**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

# Solvent Hold Tank Sample Results for MCU-18-425-427 (October 2018), MCU-18-459-460-461 (November 2018), and MCU-18-487-488-489 (December 2018): Quarterly Report

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July 2019

SRNL-STI-2019-00233, Revision 0

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**Prepared for**
**U.S. Department of Energy**

**Keywords:** *MCU, ARP, ISDP, NGS*

**Retention:** *Permanent*

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory®

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# EXECUTIVE SUMMARY

A trend summary of three Solvent Hold Tank (SHT) monthly samples MCU-18-425-426-427, MCU-18-459-460-461 and MCU-18-487-488-489 are reported. Most of the conclusions are based on the December SHT sample (MCU-18-487-488-489). Analyses of the December SHT sample (MCU-18-487-488-489 indicated that the Modifier (Cs-7SB) and the extractant (MaxCalix) concentrations were below their nominal recommended concentrations (169,000 mg/L and 46,400 mg/L respectively) by 2% and 9% respectively. The suppressor (*N,N',N"*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has decreased since the October 2018 measurement (Modular Caustic-Side Solvent Extraction Unit or MCU resumed processing (from May through November 2018) to 528 mg/L, but it is above the minimum recommended concentration (479 mg/L). These new levels are consistent with the concentrations observed when MCU was fully operational in 2016.

The Semi-Volatile Organic Analysis (SVOA) did not detect any impurities. However, the Fourier Transform Hydrogen Nuclear Magnetic Resonance (FT-HNMR) analysis detected presence of phthalates at a few ppm. The impurity concentration was highest in the October sample and consistently detected in the November and December samples (but always a few ppm or less). Another impurity observed in the samples was mercury. Based on the December SHT sample, up to 24 ± 5 micrograms of mercury per mL of solvent was detected (as the average of the Direct Mercury Analysis (DMA) and X-Ray Fluorescence (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 9 and 10.

The gamma concentration (~3.6E5 dpm/mL) measured in the December SHT samples was consistent with previous values observed when MCU was fully operational (for example, between December 2016 and January 2017) but it was lower than the April SHT measurement. The "dip" in the gamma measurement for the May 2018 SHT sample was due to an Isopar™ L addition to MCU during April and May 2018.

The laboratory will continue to monitor the quality of the solvent for any new impurities or degradation of the solvent components.

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| | |
|---|---|
| BOBCalixC6 | Calix[4]arene-bis(*tert*-octylbenzo-crown-6) |
| CSSX | Caustic-Side Solvent Extraction |
| CVAA | Cold Vapor Atomic Absorption |
| DMA | Direct Mercury Analysis |
| FT-HNMR | Fourier Transform Hydrogen Nuclear Magnetic Resonance |
| HNMR | Hydrogen Nuclear Magnetic Resonance |
| HPLC | High Performance Liquid Chromatography |
| 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 |
| 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, 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 calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalixC6) and trioctylamine (TOA). For process monitoring, SHT samples are sent to Savannah River National Laboratory (SRNL) to examine solvent composition changes over time.[1] 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 three SHT samples: MCU-18-425-426-427, MCU-18-459-460-461, and MCU-18-487-488-489. A summary report for each of the SHT samples was issued earlier.[2,3,4] This report examines the cumulative results from these and several past monthly reports.

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 of the composition that approximates the blend of cocktail[5] and heel solvent – was prepared in the lab (May 2018) and used for comparison and evaluation. The results from the analyses are presented in this document.

## 2.0 Experimental Procedure

### 2.1 Experimental Procedure

Table 2-1 lists a summary of relevant and recent trims to the MCU solvent as well as the arrival date of the samples currently being studied. On November 9, 2018, an Isopar™ L addition was made to MCU.[6]

**Table 2-1 Log of trims to MCU solvent since 2018 and SHT sampling dates**

| Event | Date |
|---|---|
| SHT sample MCU-18-1-2-3 | January 10, 2018 |
| SHT sample MCU-18-18-19-20 | February 22, 2018 |
| SHT sample MCU-18-108-109-110 | March 19, 2018 |
| SHT sample MCU-18-123-124-125 | April 23, 2018 |
| 15 gallons Isopar™ L added to MCU | April 28, 2018 |
| 10 gallons Isopar™ L added to MCU | May 14, 2018 |
| SHT sample MCU-18-135-136-137 | May 21, 2018 |
| SHT sample MCU-18-192-193-194-195-196-197 | June 18, 2018 |
| 14 gallons Isopar™ L added to MCU | July 2, 2018 |
| SHT sample MCU-18-301-302-303 | July 14, 2018 |
| 13 gallons Isopar™ L added to MCU | August 9, 2018 |
| SHT sample MCU-18-357-359-360 | August 20, 2018 |
| SHT sample MCU-18-402-403-404-405-406-407-409-410 | September 18, 2018 |
| 21 gallons of solvent trim added to MCU | October 24, 2018 |
| SHT sample MCU-18-425-426-427 | October 25, 2018 |
| 11 gallons Isopar™L added to MCU | October 31, 2018 |
| 13 gallons Isopar™ L added to MCU | November 9, 2018 |
| SHT sample MCU-18-459-460-461 | November 20, 2018 |
| SHT sample MCU-18-487-488-489 | December 11, 2018 |

Samples shown in Table 2-1 were received in P-nut vials containing ~10 mL each (see Figure 1). Once taken into a radioactive hood, the samples were visually inspected and analyzed for pH. Contents of the P-nut vials for each monthly SHT sample were composited before use. Aliquots of the composited sample were removed to perform the following analyses: density, SVOA, HPLC, titration for TiDG, gamma counting, DMA, XRF, and FT-HNMR. Results from analytical measurements were compared with the theoretical values shown in Table 2-2. Please note that the SVOA, HPLC, XRF, DMA, density, titration for TiDG, and FT-HNMR results for each SHT sample are shown in the respective monthly reports. All reported values were checked against the values obtained from a Scratch solvent made in May 2018. All error bars represent one-sigma (one standard deviation). In the case of the physical measurements (density, surface tension, and viscosity measurements), the one-sigma was obtained from three replicates (observations). Suppressor concentration derived from titration was performed three times. Except for the data from the HPLC, FT-HNMR, and Gamma counting where one observation was made, the one-sigma from the DMA measurement was obtained from duplicate observations (replicates). Therefore, the error bars shown in this report are the variations within replicates (or fidelity of the analytical measurements).

**Table 2-2 Nominal concentrations of the relevant components in NGS Blend at 25 °C (Ref. 5)**

| 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 | ~1,440♥ | ~ 0.003 |
| Isopar™ 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 an NGS-CSSX blend formulation.

