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Solvent Hold Tank Sample Results for MCU-19-2-3-4 (January 2019), MCU-19-83-84-85 (February 2019), MCU-19-208-209-210 (March 2019), and MCU-19-138-139-140 (March special trim): Quarterly Report

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EXECUTIVE SUMMARY

A trend summary of three sets of Solvent Hold Tank (SHT) monthly samples (MCU-19-2-3-4, MCU-19-83-84-85, MCU-19-208-209-210); and a set from a special trim (MCU-19-138-139-140) are reported. Most of the conclusions are based on the March SHT sample (MCU-18-208-209-210). Analyses of the March SHT sample (MCU-19-208-209-210) indicated that the Modifier (Cs-7SB) and the Extractant (MaxCalix) concentrations were below their nominal recommended concentrations (169,000 mg/L and 46,900 mg/L, respectively) by 3% and 6%, respectively. The Suppressor (*N,N',N"*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has increased since the January 2019 measurement to 1141 mg/L, which is above the minimum recommended concentration (479 mg/L). These new concentrations 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 January sample and consistently detected in the February and March samples (but always registered as a few ppm or less). Another impurity observed in the samples was mercury. Based on the March SHT sample, up to 25 ± 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 (~2.55E5 dpm/mL) measured in the March 2019 SHT samples was consistent with previous values observed when MCU was operating continuously (for example, between December 2016 and January 2017).

Statistical analysis of the different analytical methods detected a bias (a statistical difference at 5% level) between the FT-HNMR and HPLC methods when measuring the MaxCalix and Modifier concentration; the FT-HNMR gave a higher concentration possibly due to peak overlapping in the measured data. A bias was also detected when measuring total mercury by the DMA method versus the XRF method with the XRF method reported higher mercury concentrations.

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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LIST OF ABBREVIATIONS

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
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 four sets of SHT samples: MCU-19-2-3-4, MCU-19-83-84-85, MCU-19-208-209-210, and MCU-19-138-139-140 (special March trim sample). A summary report for each of the SHT monthly samples was issued previously.[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 (September 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 March 2019, 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-19-2-3-4	January 26, 2019
9 gallons of Isopar^{TM} L added to MCU	February 4, 2019
11 gallons Isopar^{TM} L added to MCU	February 21, 2019
SHT sample MCU-19-83-84-85	February 17, 2019
SHT sample MCU-19-138-139-140 special trim	March 5, 2019
SHT sample MCU-19-208-209-210	March 19, 2019
9 gallons of Isopar^{TM} L added to MCU	March 27, 2019

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. 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 the scratch solvent made in September 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 Technical Task Request (TTR) X-TTR-H-00026. The recorded data, analysis, and conclusions satisfy the production support requirements in the Task Technical and Quality Assurance Plan (TTQAP) associated with this TTR, SRNL-RP-2013-00536. The requested QA level for this work is for Production Support (PS) as stated in "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. The work performed, all analyses, and the review process for this report complies with those requirements.

3.0 Results and Discussion

Each sample (and its corresponding P-nut vial) was visually examined. No floating debris or foam were observed (see Figure 1). However, the bottom wall of the P-nut vials for samples MCU-19-2 and MCU-19-3 showed a film composed of degraded Modifier and 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. Large caustic droplets were found in the P-nut vials for samples MCU-19-83, MCU-19-84, MCU-19-208, and MCU-19-209. No droplets were found in the trim samples MCU-19-138-140. 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.

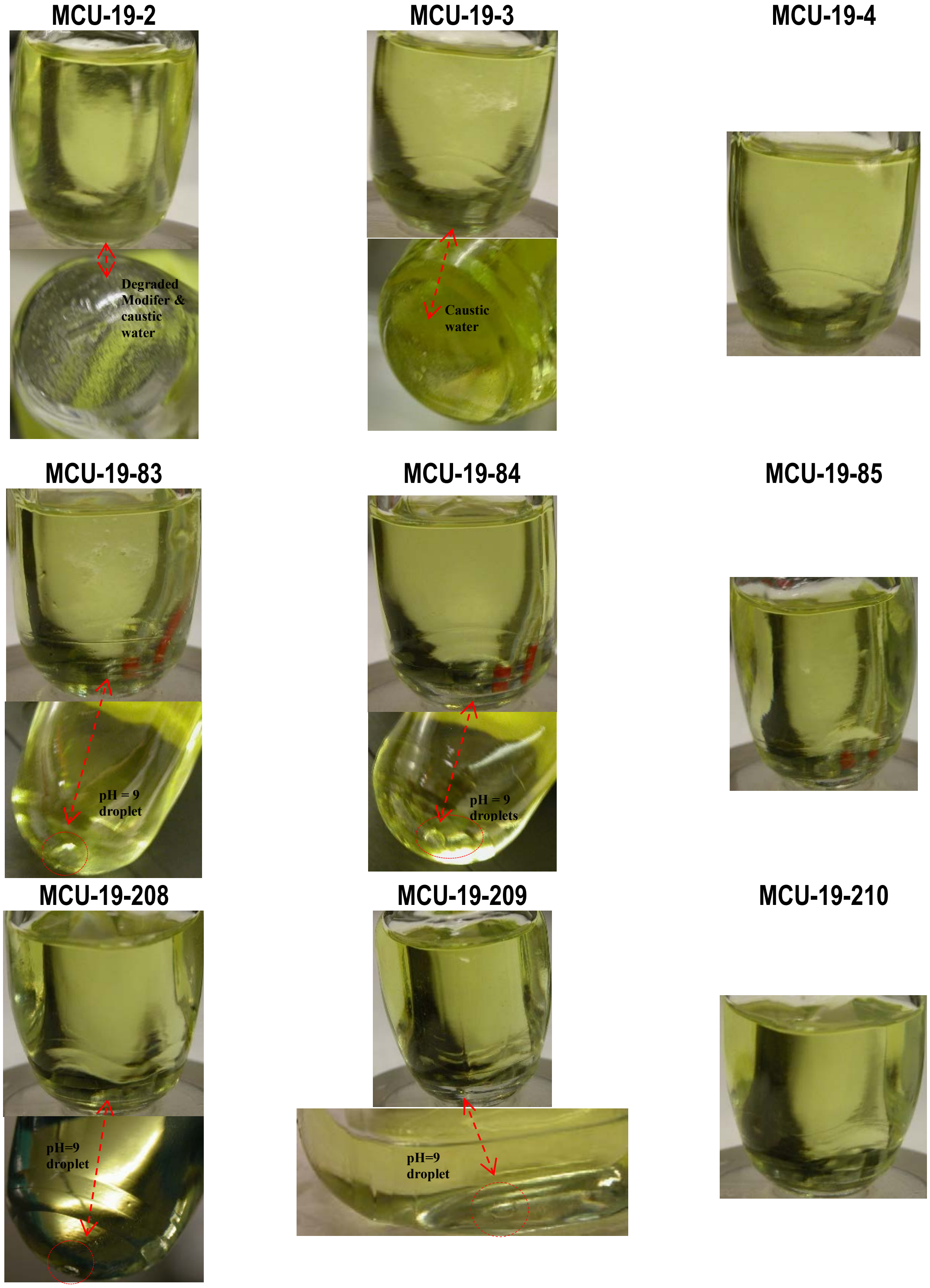


Figure 1 A picture of samples MCU-19-2-4 (top), MCU-19-83-85 (middle), and MCU-19-208-210 (bottom).

