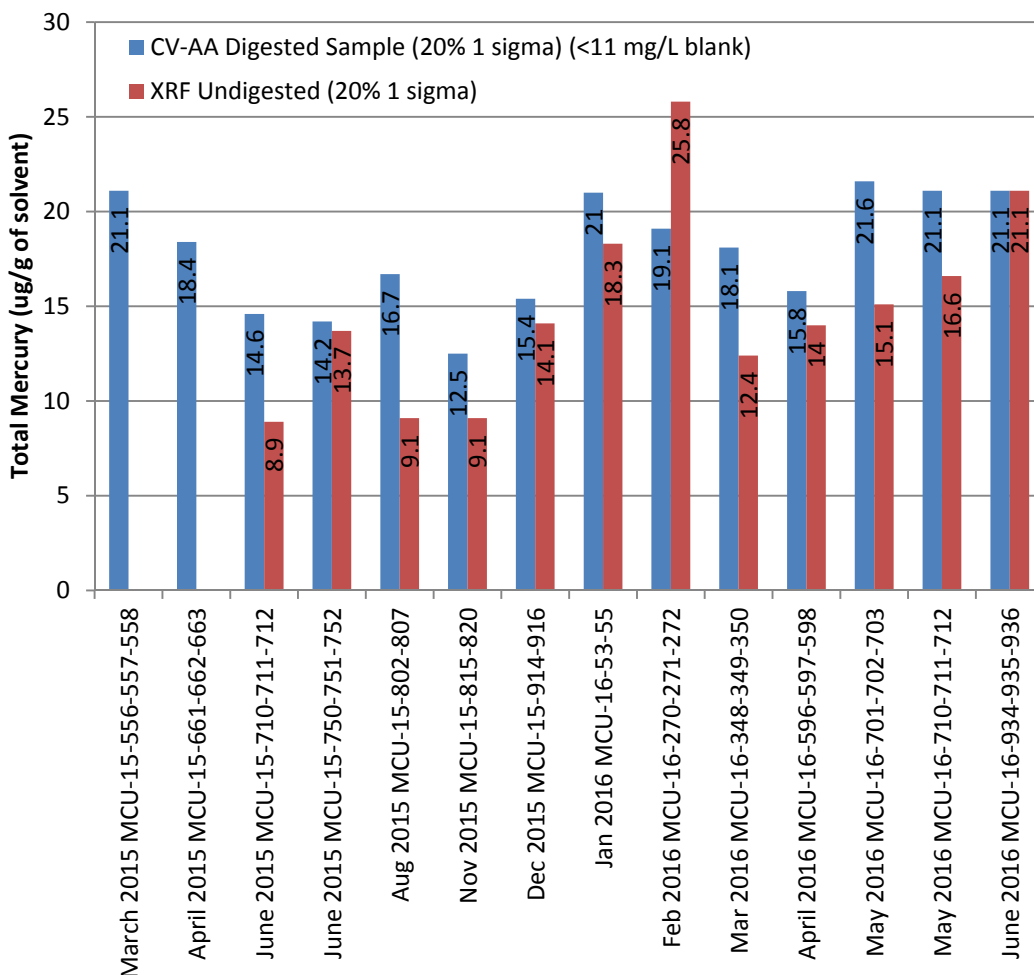
### Impurities

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-16-934-935-936 was digested and analyzed for total mercury by the CVAA method. The CV-AA method detected  $21.1 \pm 4.2 \text{ ug/g}_{\text{solvent}}$  of mercury. The XRF method also detected a concentration of  $21.1 \pm 4.2 \text{ ug/g}_{\text{solvent}}$  of mercury (or  $17.5 \text{ ug/mL}_{\text{solvent}}$  at  $25^\circ\text{C}$ ) of the undigested MCU-16-934-935-936 sample.

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  $0.8289 \text{ g/mL}$ , the solvent could contain a total of  $14 \pm 2 \text{ g}$  of mercury. 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 8 (Tank 49H).



**Figure 6. Total mercury in recent SHT samples. One standard deviation 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 (92% of its nominal concentration) and TiDG (71%) levels, but it has slightly higher levels of Isopar™ (101%) relative to the standard. The lower MaxCalix concentration is 95% of its nominal level. The TiDG, MaxCalix, modifier, and Isopar™ levels are expected to trend downward with time. 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 and trimming additions to the solvent. Based on the June sample results, there is no need to add MaxCalix to the solvent at this time. In the case of gross bacteria particulates in the solvent that most likely come from the strip acid solution, filtration of the strip acid is recommended before it contacts the solvent.

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-16-934-935-936), pulled on 07/01/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-934-935-936 indicated the Isopar<sup>TM</sup>L concentration is above its nominal level (101%). The modifier (CS-7SB) and the TiDG concentrations are 8% and 29 % below their nominal concentrations. This analysis confirms the solvent may require the addition of TiDG, and possibly of modifier. 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.

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  $21.1 \pm 4$  micrograms of mercury per gram of solvent (or 17.5  $\mu\text{g/mL}$ ) was detected in this sample (as determined by the XRF method of undigested sample). 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 8 (Tank 49H).

The current gamma level (1.41E5 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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