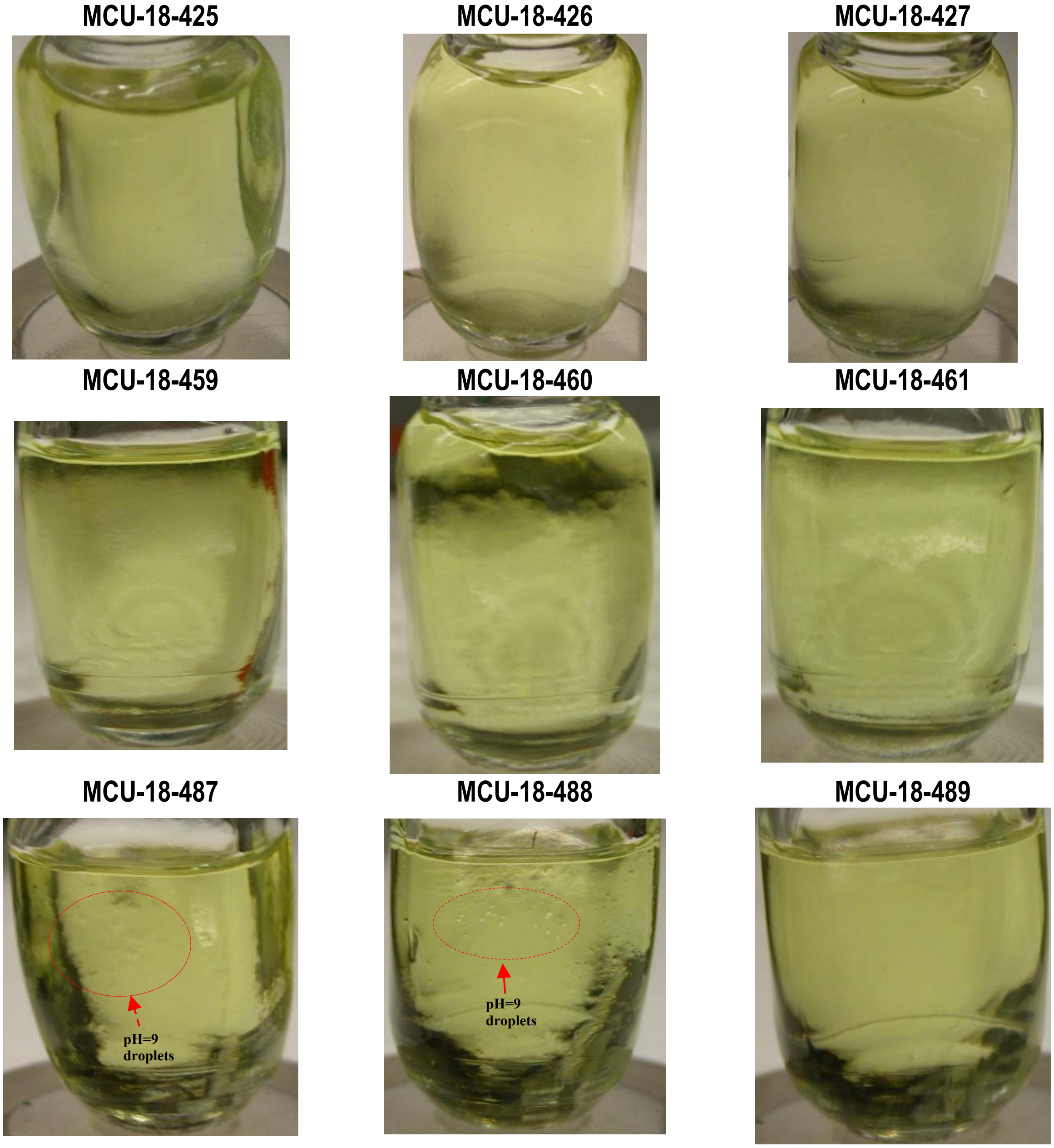
♥Assuming a molecular weight for caustic-washed TiDG of 479 g/mol (516 g/mol for TiDG*HCl).

2.2 Quality Assurance

This work was performed under the following production support request: Q. L. Nguyen, “Analyzing MCU Routine Samples” TTR-H-00026, Rev. 0 July 2013. The recorded data, analysis, and conclusions satisfied the requirements listed in T.B. Peters, A.L. Washington, II, and F. F. Fondeur, “Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU,” SRNL-RP-2013-00536, Rev. 2, January 2019. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60 (design check requirements). 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 floating debris or foam were observed (see Fig. 1). However, the side walls of the P-nut vials MCU-18-487 and MCU-18-488 showed adsorbed droplets with a pH value of 9. SRNL believes these caustic droplets are evidence that the solvent contacted a caustic solution which is consistent with the caustic wash step of the solvent at MCU. All solvent samples had a pH value of 5.5. No unusual reactions, solids, foaming, or immiscible layers were observed after combining the samples into one Teflon container for each set of monthly SHT samples.


MCU-18-425 MCU-18-426 MCU-18-427

MCU-18-459 MCU-18-460 MCU-18-461

MCU-18-487 MCU-18-488 MCU-18-489

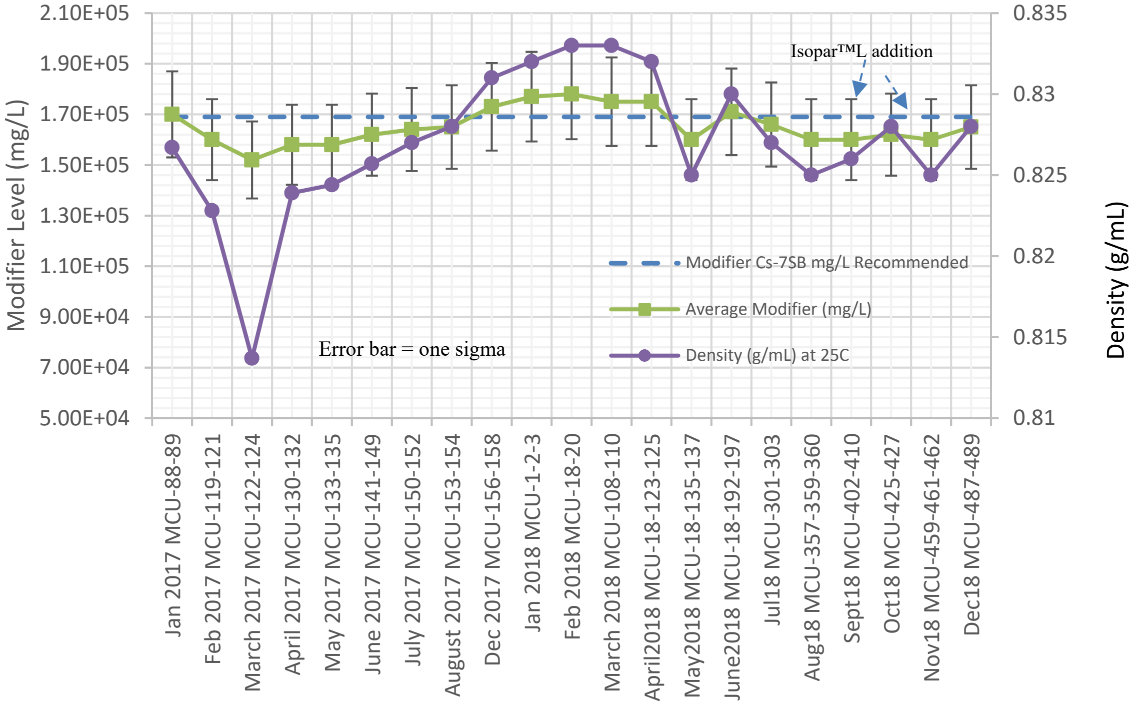
**Figure 1 A picture of samples MCU-18-425-427 (top), MCU-18-459-461 (middle), and MCU-18-487-489 (bottom).**

*Modifier Concentrations and Density Measurements*

MCU resumed operations in May 2018 (after suspending operations in January 2017) and since then, four Isopar™L additions and one trim addition were made to the solvent. Based on the October-November-December results, both the density measurements and the Modifier concentration levels were steady (flat) and the corresponding error intervals included the nominal (0.830 mg/L at 25 °C in the case of the density measurement) and/or recommended value (in the case of the Modifier, the recommended level is 1.69E5 mg/L) [see Fig. 2 and the tabulated data in Appendix A]. [2,4] The reported density measurements were obtained from triplicate measurements of the sample (the density was measured by the vibrations of an especially calibrated tube filled with the organic liquid and corrected for temperature using the CSSX temperature correction formula).[7] The uncertainty (one sigma) by this method is 3%. Unlike the gravimetric measurement that uses calibrated 2 mL flasks (for limited samples) where manufacturing errors of the flask's geometry such as camber, concentricity, roundness, cylindricity, and thick marked lines for visual detection of the meniscus raised the measurement error to 9% (excluding human error). And after comparing the density of several SHT samples by the two methods and determined no statistical difference between the two methods, the more precise density measuring method is reported.

The slightly fluctuating values observed in the density (and also in the Modifier concentration) for the October-November-December samples relative to the same measurements done earlier in 2018 are likely due to aliasing between the monthly samples and the monthly additions to the solvent. However, the observed density and Modifier values from the October-November-December samples were consistent with previous measurements when MCU was fully operational (for example in 2016). Both the density data and the Modifier concentration correlated strongly with each other as expected (see Fig. 2).[7] Statistically, there were no differences between the values reported by HPLC and FT-HNMR (see Fig. 3, Fig.4, and Table 3-1). In Table 3-1, the symbol "t" stands for the ratio of the difference between the means estimated from two samples (or sample means versus a hypothetical mean) and the t-weighted standard pooled error (t values comes from a statistical table for t-values ranked by the degree of freedoms of the sample). The symbol "T" is the critical t-value obtained from t-values statistical for the degrees of freedom of the sample measurements. The Isopar™ L concentration (not shown) in the December sample was similar to that of the baseline solvent (scratch made on May 2018). This finding is expected since the solvent density is a volume-weighed linear combination of the Modifier and Isopar™ L densities. Other physical measurements of the October, November, and December SHT samples such as viscosity and surface tension were similar to the baseline solvent measurements (see Fig. 5 and Fig. 6). However, a bias was detected in the surface tension measurements of the SHT samples relative to the control scratch.