Modifier Concentrations and Density Measurements

MCU resumed operations in May 2018 (after suspending operations in January 2017) and since then, several Isopar™L additions and three trim additions were made to the solvent. Based on the January-February-March results, both the density measurements and the Modifier concentration 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) or recommended value (in the case of the Modifier, the recommended concentration is 1.69E5 mg/L) [see Figure 2 and the tabulated data in Appendix A].[2,4] The reported density measurements were obtained from triplicate measurements of the sample (with the density measured by the vibrations of a specially 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). 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 in the Modifier concentration) for the January-February-March 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 January-February-March samples were consistent with previous measurements when MCU was operating continuously (for example in 2016). Both the density data and the Modifier concentration correlated strongly with each other as expected (see Figure 2).[7] Statistically, there were differences between the values reported by HPLC and FT-HNMR (see Figure A1, Figure A2, and Table A-1 in Appendix A). The Isopar™ L concentration (not shown) in the March sample was similar to that of the baseline solvent (scratch made on September 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 January, February, and March SHT samples such as viscosity and surface tension were like the baseline solvent measurements (see Figure 3). No evidence of bias was determined relative to the scratch baseline solvent (Figure A3 in Appendix A).

All measurements indicate (based on the January, February, and March 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.

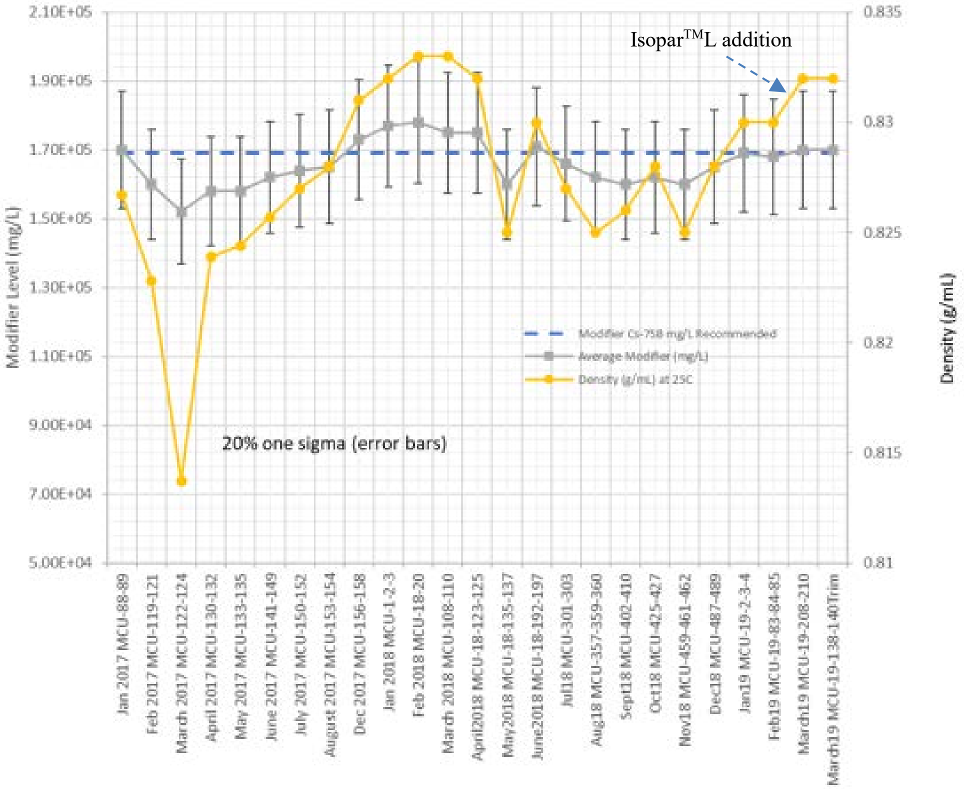


Figure 2. Modifier concentration in the solvent as measured by HPLC (one sigma is 10%).

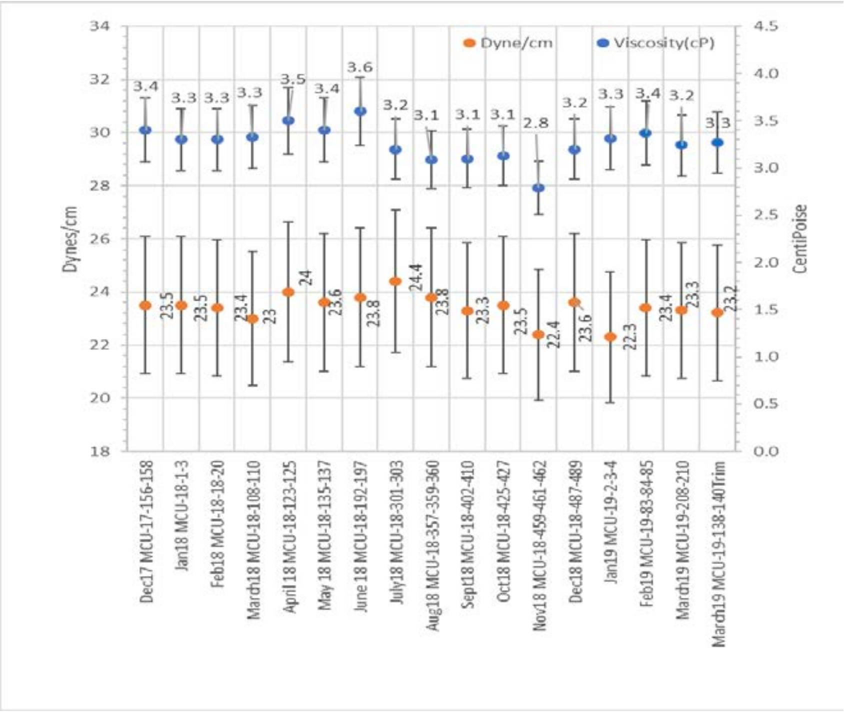


Figure 3. Viscosity and surface tension measurements of the last 17 SHT samples. The scratch blend measured a viscosity of 3 ± 0.3 cP and a surface tension of 23 ± 0.6 dynes/cm (at 25˚C).

Suppressor Concentrations

The average TiDG concentrations for MCU-19-2-3-4, MCU-19-83-84-85, MCU-19-208-209-210, and MCU-19-138-139-140 are shown in Figure 4. As can be seen in Figure 4, the TiDG concentration has increased since January 2019. The addition of TiDG to the solvent in early March 2019 raised the concentration to 1140 mg/L (March SHT sample). Although the March sample was obtained after trimming and mixing, the TiDG level in the March samples was still much lower than that observed after previous trims (such as Nov. 2016 and Dec 2017 in Figure 4). Considering the January sample (1080 mg/L TiDG) and the February sample (914 mg/L TiDG), the upward trend has previously been observed before (for example from September to November 2016 in Figure 4). Based on the March SHT sample, the Suppressor concentration (1.14 ± 0.11E3 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 132 ± 21 mg/L. Since May 2016, the TOA level range can be estimated by 196 ± 32 mg/L. Since MCU no longer adds TOA, a drop in TOA concentration is expected with time. However, a detectable and steady TOA concentration level persists with time, perhaps due to a slower than expected degradation rate, a slower transfer rate to the aqueous streams during operation, or a bias resulting from 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]