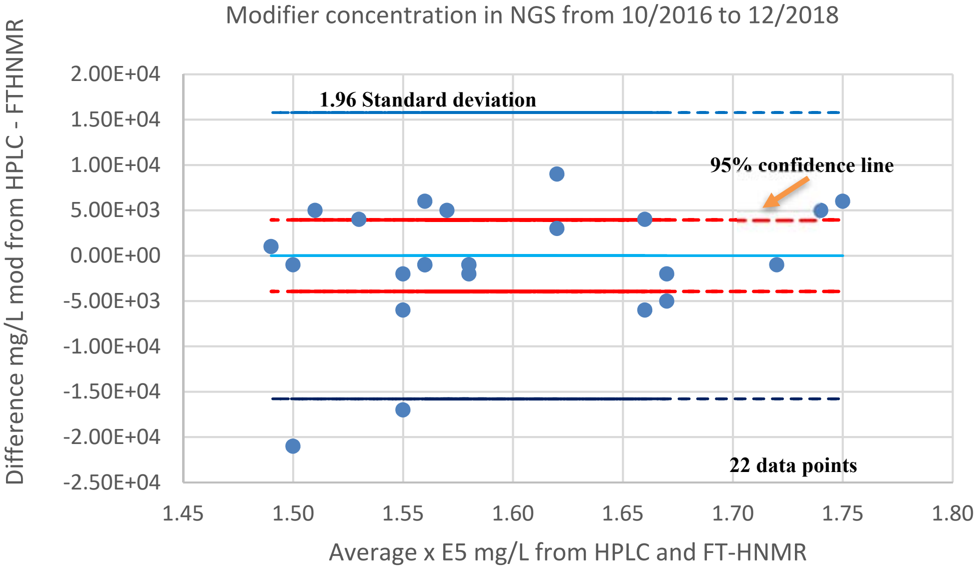
All measurements indicate (based on the October, November, and December samples) that the Isopar™ L concentration was at its nominal value. Isopar™ L is added to the solvent more frequently (compared to the modifier) to compensate for its high evaporation rate.



Isopar™L addition

Error bar = one sigma

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



Modifier concentration in NGS from 10/2016 to 12/2018

1.96 Standard deviation

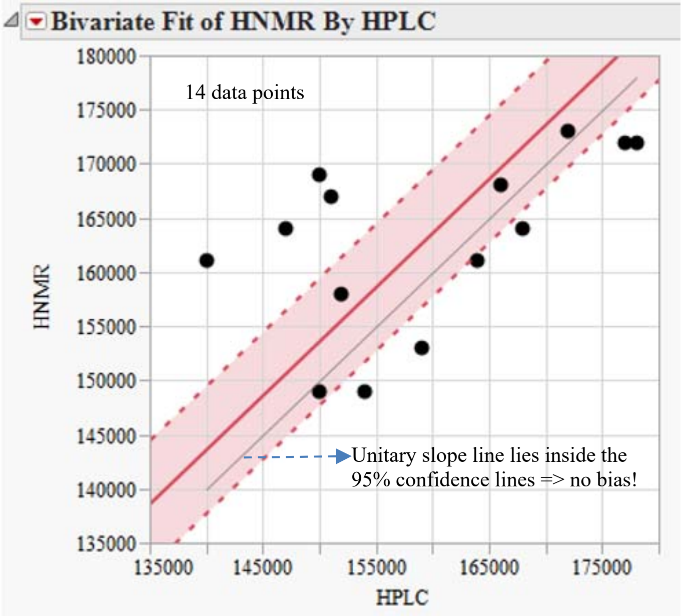
95% confidence line

22 data points

**Figure 3. A comparison of the HPLC and FT-HNMR methods for measuring the Modifier.**

**Table 3-1 t-Test: Paired Two Sample for Means (HPLC versus FT-HNMR)**

| *Parameter* | *HPLC* | *FT-HNMR* |
|---|---|---|
| Mean (mg/L) | 1.58E5 | 1.61E5 |
| Variance | 9E7 | 6E7 |
| Observations | 23 | 23 |
| Pearson Correlation | 0.56 | |
| Hypothesized Mean Difference | 0 | |
| df | 22 | |
| t Stat | -1.71 | |
| P(T<=t) one-tail (< 0.05) | 0.051 → | Not significant |
| t Critical one-tail | 1.72 | |
| P(T<=t) two-tail (<0.05) | 0.102 → | Not significant |
| t Critical two-tail | 2.074 | |



14 data points

Unitary slope line lies inside the 95% confidence lines => no bias!

**Figure 4. A regression fit between the FT-HNMR and HPLC data for the Modifier. Also shown the 95% confidence lines (broken lines). The unitary slope line is also shown and lies inside the confidence line.**

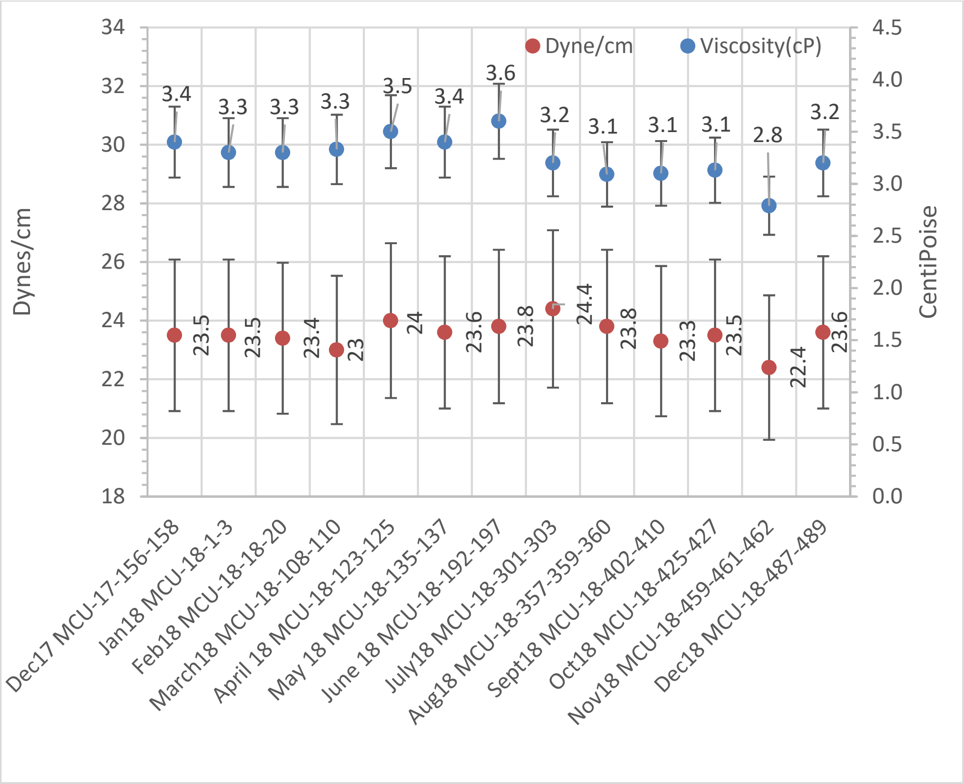
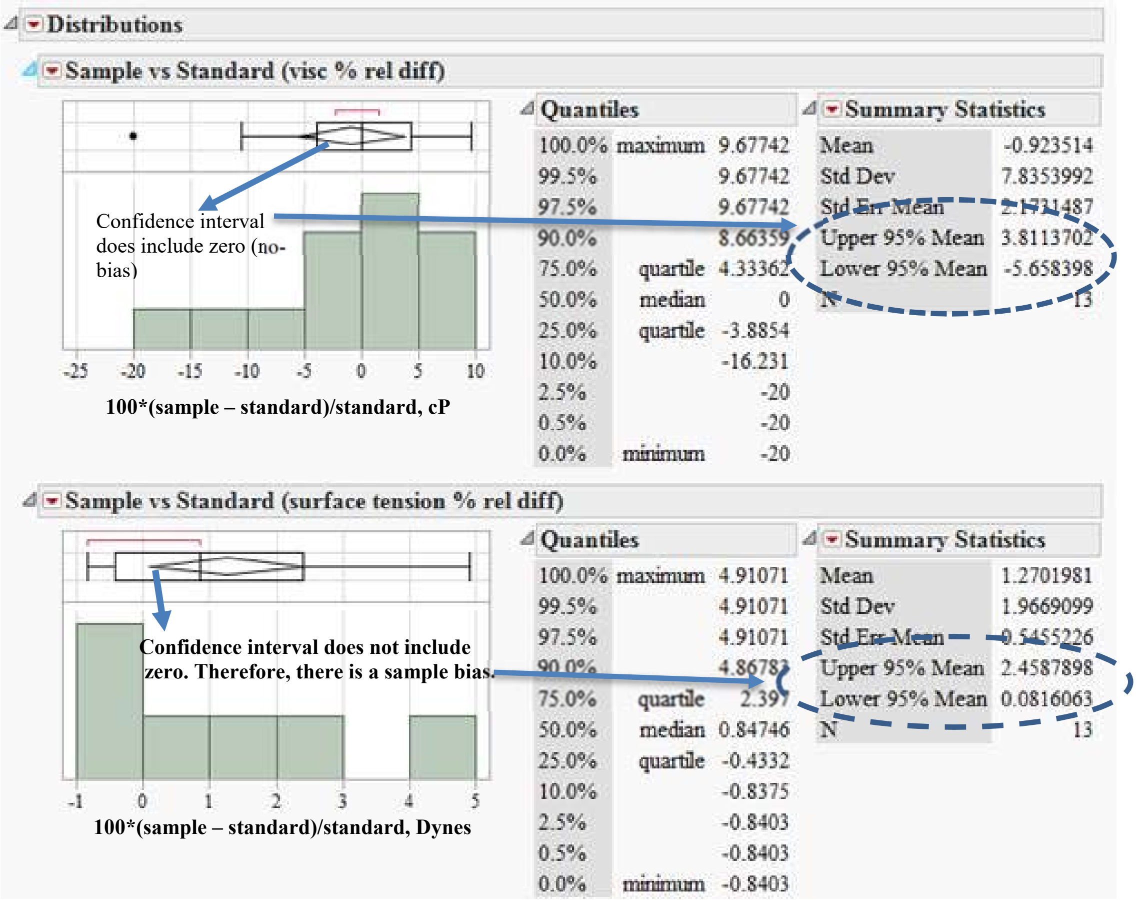