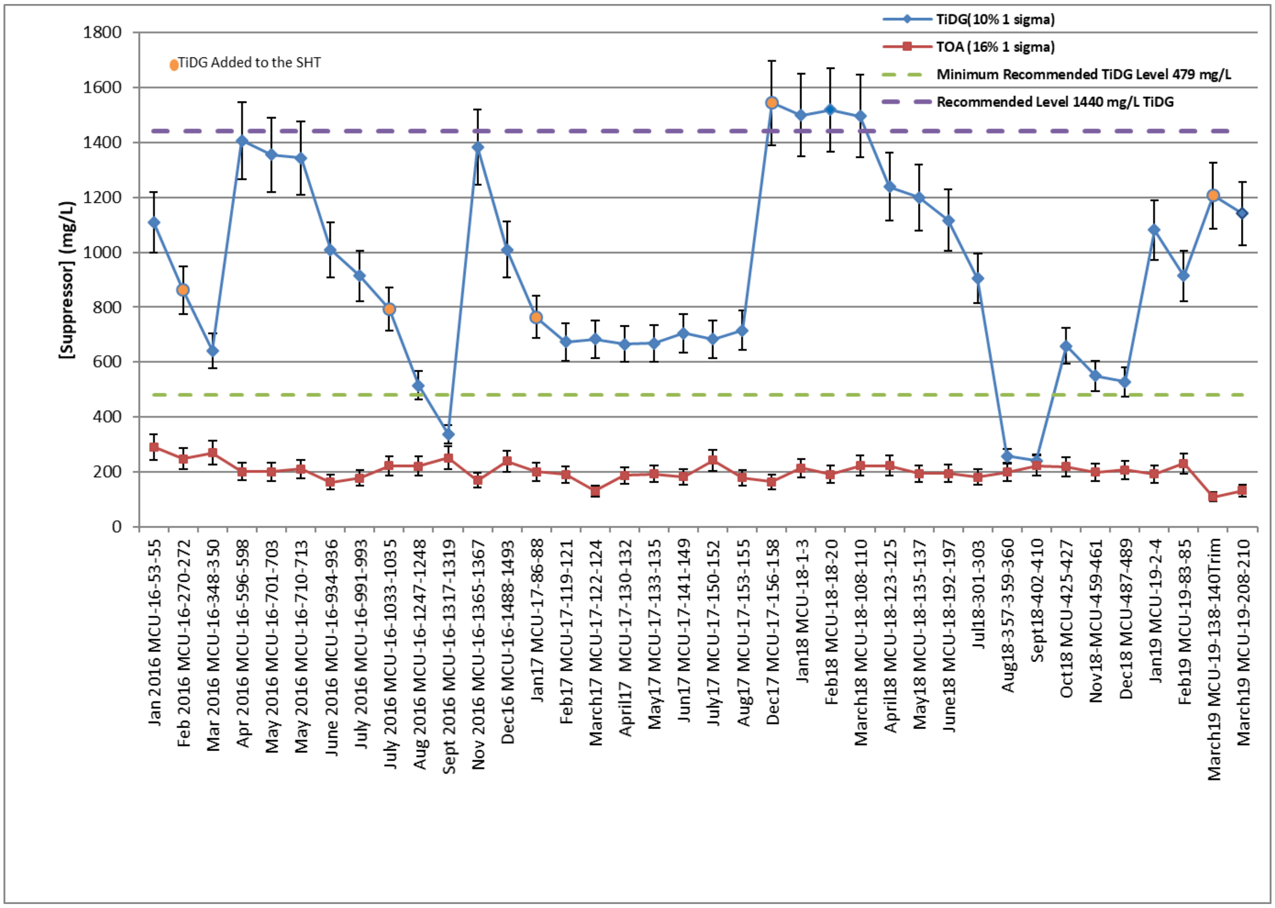


Figure 4. Suppressor concentration as measured by titration in the SHT samples since NGS implementation. The minimum recommended concentration is 479 mg/L for TiDG.

Extractant Concentrations

The calculated MaxCalix concentration has remained nearly steady around an average of 4.37E4 mg/L in the last 4 SHT samples (see Figure 5). 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 46,883 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 (917 mg/L in the March sample). The recent variations in the MaxCalix concentration seen in Figure 5 (including a concentration minimum observed in the November 2018 SHT sample) is within the uncertainty range for this measurement. The pseudo-linear trends observed in Figure 5 correlate (correlation coefficient of 0.82) with the trends observed in the Modifier levels (see Figure A4 in Appendix A 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 is (based on the March sample) at 23% 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.

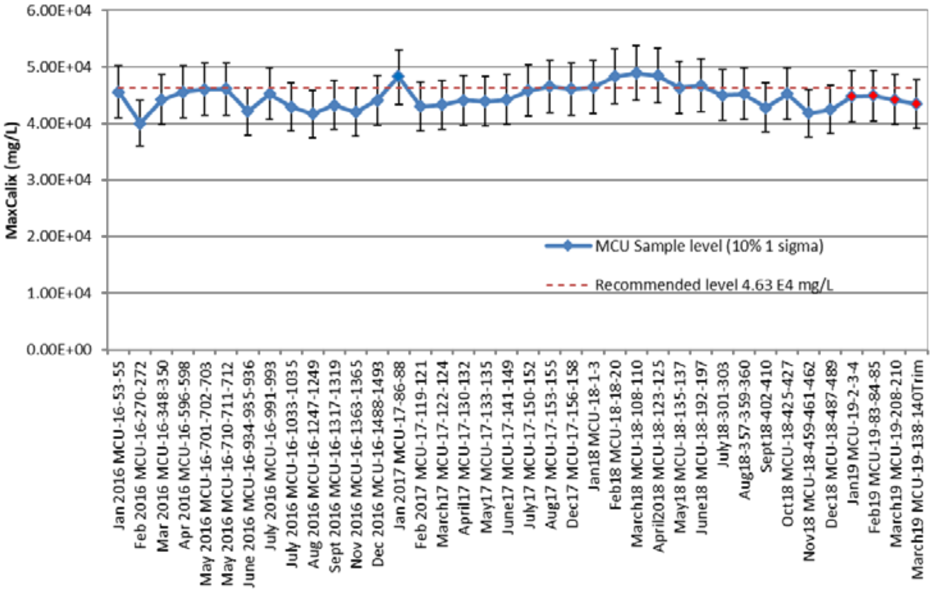


Figure 5. Average MaxCalix concentration from the average of the HPLC and FT-HNMR of recent samples since NGS implementation (46,000 mg/L is the nominal concentration).

A closer look at the MaxCalix concentration data obtained from the HPLC and FT-HNMR methods from January 2018 to March 2019 is shown in Figure A5. In Figure A5, 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 Figure A5, for several samples, the FT-HNMR method reported higher 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 September 2018 standard). A significant number of data points lie outside the 95% confidence interval (as shown in Figure A5) that does not include the origin. The observed bias is not constant (not displayed through the whole domain in Figure A5), but it is noticeable at the higher magnitude of the average MaxCalix measurements and it is statistically significant (see Table A-2 in Appendix A).

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. In Figure A6 the extent of the bias that caused the 95% confidence interval to exclude the line with unitary slope.

Gamma Measurements

The gamma measurements for the January, February, March (and the special March trim) samples are shown in Figure 6 (colored red) in relation to past measurements. The values in the January, February, and March 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 January, February, and March 2019 SHT samples are consistent with routine MCU processing salt solutions before January 2017.

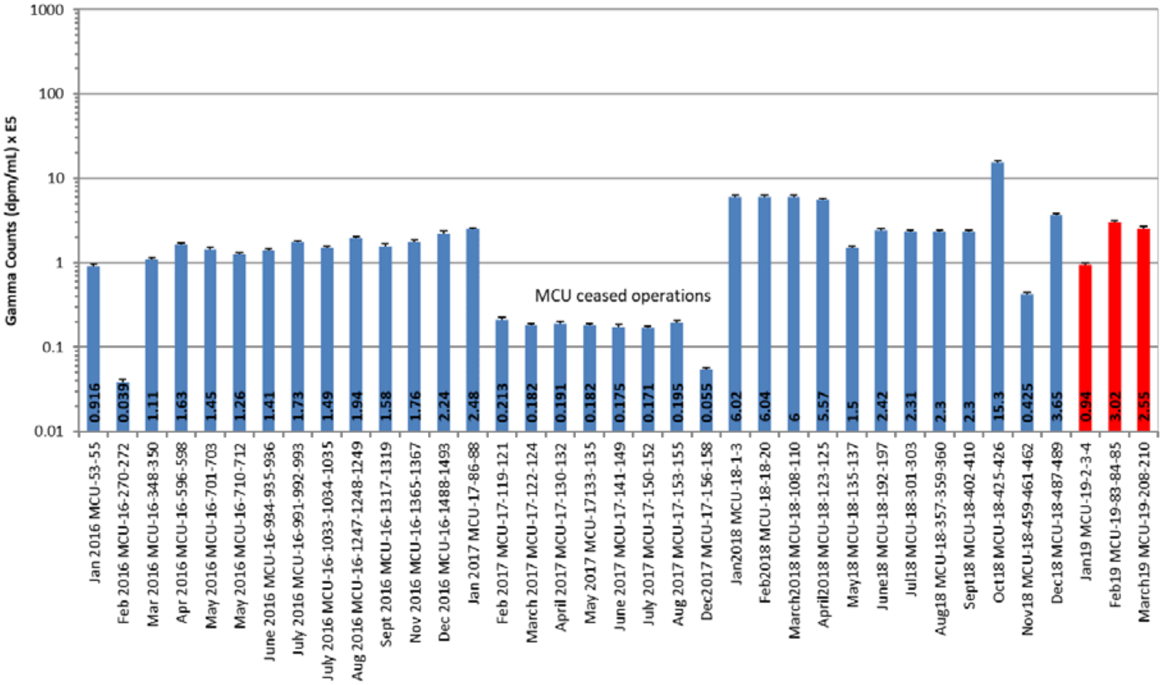


Figure 6. The gamma counts of selected SHT samples.

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 Figure 7). These peaks are believed to be due to phthalate (for example, diethyl heptyl phthalate or di-octylphthalate). This impurity concentration decreases from the January to the March 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 January, February, and March SHT samples were 33 ± 7 ug/g, 37 ± 7 ug/g, and 31 ± 6 ug/g, respectively (see Figure 8). 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 organics like kerosene). The effect is statistically significant (see Table A-3 in Appendix A), giving a higher concentration than DMA. Measurements of the January, February, and March SHT samples are consistent with the measurements obtained since August 2016 possibly (since Salt Batch 9 and Salt Batch 10) 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 seen after July 2016. The average mercury before July 2016 was 17 ± 4 ug/g and after was 29 ± 4 ug/g (see insert table in Figure 8). 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 January, February, and March 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 March 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 Figure 8). 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.

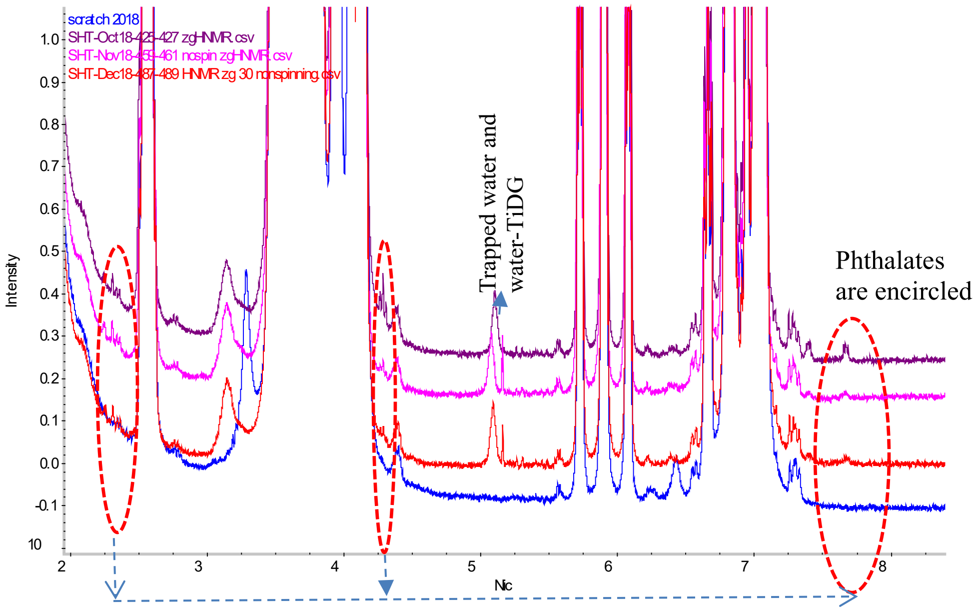
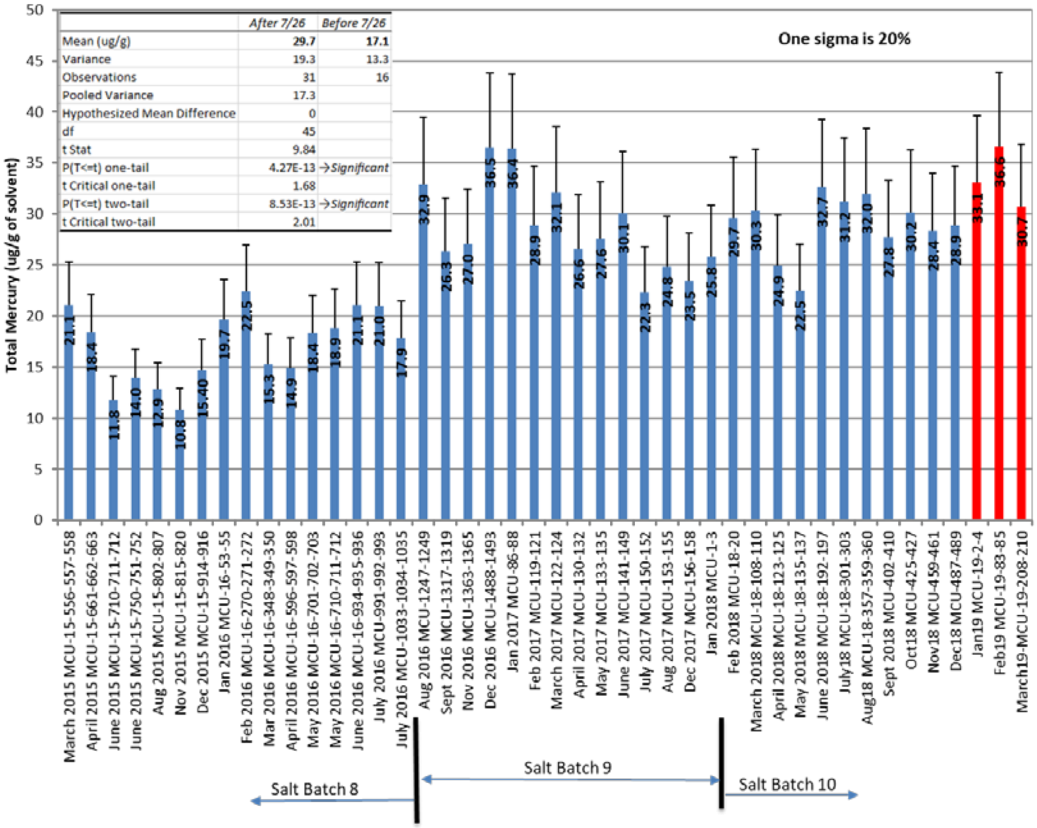