**Figure 5. Viscosity and surface tension measurements of the last 10 SHT samples. The scratch blend measured a viscosity of 3 ± 0.3 cP and a surface tension of 23 ± 0.6 dynes/cm (at 25˚C).**



**Distributions**

**Sample vs Standard (visc % rel diff)**

Confidence interval does include zero (no-bias)

**Quantiles**

| | | |
|---|---|---|
| 100.0% | maximum | 9.67742 |
| 99.5% | | 9.67742 |
| 97.5% | | 9.67742 |
| 90.0% | | 8.66359 |
| 75.0% | quartile | 4.33362 |
| 50.0% | median | 0 |
| 25.0% | quartile | -3.8854 |
| 10.0% | | -16.231 |
| 2.5% | | -20 |
| 0.5% | | -20 |
| 0.0% | minimum | -20 |

**Summary Statistics**

| | |
|---|---|
| Mean | -0.923514 |
| Std Dev | 7.8353992 |
| Std Err Mean | 2.1731487 |
| Upper 95% Mean | 3.8113702 |
| Lower 95% Mean | -5.658398 |
| N | 13 |

**Sample vs Standard (surface tension % rel diff)**

**Confidence interval does not include zero. Therefore, there is a sample bias.**

**Quantiles**

| | | |
|---|---|---|
| 100.0% | maximum | 4.91071 |
| 99.5% | | 4.91071 |
| 97.5% | | 4.91071 |
| 90.0% | | 4.86783 |
| 75.0% | quartile | 2.397 |
| 50.0% | median | 0.84746 |
| 25.0% | quartile | -0.4332 |
| 10.0% | | -0.8375 |
| 2.5% | | -0.8403 |
| 0.5% | | -0.8403 |
| 0.0% | minimum | -0.8403 |

**Summary Statistics**

| | |
|---|---|
| Mean | 1.2701981 |
| Std Dev | 1.9669099 |
| Std Err Mean | 0.5455226 |
| Upper 95% Mean | 2.4587898 |
| Lower 95% Mean | 0.0816063 |
| N | 13 |

**Figure 6. Descriptive analysis of the relative difference (top is viscosity and the bottom is surface tension) between the SHT samples and the May 2018 scratch control sample.**

*Suppressor Concentrations*

The average TiDG concentrations for MCU-18-425-426-427, MCU-18-459-460-461, and MCU-18-487-488-489 are shown in Figure 7. As can be seen in Fig. 7, the TiDG concentration has steadily declined since MCU restarted operations in May 2018 (the April measurement was also lower probably due to Processing Runs at MCU in December 2017). The addition of TiDG to the solvent in October 2018 raised the concentration to 659 mg/L (October SHT sample). Although the October sample was obtained after trimming and mixing, the TiDG level in the October samples was still much lower than that observed after previous trims (such as Nov. 2016 and Dec 2017 in Fig. 7). Considering the November sample (550 mg/L TiDG) and the December sample (528 mg/L TiDG), the downward trend has previously been observed before (for example from July to September 2016 in Fig. 7). The mechanisms for the downward trends are unclear at this time. Based on the December SHT sample, the suppressor concentration (528 ± 53 mg/L) is above its minimum recommended operating concentration (479 mg/L for caustic washed TiDG: See the communication that set the minimum level in Appendix B). The TOA concentration appears to have remained steady and it was at 208 ± 33 mg/L. Since May 2016, the TOA level range can be estimated by 198 ± 29 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 a slower than expected degradation rate, or a slower transfer rate to the 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 ºC, 25 ºC and 36 ºC).[8] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide, and therefore difficult to distinguish.[9]

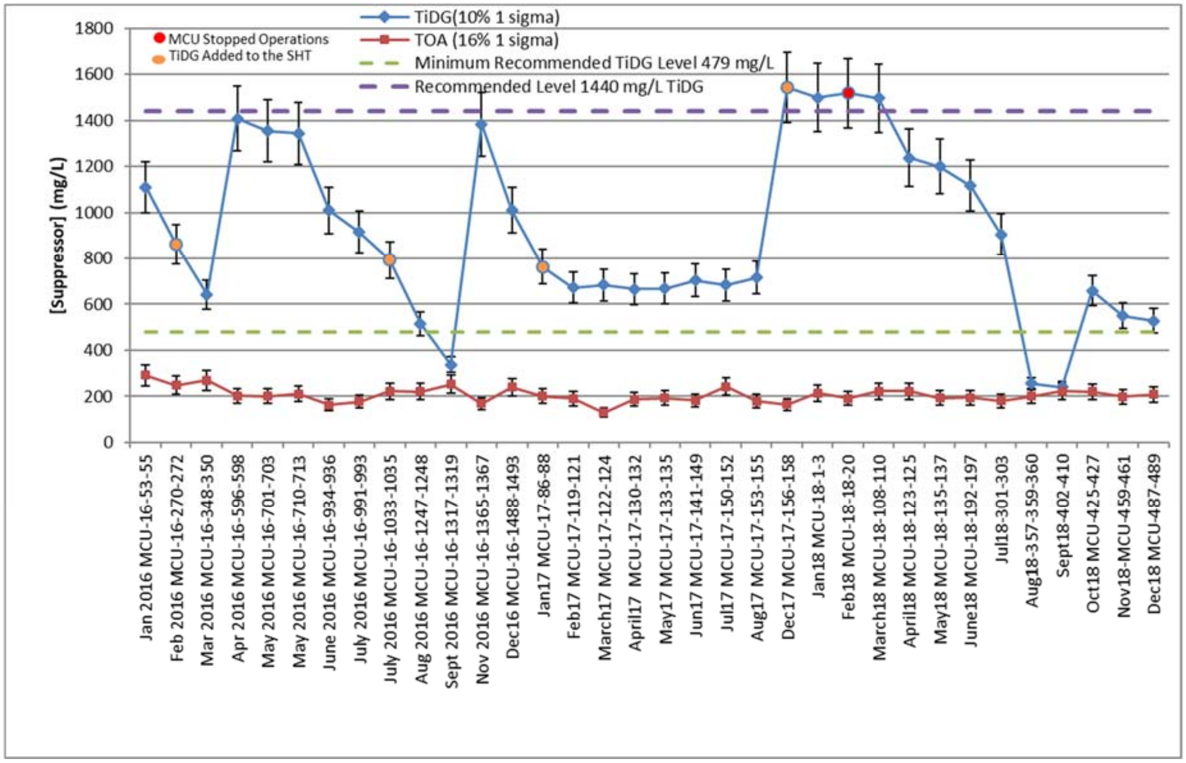


**Figure 7. Suppressor concentration as measured by titration in the SHT samples since NGS implementation. The minimum recommended concentration is 479 mg/L for TiDG.**