Figure 7. FT-HNMR of the January, February, and March SHT samples and the September 2018 Scratch baseline solvent



	After 7/26	Before 7/26
Mean (ug/g)	**29.7**	**17.1**
Variance	19.3	13.3
Observations	31	16
Pooled Variance	17.3	
Hypothesized Mean Difference	0	
df	45	
t Stat	9.84	
P(T<=t) one-tail	4.27E-13	→*Significant*
t Critical one-tail	1.68	
P(T<=t) two-tail	8.53E-13	→*Significant*
t Critical two-tail	2.01	

Figure 8. Total mercury in recent SHT samples.

4.0 Conclusions

A trend summary of three sets of Solvent Hold Tank (SHT) monthly samples (MCU-19-2-3-4, MCU-19-83-84-85, MCU-19-208-209-210); and a set from a special trim (MCU-19-138-139-140) are reported. Most of the conclusions are based on the March SHT sample (MCU-18-208-209-210). Analyses of the March SHT sample (MCU-19-208-209-210) indicated that the Modifier (Cs-7SB) and the Extractant (MaxCalix) concentrations were below their nominal recommended concentrations (169,000 mg/L and 46,900 mg/L, respectively) by 3% and 6%, respectively. The Suppressor (*N,N',N"*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has increased since the January 2019 measurement to 1141 mg/L, which is above the minimum recommended concentration (479 mg/L). These new concentrations are consistent with the concentrations observed when MCU was fully operational in 2016.

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

5.0 References

[1] T. B. Peters, A. L. Washington, II, F. F. Fondeur, "Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU", SRNL-RP-2013-00536.

[2] F. Fondeur, "Solvent Hold Tank Sample Results for MCU-19-2-3-4: January 2019 Monthly Sample", SRNL-L3100-2019-0003, Rev. 0, March 2019.

[3] F. F. Fondeur, 'Solvent Hold Tank Sample Results for MCU-19-83-84-85: February 2019 Monthly Sample" SRNL-L3100-2019-00005, Rev. 0, April 2019.

[4] F. F. Fondeur, "Solvent Hold Tank Sample Results for MCU-19-208-209-210: March 2019 Monthly Sample", SRNL-L3160-2019-00007, Rev. 0, June 2019.

[5] M. R. Williams, "Next Generation Solvent Preparation." Manual L29, Procedure ITS-0173, Rev. 3, January 20, 2016.

[6] C. M. Santos, "Engineering Evaluation of MCU Solvent and Recommended Trim and Isopar-L Additions to Maintain Specifications: March 2019," X-ESR-H-00989, Rev. 0, March 2019.

[7] L.H. Delmau, J. F. Birdwell, P. V. Bonnesen, L. J. Foote, T. J. Haverlock, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloope, Jr., B. A. Tomkins, "Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent", ORNL/TM-2002/190, October 2002.

[8] B. A Moyer, L. H. Delmau, B. D. Roach, and N. J. Williams, "Thermal Degradation of Next Generation Solvent using Triisodecylguanidine Suppressor: Impacts on Solvent Performance and Organic Content of Aqueous Effluents" ORNL-LTR-NGCSSX-020, Rev. 1, October 2013.

[9] K. M. L. Taylor-Pashow, F. F. Fondeur, T. L. White, D. P. Diprete, and C. E. Milliken, "Development of Analytical Methods for Determining Suppressor Concentration in the MCU Next Generation Solvent (NGS)" SRNL-STI-2013-00435, Rev. 0, October 2013.

[11] C. J. Bannochie, "Result of Preliminary Hg Speciation Testing on Tank 22 and Waste Concentrate Hold Tank (WCHT) Material", SRNL-L3100-2015-00079, Rev. 1, May 4, 2015.

[12] C. J. Bannochie, "Results of Hg Speciation Testing on 3Q16 and 4Q16 Tank 50 WAC samples", SRNL-L3100-2016-00222, Rev. 1, January 2017.

Appendix A Average Modifier concentration in the SHT samples

SHT Sample (Modifier)	Average (mg/L)	HPLC (mg/L)	FT-HNMR (mg/L)
Jan 2017 MCU-88-89	1.68E+05	1.65E+05	1.70E+05
Feb 2017 MCU-119-121	1.53E+05	1.55E+05	1.51E+05
March 2017 MCU-122-124	1.51E+05	1.50E+05	1.51E+05
April 2017 MCU-130-132	1.59E+05	1.58E+05	1.59E+05
May 2017 MCU-133-135	1.57E+05	1.56E+05	1.57E+05
June 2017 MCU-141-149	1.58E+05	1.57E+05	1.59E+05
July 2017 MCU-150-152	1.57E+05	1.56E+05	1.57E+05
August 2017 MCU-153-154	1.59E+05	1.58E+05	1.59E+05
Dec 2017 MCU-156-158	1.66E+05	1.63E+05	1.69E+05
Jan 2018 MCU-1-2-3	1.73E+05	1.72E+05	1.73E+05
Feb 2018 MCU-18-20	1.75E+05	1.77E+05	1.72E+05
March 2018 MCU-108-110	1.75E+05	1.78E+05	1.72E+05
April2018 MCU-18-123-125	1.75E+05	1.66E+05	1.68E+05
May2018 MCU-18-135-137	1.60E+05	1.59E+05	1.53E+05
June2018 MCU-18-192-197	1.71E+05	1.68E+05	1.64E+05
Jul18 MCU-301-303	1.63E+05	1.64E+05	1.61E+05
Aug18 MCU-357-359-360	1.52E+05	1.54E+05	1.49E+05
Sept18 MCU-402-410	1.50E+05	1.50E+05	1.49E+05
Oct18 MCU-425-427	1.51E+05	1.40E+05	1.61E+05
Nov18 MCU-459-461-462	1.55E+05	1.52E+05	1.58E+05
Dec18 MCU-487-489	1.56E+05	1.47E+05	1.64E+05
Jan19 MCU-19-2-3-4	1.59E+05	1.51E+05	1.67E+05
Feb19 MCU-19-83-84-85	1.60E+05	1.50E+05	1.69E+05
March19 MCU-19-208-210	1.54E+05	1.48E+05	1.59E+05
March19 MCU-19-138-140Trim	1.52E+05	1.48E+05	1.55E+05

Viscosity and surface tension of the SHT samples

SHT sample (Rheology)	Viscosity (cP)	Surface Tension (Dyne/cm)	Control Viscosity (cP)	Control Surface Tension (dyne/cm)
Dec17 MCU-17-156-158	3.4	23.5	3.1	22.4
Jan18 MCU-18-1-3	3.3	23.5	3.08	22.9
Feb18 MCU-18-18-20	3.3	23.4	3.08	23.44
March18 MCU-18-108-110	3.3	23	3.28	22.6
April 18 MCU-18-123-125	3.5	24	3.47	22.9
May 18 MCU-18-135-137	3.4	23.6	3.6	23.7
June 18 MCU-18-192-197	3.6	23.8	3.6	23.6
July18 MCU-18-301-303	3.2	24.4	4	24
Aug18 MCU-18-357-359-360	3.1	23.8	3.16	24

Viscosity and surface tension of the SHT samples

Sept18 MCU-18-402-410	3.1	23.3	3.11	23.2
Oct18 MCU-18-425-427	3.1	23.5	3.15	23
Nov18 MCU-18-459-461-462	2.8	22.4	3.12	22.5
Dec18 MCU-18-487-489	3.2	23.6	3.17	23.8
Jan19 MCU-19-2-3-4	3.3	22.3	3.17	23.7
Feb19 MCU-19-83-84-85	3.4	23.4	3.2	23.2
March19 MCU-19-208-210	3.2	23.3	3.18	22.9
March19 MCU-19-138-140Trim	3.3	23.2	3.21	23.4

Average MaxCalix concentration in the SHT samples

SHT Sample (MaxCalix)	HPLC (mg/L)	FT-HNMR (mg/L)	Average (mg/L)
Jan 2017 MCU-17-86-88	4.82E+04	49300	48597
Feb 2017 MCU-17-119-121	4.30E+04	43700	43255
March17 MCU-17-122-124	4.33E+04	44300	43661
April17 MCU-17-130-132	4.41E+04	46000	44769
May17 MCU-17-133-135	4.39E+04	44700	44191
June17 MCU-17-141-149	4.42E+04	45800	44768
July17 MCU-17-150-152	4.58E+04	45600	45725
Aug17 MCU-17-153-155	4.65E+04	46000	46312
Dec17 MCU-17-156-158	4.61E+04	46900	46391
Jan18 MCU-18-1-3	4.64E+04	48300	47071
Feb18 MCU-18-18-20	4.83E+04	49600	48767
March18 MCU-18-108-110	4.89E+04	48100	48596
April2018 MCU-18-123-125	4.84E+04	48100	48288
May18 MCU-18-135-137	4.63E+04	44200	45473
June18 MCU-18-192-197	4.67E+04	47100	46847
July18-301-303	4.50E+04	44400	44773
Aug18-357-359-360	45200	48400	46289
Sept18-402-410	4.28E+04	40700	41969
Oct18 MCU-18-425-427	4.52E+04	48400	46289
Nov18 MCU-18-459-461-462	4.18E+04	47600	43617
Dec18 MCU-18-487-489	4.24E+04	48500	44300
Jan19 MCU-19-2-3-4	44800	47600	45763
Feb19 MCU-19-83-84-85	44900	48800	46202
March19 MCU-19-208-210	4.42E+04	48800	45703
March19 MCU-19-138-140Trim	4.34E+04	48800	45122

Mercury concentration measured by the DMA and XRF Methods

SHT Sample (mercury)	DMA (ug/g)	XRF (ug/g)
April 2018 MCU-18-123-125	24.40	25.44
May 2018 MCU-18-135-137	19.90	25.11
June 2018 MCU-18-192-197	33.20	32.15
July18 MCU-18-301-303	28.60	33.75
Aug18 MCU-18-357-359-360	26.20	37.79
Sept 2018 MCU-402-410	26.70	28.82
Oct18 MCU-425-427	28.00	32.4
Nov18 MCU-459-461	25.90	30.8
Dec18 MCU-487-489	25.80	32.0
Jan19 MCU-19-2-4	25.10	41.0
Feb19 MCU-19-83-85	38.50	34.61
March19-MCU-19-208-210	29.00	32.43

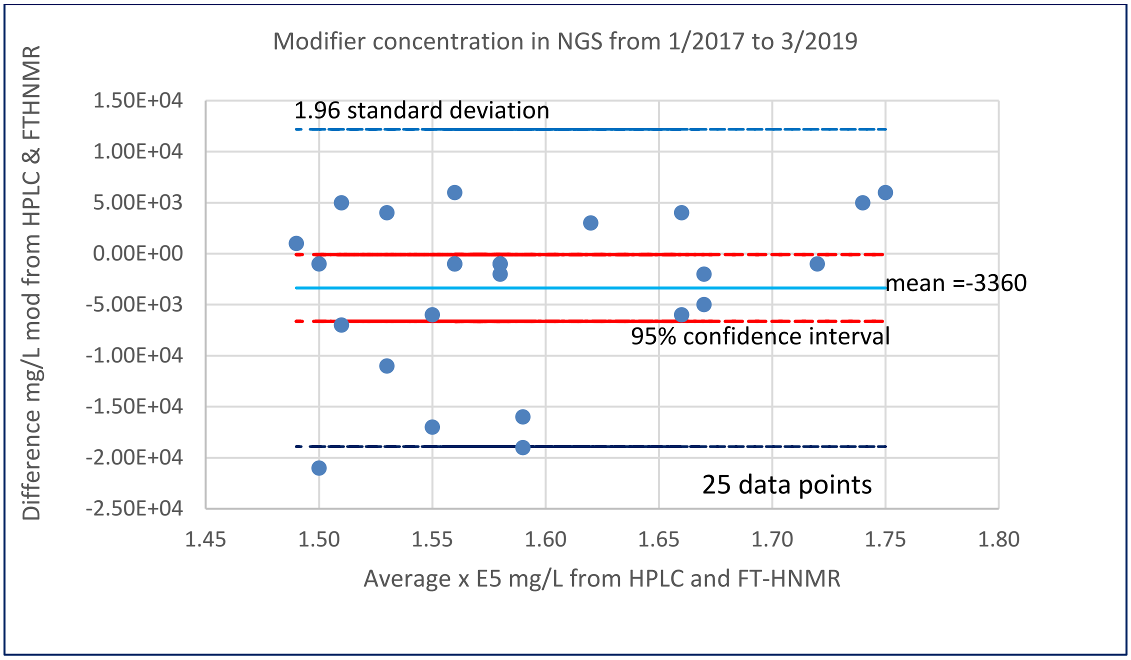


Figure A1. A comparison of the HPLC and FT-HNMR methods for measuring the Modifier.

Figure A1 shows the difference between the HPLC and the FT-HNMR results as a function of their average results. The confidence interval does not contain the number zero. Therefore, there is evidence of statistical differences between the methods. Also, the differences are not increasing or decreasing with the magnitude of the measurement. Figure A2 show the linear fitting and interval of the HPLC and FT-HNMR results that contain the unitary slope line. It shows that the unitary slope line is outside the 95% confidence interval indicating the two measuring methods are different at the 5% significance level.