*Extractant Concentrations*

The calculated MaxCalix concentrations declined from 4.9E4 to 4.3E4 mg/L in the last 10 SHT samples, but the decline is not statistically significant given the 10% uncertainty (see Fig. 8). Furthermore, this apparent trend and levels have been previously observed (for example, February 2017 to February 2018) when MCU operated as expected. Note the current recommended value of 46,300 mg/L is the difference between 47,800 mg/L (50 mM MaxCalix as referred to in Table 2.2) and the BOBCalixC6 concentration in the SHT (1.30E3 mg/L in the December sample). The recent variations in the MaxCalix concentration seen in Fig. 8 (including a concentration maximum observed in the January 2018 SHT sample) is within the uncertainty range for this measurement despite the addition of MaxCalix to the solvent on December 3, 2017. The pseudo-linear trends observed in Fig. 8 correlates (correlation coefficient of 0.82) with the trends observed in the Modifier levels (see Fig. 9 for residual plots of the Modifier and MaxCalix). This indicates that the MaxCalix is lost through whole solvent carry-over into the aqueous phase.

The residual concentration of BOBCalixC6 concentration is (based on the December sample) at 26% of the concentration measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). This concentration is approximately the same concentration 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 (the standard deviation of the BOBCalixC6 concentration since January 2018 is 9.3% which is similar to the 10% method of uncertainty reported by HPLC). Since January 2018, the BOBCalixC6 concentration range can be estimated by 1.4 ± 1E3 mg/L. Given that no BOBCalixC6 is added to the solvent, the concentration is expected to decrease with time.

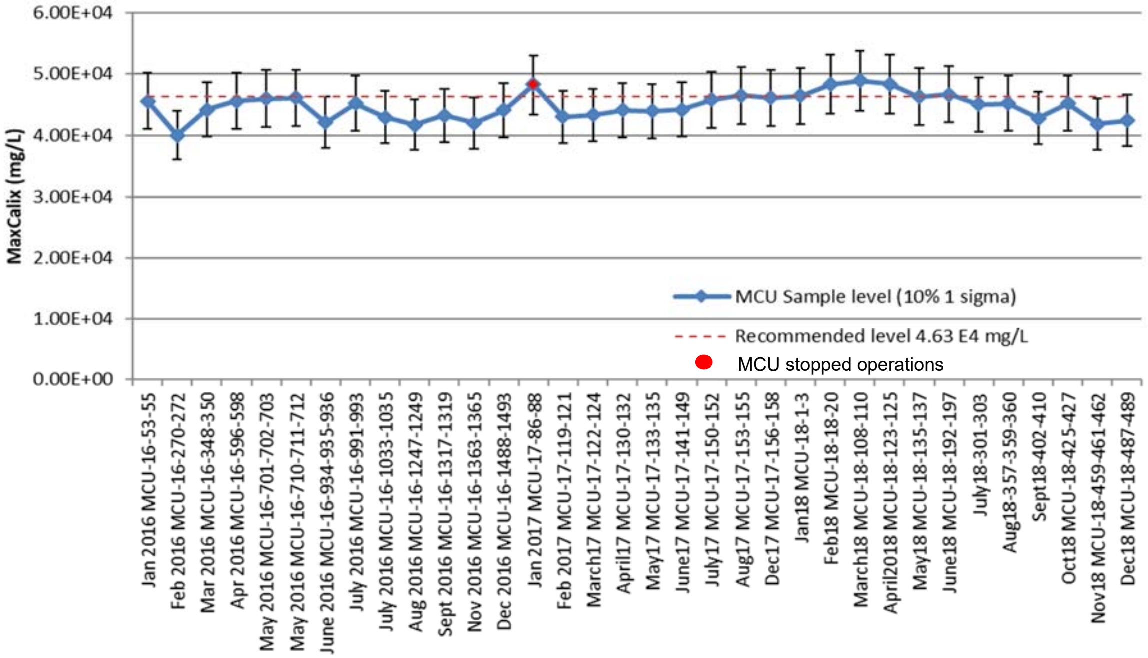


**Figure 8. Average MaxCalix concentration from the average of the HPLC and FT-HNMR of recent samples since NGS implementation (46,000 mg/L is the nominal concentration).**