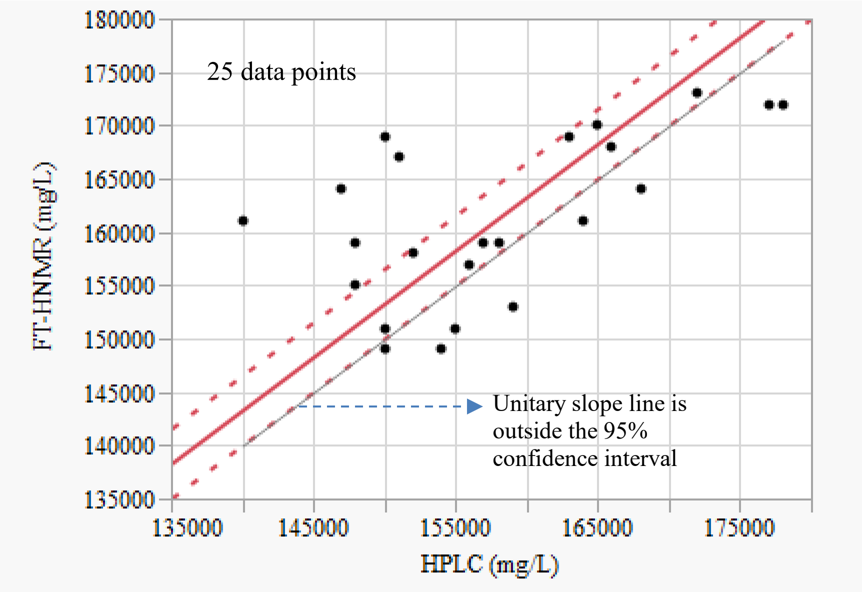
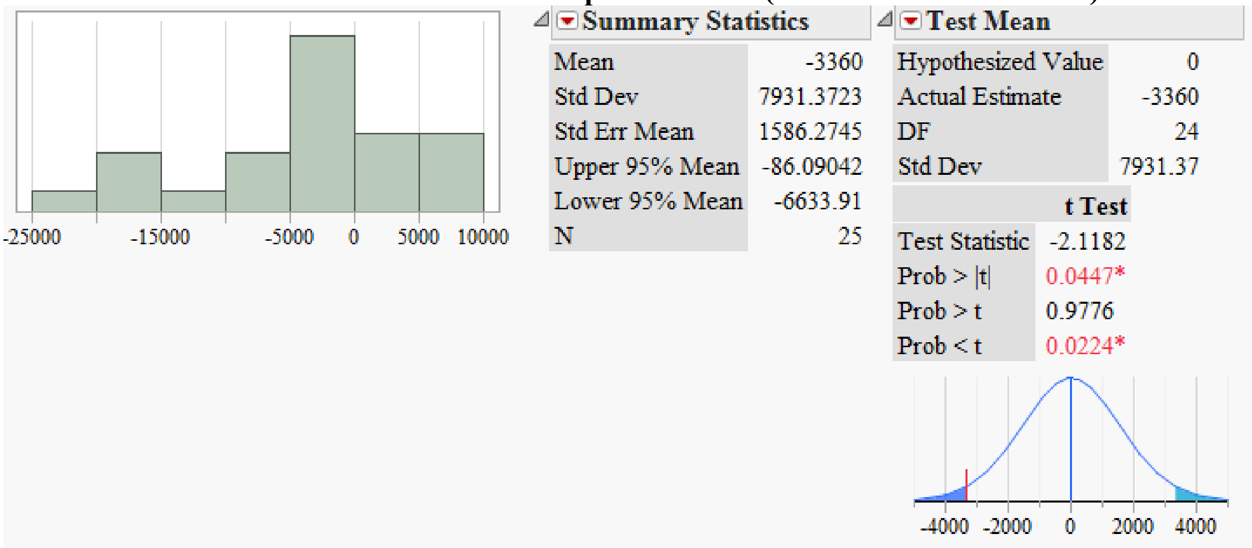


Figure A2. A regression fit between the FT-HNMR and HPLC data for the Modifier. Also shown the 95% confidence lines (broken lines). The unitary slope line is also shown and lies inside the confidence line.

Table A1 shows a different presentation of the statistical analysis of the HPLC and FT-HNMR results showing that their answers are statistically different at the 5% significance level.

Table A1. t-Test: Paired Two Sample for Means (HPLC versus FT-HNMR)



Summary Statistics

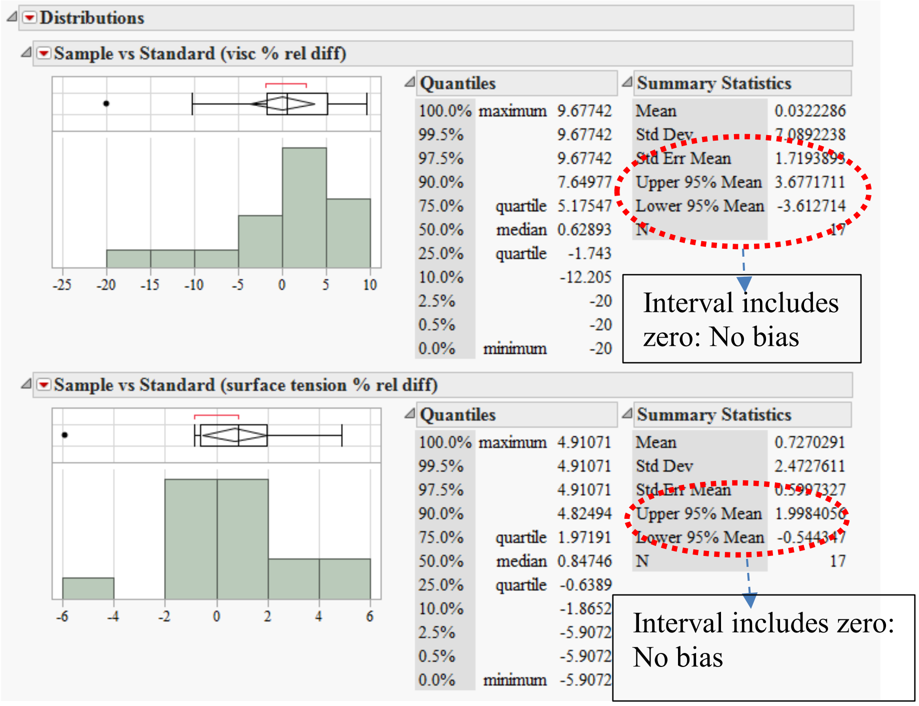
Mean	-3360
Std Dev	7931.3723
Std Err Mean	1586.2745
Upper 95% Mean	-86.09042
Lower 95% Mean	-6633.91
N	25

Test Mean

Hypothesized Value	0
Actual Estimate	-3360
DF	24
Std Dev	7931.37

	t Test
Test Statistic	-2.1182
Prob > |t|	0.0447*
Prob > t	0.9776
Prob < t	0.0224*

Figure A3 shows the 95% confidence interval (CI) of the viscosity and surface tension of the SHT samples relative to the control. The 95% CI of the relative viscosity measurements contain the zero number (indicating no difference with the control). Similarly, there is no evidence of bias in the relative surface tension measurements.



Sample vs Standard (visc % rel diff)

Quantiles		
100.0%	maximum	9.67742
99.5%		9.67742
97.5%		9.67742
90.0%		7.64977
75.0%	quartile	5.17547
50.0%	median	0.62893
25.0%	quartile	-1.743
10.0%		-12.205
2.5%		-20
0.5%		-20
0.0%	minimum	-20

Summary Statistics	
Mean	0.0322286
Std Dev	7.0892238
Std Err Mean	1.7193893
Upper 95% Mean	3.6771711
Lower 95% Mean	-3.612714
N	17

Interval includes zero: No bias

Sample vs Standard (surface tension % rel diff)

Quantiles		
100.0%	maximum	4.91071
99.5%		4.91071
97.5%		4.91071
90.0%		4.82494
75.0%	quartile	1.97191
50.0%	median	0.84746
25.0%	quartile	-0.6389
10.0%		-1.8652
2.5%		-5.9072
0.5%		-5.9072
0.0%	minimum	-5.9072

Summary Statistics	
Mean	0.7270291
Std Dev	2.4727611
Std Err Mean	0.5997327
Upper 95% Mean	1.9984056
Lower 95% Mean	-0.544347
N	17

Interval includes zero: No bias

Figure A3. Descriptive analysis of the relative difference (top is viscosity and the bottom are surface tension) between the SHT samples and the September 2018 scratch control sample.