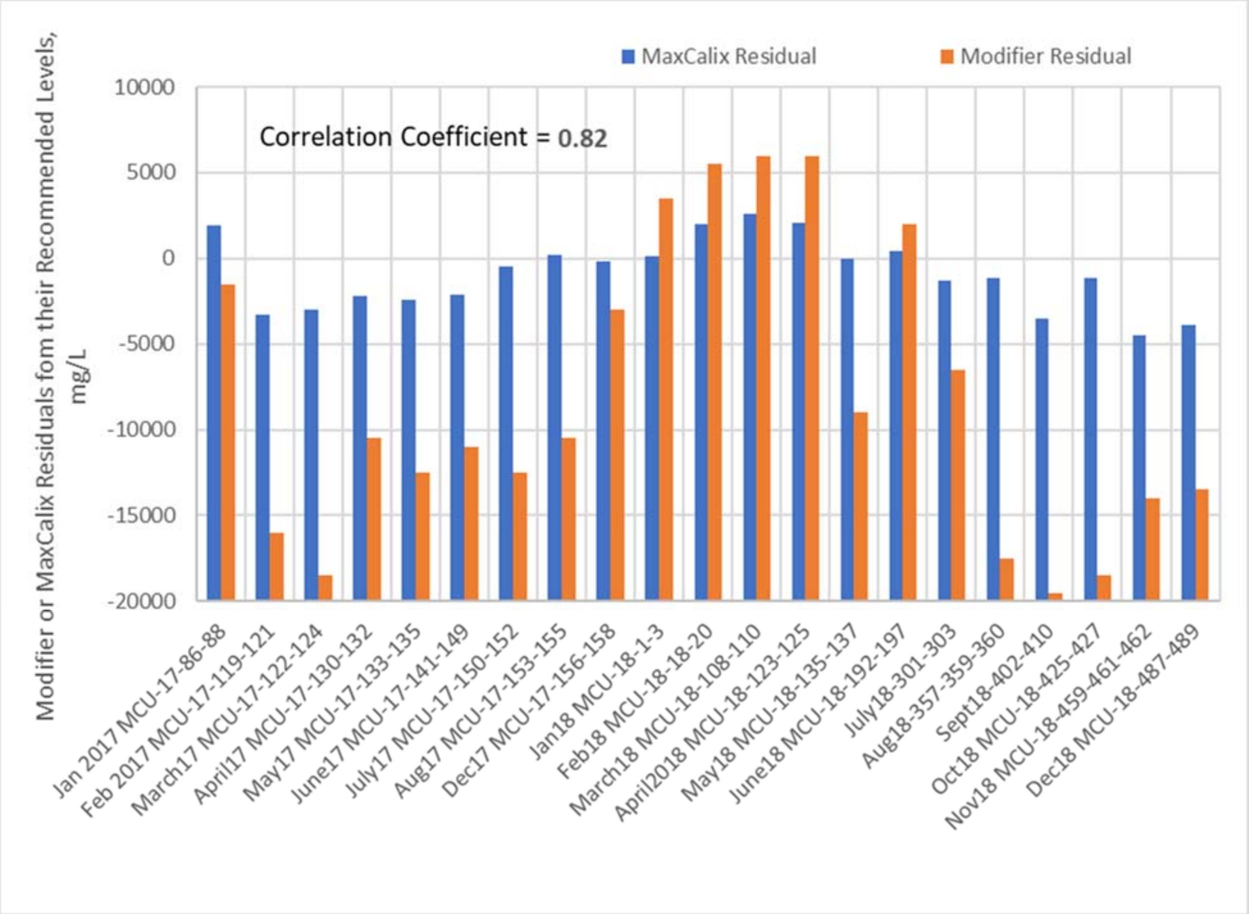


**Figure 9 MaxCalix and Modifier residuals from their recommended levels**

A closer look at the MaxCalix concentration data obtained from the HPLC and FT-HNMR methods from January 2018 to December 2018 is shown in Figure 10. In Fig. 10, the ordinate axis presents the difference of the measurements from the two methods while the coordinate axis presents the average value. As can be seen from Fig.10, for several samples, the FT-HNMR method reported lower values than the HPLC. SRNL believes this is due to overlapping at the base of the peaks between the aromatic peak assigned to MaxCalix and the aromatic peaks assigned to the Modifier. The area of the aromatic peak assigned to MaxCalix is computed without conducting any effort to deconvolute it from neighboring peaks (the same arithmetic treatment is done to the spectrum of the Scratch May 2018 standard). A significant number of the difference data lies outside the 95% confidence interval (as shown in Fig. 10) that include the origin. The observed bias is not constant (not displayed through the whole domain in Fig. 10), but it is noticeable at the lower magnitude of the average MaxCalix measurements and it is statistically significant (see Table 3-2).

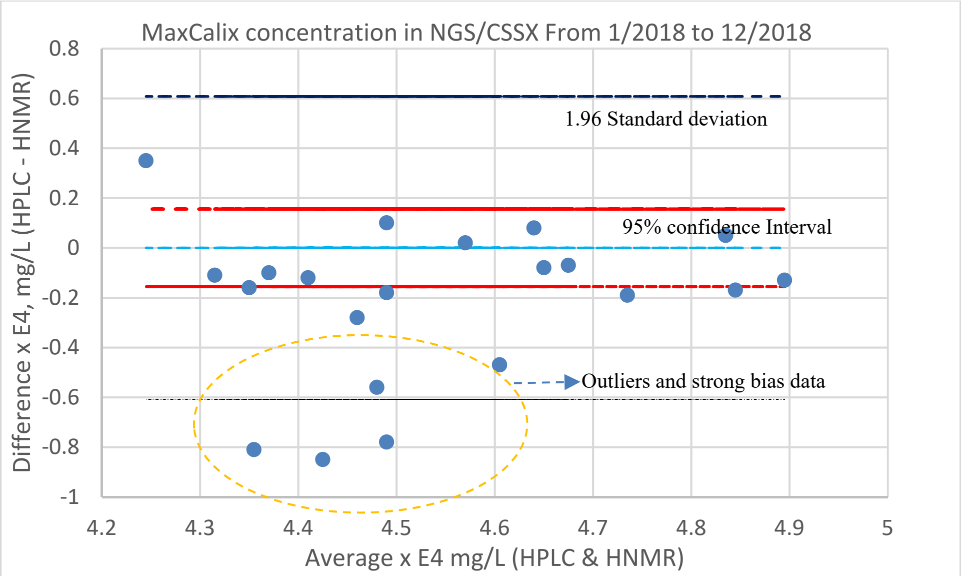


**Figure 10. A comparison of the HPLC and HNMR analytical methods for measuring MaxCalix. The ordinate is the subtraction of the results of the two methods and the coordinate is their average.**

**Table 3-2 t-Test: Paired Two Sample for Means. HPLC versus FT-HNMR**

| *Parameter* | *HPLC* | *FT-HNMR* |
|---|---|---|
| Mean (mg/L) | 4.45 E4 | 4.66 E4 |
| Variance | 0.069 E4 | 0.05 E4 |
| Observations | 23 | 23 |
| Pearson Correlation | 0.182 | |
| Hypothesized Mean Difference | 0.000 | |
| df (Jan. 2017 to Feb. 2019) | 22.000 | |
| t Stat | -3.280 | |
| P(T<=t) one-tail (<0.05) | 0.002 | Significant |
| t Critical one-tail | 1.717 | |
| P(T<=t) two-tail (<0.05) | 0.003 | Significant |
| t Critical two-tail | 2.074 | |

A linear regression analysis of the FT-HNMR and HPLC MaxCalix data also proved that there is a bias in the FT-HNMR data as explained before (see in Fig. 11 the extent of the bias that caused the 95% confidence interval to exclude the line with unitary slope).

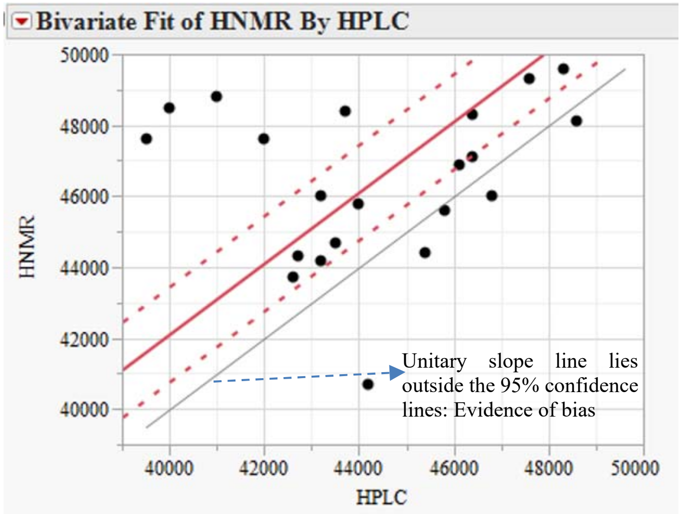


**Figure 11. Linear regression of the FT-HNMR and HPLC data for MaxCalix. The broken lines represent the 95% confidence limits. The unitary slope line lies outside the confidence lines.**

*Gamma Measurements*

The gamma measurements for the October, November, and December samples are shown in Fig. 12 in relation to past measurements. The values in the November and December samples are consistent with previous levels observed during normal operation (for example in 2016). The variability in the gamma measurements is due to several factors that include the Isopar™ L addition (sometimes 12% dilution or 25 gallons of Isopar™ L to 200 gallons of solvent), processing start-up, and measurement imprecision. The gamma counts in the October, November, and December 2018 SHT samples are consistent with routine MCU processing salt solutions before January 2017.

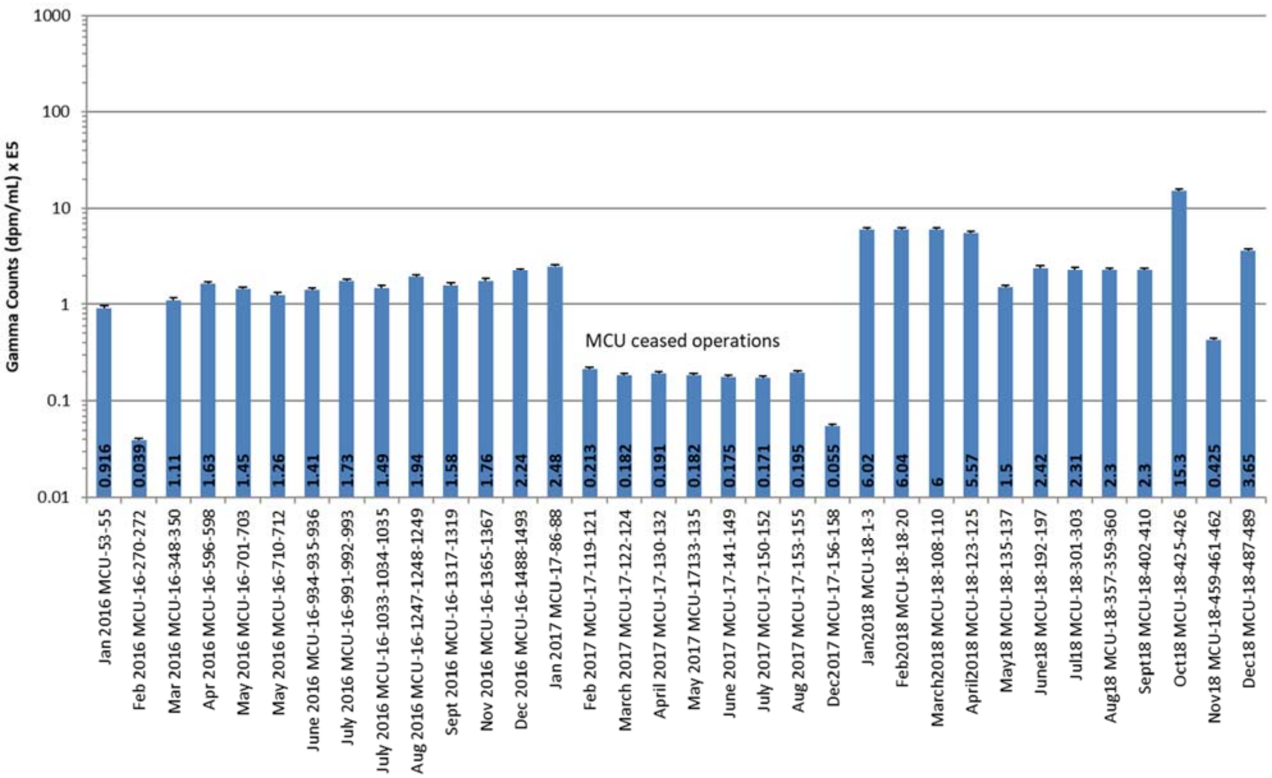


**Figure 12. The gamma count of selected SHT samples. One sigma is 5%.**

*Impurities*

No impurities were observed when performing the SVOA. However, the FT-HNMR analysis revealed the presence of three visible peaks (7.7, 7.4, 4.3, and 2.4 ppm) not observed in the solvent spectrum (see Fig. 13). These peaks are believed to be due to phthalates (for example, diethyl heptyl phthalate or di-octylphthalate). The phthalate concentration decreases from the October to the December sample. There is the potential that other new peaks may also be present, but if any are, they overlap with the solvent peaks and are indistinguishable.

Another impurity being tracked in the SHT solvent is the concentration of mercury. A few mL of each sample was analyzed by XRF and then digested and analyzed for total mercury by the DMA method. The average mercury concentrations in the October, November, and December 2018 SHT samples were 30 ± 6 ug/g, 38 ± 8 ug/g, and 29 ± 6 ug/g, respectively (see Fig. 14). Please note that the calculated mercury concentration of the samples obtained after April 2018 were averages of the XRF and DMA measurements (prior to April, averages of the XRF and Cold Vapor Atomic Adsorption (CVAA) were reported). SRNL measures total mercury by two different analytical techniques to eliminate single method bias in the reported results. Recall that XRF method calculates a higher mercury concentration due to the application of an adjustment factor from using a water standard (water absorbs more X-rays than aliphatic organic like kerosene). The effect is statistically significant (see Table 3-3) giving higher concentration than DMA. Measurements of the October, November, and December SHT samples are consistent with the measurements obtained in early 2016 possibly indicating variability in the mercury concentration of the salt batches sent to ARP/MCU. An example of this is the noticeable jump in the mercury concentration of the SHT is seen after July 2016. The average mercury before July 2016 was 17 ± 4 ug/g and after was 29 ± 4 ug/g (see Table 3-4). SRNL believes this jump is due to a feed stream with a higher mercury concentration (possibly Salt Batch 9) sent to MCU rather than an analytical measurement outlier.

The concentration of mercury observed in the October, November and December samples is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm),[10] implying that other solubility-enhancing mechanisms are at play (for example extraction by an extractant or sorption on trapped solids: Solids were not observed in these samples) 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.[11] Based on the December SHT sample DMA mercury measurements, for 200 gallons of solvent (757.1 L), the solvent could contain up to 18 ± 4 g of mercury. A comparison of these measurements with previous months (especially 2016 samples) confirms a higher mercury concentration in the solvent (data are shown in Fig. 14). This finding may be consistent with the higher concentrations of total mercury (~104 ppm) observed in Tank 50H in the third (7/2016-9/2016) and fourth (10/2016-12/2016) quarters surveillance samples.[12] It appears that the solvent may hold on to the mercury it receives (as no statistically detected downward trend in the mercury data is observed). Note that all the XRF data since November 2017 were renormalized and compensated for solvent density variation in this report. Thus, these values differ (slightly lower values) from previous reports.