Figure A4 shows the residuals (relative to their recommended levels) of the Modifier and MaxCalix and it shows a strong correlation between the two measurements.

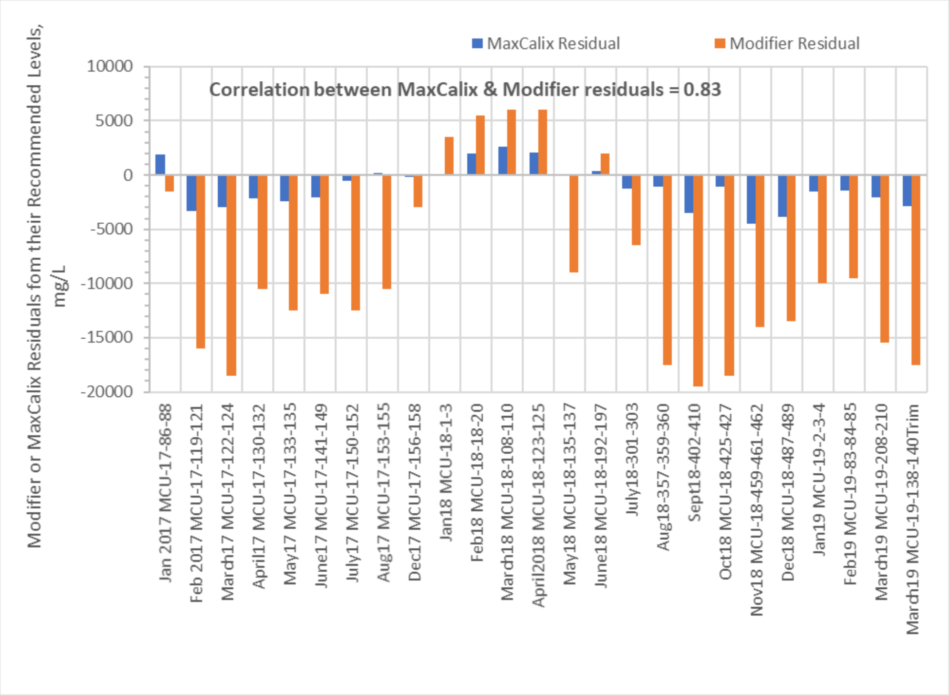


Figure A4. MaxCalix and Modifier residuals from their recommended levels

Figure A5 shows the 95% CI of the difference between the HPLC and FT-HNMR results for MaxCalix and its shows the two-measuring method are statistically different at the 5% significance level.

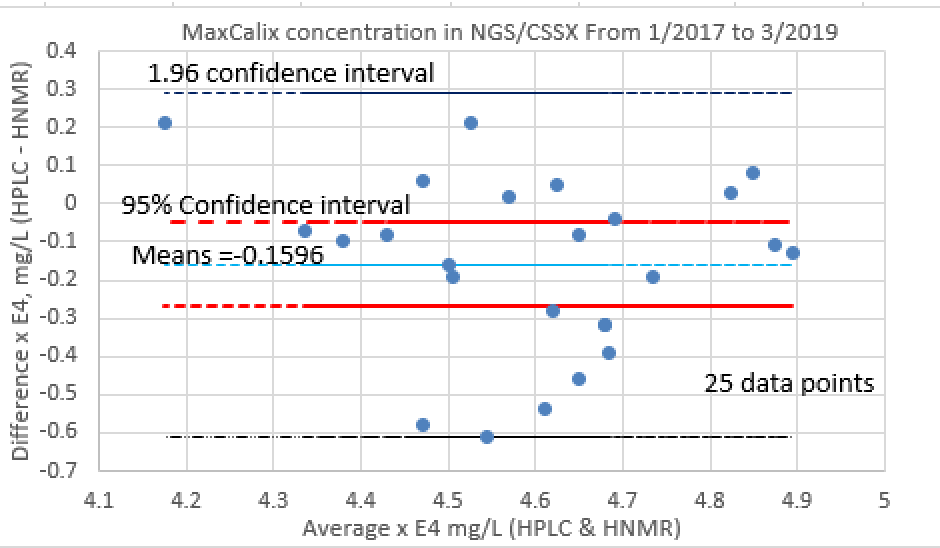
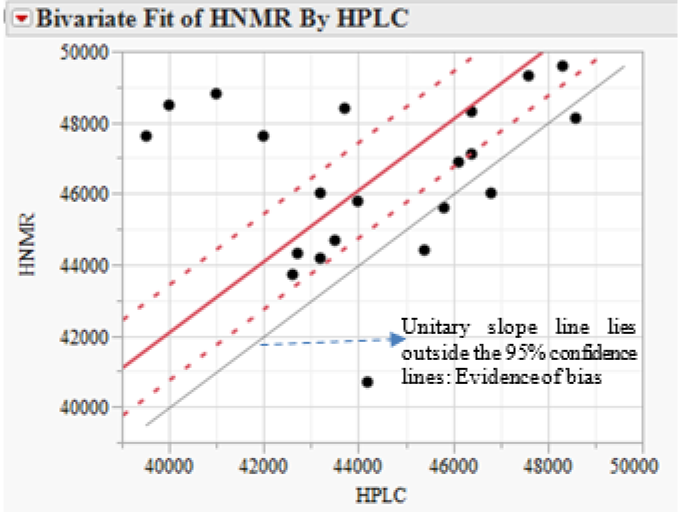


Figure A5. A comparison of the HPLC and FT-HNMR analytical methods for measuring MaxCalix.
The ordinate is the subtraction of the two methods and the coordinate is their average

Table A2 shows the t-statistics of the mean of the HPLC and FT-HNMR MaxCalix results showing a significant difference between the HPLC and FT-HNMR results (evidence for bias). Similarly, Figure A6 shows the linear fitting and corresponding 95% CI of the HPLC and FT-HNMR results that doesn't include the unitary slope line (evidence for bias).

Table A2. t-Test: Paired Two Sample for Means of MaxCalix (HPLC versus FT-HNMR)

	FT-HNMR	*HPLC*
Mean *(mg/L)*	4.68E+04	4.52E+04
Variance	4.78E+06	3.85E+06
Observations	25	25
Pearson Correlation	0.390	
Hypothesized Mean Difference	0	
df	24	
t Stat	3.471	
P(T<=t) one-tail	0.001	*Significant*
t Critical one-tail	1.711	
P(T<=t) two-tail	0.002	*Significant*
t Critical two-tail	2.064	



Unitary slope line lies outside the 95% confidence lines: Evidence of bias

Figure A6. 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.

Table A3 shows the t-statistical analysis of the total mercury results obtained by DMA and XRF. The low probability is evidence of a significant difference between the two tests for the same samples at the 5% significance level.

Table A3. t-Test: Paired Two Sample for Means. DMA versus XRF for mercury.

	XRF	*DMS*
Mean *(ug/g)*	32.2	27.6
Variance	20.6	21.6
Observations	12	12
Pearson Correlation	0.345	
Hypothesized Mean Difference	0	
df	11	
t Stat	3.020	
P(T<=t) one-tail	0.006	► *Significant*
t Critical one-tail	1.796	
P(T<=t) two-tail	0.012	► *Significant*
t Critical two-tail	2.201	

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 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 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
Savannah River Nuclear Solutions
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Aiken, SC 29808
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