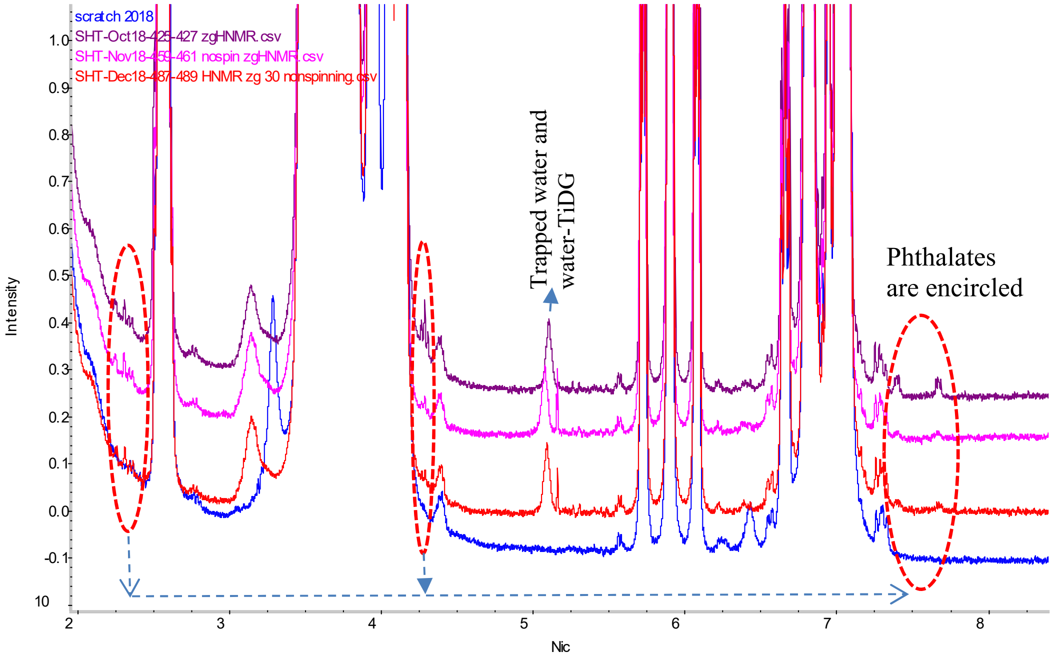


**Figure 13. FT-HNMR of the October, November and December SHT samples and the May 2018 Scratch baseline solvent**

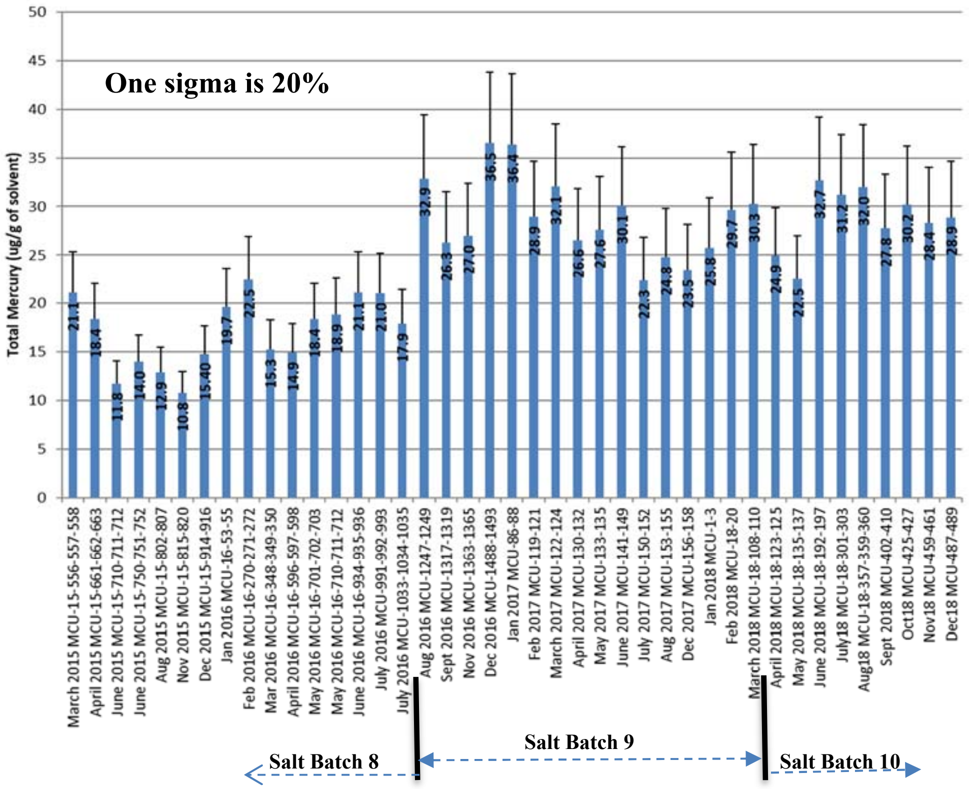


**Figure 14. Total mercury in recent SHT samples.**

**Table 3-3 t-Test: Paired Two Sample for Means. DMA versus XRF for mercury.**

| *Parameter* | *DMA* | *XRF* |
|---|---|---|
| Mean (ug/g) | 26.38 | 31.93 |
| Variance | 11.37 | 24.42 |
| Observations | 10 | 10 |
| Pearson Correlation | 0.335 | |
| Hypothesized Mean Difference | 0.000 | |
| df | 9.000 | |
| t Stat | -3.534 | |
| P(T<=t) one-tail (<0.05) | 0.003 | Significant |
| t Critical one-tail | 1.833 | |
| P(T<=t) two-tail (<0.05) | 0.006 | Significant |
| t Critical two-tail | 2.262 | |

**Table 3-4 t-Test: Two-Sample Assuming Equal Variances for determining a “step” jump in the data after July 2016.**

| *Parameter* | *Hg (ug/g) before 7/2016* | *Hg (ug/g) after 7/2016* |
|---|---|---|
| Mean (ug/g) | 17.1 | 28.9 |
| Variance | 13.3 | 14.7 |
| Observations | 16 | 26 |
| Pooled Variance | 14.16 | |
| Hypothesized Mean Difference | 0.00 | |
| df | 40 | |
| t Stat | -9.92 | |
| P(T<=t) one-tail (<0.05) | 1.21E-12 | Significant |
| t Critical one-tail | 1.68 | |
| P(T<=t) two-tail (<0.05) | 2.42E-12 | Significant |
| t Critical two-tail | 2.02 | |

## 4.0 Conclusions

A trend summary of three SHT monthly samples; MCU-18-425-426-427, MCU-18-459-460-461 and MCU-18-487-488-489 are reported. Most of the conclusions are based on the December SHT sample (MCU-18-487-488-489). Analyses of the December SHT sample (MCU-18-487-488-489 indicated that the Modifier (Cs-7SB) and the extractant (MaxCalix) concentrations were below their nominal recommended concentrations (169,000 mg/L and 46,400 mg/L respectively) by 2% and 9% respectively. The suppressor (*N,N’,N”*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has decreased since the October 2018 measurement (MCU resumed processing from May through November 2018) to 528 mg/L, but it is above the minimum recommended concentration (479 mg/L). These new levels are consistent with the concentrations observed when MCU was fully operational in 2016.

The SVOA did not detect any impurities. However, FT-HNMR analysis detected presence of phthalates at a few ppm. The impurity concentration was highest in the October sample and consistently detected in the November and December samples (but always a few ppm or less). Another impurity observed in the samples was mercury. Based on the December SHT sample, up to 24 ± 5 micrograms of mercury per mL of solvent was detected (as the average of the Direct Mercury Analysis (DMA 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 9 and 10.

The gamma concentration (~3.6E5 dpm/mL) measured in the December SHT samples was consistent with previous values observed when MCU was fully operational (for example, between December 2016 and January 2017) but it was lower than the April SHT measurement. The “dip” in the gamma measurement for the May 2018 SHT sample was due to an Isopar™ L addition to MCU during April and May 2018.

The laboratory will continue to monitor the quality of the solvent for any new impurities or degradation of the solvent components.

## 5.0 References

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## Appendix A: Average Modifier concentration in the SHT samples

| Sample | Average Modifier (mg/L) | Recommended Modifier level (mg/l) |
|---|---|---|
| Jan 2017 MCU-88-89 | 167500 | 169000 |
| Feb 2017 MCU-119-121 | 153000 | 169000 |
| March 2017 MCU-122-124 | 150500 | 169000 |
| April 2017 MCU-130-132 | 158500 | 169000 |
| May 2017 MCU-133-135 | 156500 | 169000 |
| June 2017 MCU-141-149 | 158000 | 169000 |
| July 2017 MCU-150-152 | 156500 | 169000 |
| August 2017 MCU-153-154 | 158500 | 169000 |
| Dec 2017 MCU-156-158 | 166000 | 169000 |
| Jan 2018 MCU-1-2-3 | 172500 | 169000 |
| Feb 2018 MCU-18-20 | 174500 | 169000 |
| March 2018 MCU-108-110 | 175000 | 169000 |
| April2018 MCU-18-123-125 | 175000 | 169000 |
| May2018 MCU-18-135-137 | 160000 | 169000 |
| June2018 MCU-18-192-197 | 171000 | 169000 |
| Jul18 MCU-301-303 | 162500 | 169000 |
| Aug18 MCU-357-359-360 | 151500 | 169000 |
| Sept18 MCU-402-410 | 149500 | 169000 |
| Oct18 MCU-425-427 | 150500 | 169000 |
| Nov18 MCU-459-461-462 | 155000 | 169000 |
| Dec18 MCU-487-489 | 155500 | 169000 |

## Appendix B: Minimum recommended level for TiDG in NGS-CSSX solvent

### Re: Dr. Moyer, if you have the time , we have a question for you .

Moyer, Bruce A. to: fernando.fondeur@srnl.doe.gov 06/24/2014 12:36 AM

Hi Fernando,

Our laboratory tests with simulants indicate that the solvent strips adequately even if the TiDG concentration falls to 10% of its nominal value of 3 mM. My recommendation is to trim when the TiDG gets to 1 mM. That should give some margin.

That said, our study of TiDG decomposition rate is making me rethink the nominal value of 3 mM TiDG. The rate data show that the decomposition slows down as the TiDG concentration decreases. The decomposition is rather fast at 3 mM. Since you want to minimize organics going to salt stone and DWPF, it might be advisable to trim only up to 2 mM and operate in the range 1-2 mM TiDG. With more experience in operating NGS in the MCU, that range might eventually be reduced even further.

Thanks for sharing your analytical data. It would be good to see the X-axis as time, though, but I suspect you are showing data back to December. That

means the TiDG has not decomposed as fast as I would have thought based on our recent study. Perhaps the cold weather has been helpful in that regard. The TiDG concentration will bear careful watching in the warm summer months, as decomposition definitely speeds up with increasing temperature.
Bruce
From: "fernando.fondeur@srnl.doe.gov<mailto:fernando.fondeur@srnl.doe.gov>" <fernando.fondeur@srnl.doe.gov<mailto:fernando.fondeur@srnl.doe.gov>>
Date: Monday, June 23, 2014 3:49 PM
To: Bruce Moyer <moyerba@ornl.gov<mailto:moyerba@ornl.gov>>
Subject: Dr. Moyer, if you have the time, we have a question for you.
Dr. Moyer:
Please pardon my numerous e-mails on this topic. Thank you for your last reply on the effect of high [K] and low temperature on third phase formation. But we need your advice. The TiDG concentration, since the implementation of NGS-CSSX blend, is around 750 mg/L (as you may see below) which is well below the nominal concentration of 1,550 mg/L. If this condition continues (that is without trimming more TiDG), is the solvent susceptible to soaps affecting the stripping? From your extensive experience on this, do you happen to know what is the lowest level of TiDG the solvent can have without any deleterious effect on mass transfer and/or hydrodynamics in the stripping stages? Thanks.

Sincerely,
Fernando Fondeur
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