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Solvent Hold Tank Sample Results for MCU-16-348-349-350: March 2016 Monthly Sample

F. F. Fondeur
D. H. Jones

May 2016
SRNL-STI-2016-00265, Revision 0

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-16-348-349-350), pulled on 03/30/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-348-349-350 indicated the Isopar™L concentration is above its nominal level (101%). The modifier (CS-7SB) and the TiDG concentrations are 9% and 55 % 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™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 21.6 ± 4 micrograms of mercury per gram of solvent (or 18.3 µg/mL) was detected in this sample (as determined by the cold vapor atomic adsorption spectrometry (CVAA) method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in salt batch 8 (Tank 49H).

The current gamma level (1.11E5 dpm/mL) confirmed that the gamma concentration has returned to previous level (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(*tert*-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-*alt*-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	*N*,*N’*,*N”*–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.[1] On March 30 2016, Operations personnel pulled and delivered three samples from the SHT (MCU-16-348, MCU-16-349, and MCU-16-350) 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[2] 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 November 28, 2015, a trim addition was made to MCU that was 10.02 E3 grams of modifier and 765 grams of TiDG in 18.6 gallons of Isopar™L.

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

Event	Date
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™L added to MCU	March 6, 2015
9 gallons of Isopar™L added to MCU	March 13, 2015
SHT sample MCU-15-2726-2727-2728	March 16, 2015
SHT sample MCU-15-661-662-663	May 2, 2015
10 gallons of Isopar™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
October solvent trim added to MCU	October 28, 2015
SHT sample MCU-15-815-816-817-818-819-820	November 29, 2015
14 gallons of Isopar™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 26, 2016
SHT sample MCU-16-270-271-272	February 21, 2016
12 gallons of Isopar™L added to MCU	March 6, 2016
SHT sample MCU-16-348-349-350	March 30, 2016
10 gallons of Isopar™L added to MCU	March 31, 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-16-348, MCU-16-349, and MCU-16-350 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[2]

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™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-16-348, MCU-16-349, and MCU-16-350) 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-16-348-349-350). Table 3-1 contains the results for the MCU-16-348-349-350 composite sample.

Isopar™ L and Modifier Levels

A density measurement of the sample gave a result of 0.8312 g/mL (0.03% RSD) (or 0.8269 g/mL at 25°C when corrected for temperature using the CSSX temperature correction formula)[3] for MCU-16-348-349-350 at 20 °C. The calculated density (0.827 g/mL) for MCU-16-348-349-350 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).[2] Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be slightly above its nominal value (within analytical uncertainties) and the modifier concentration should be slightly below its nominal value.

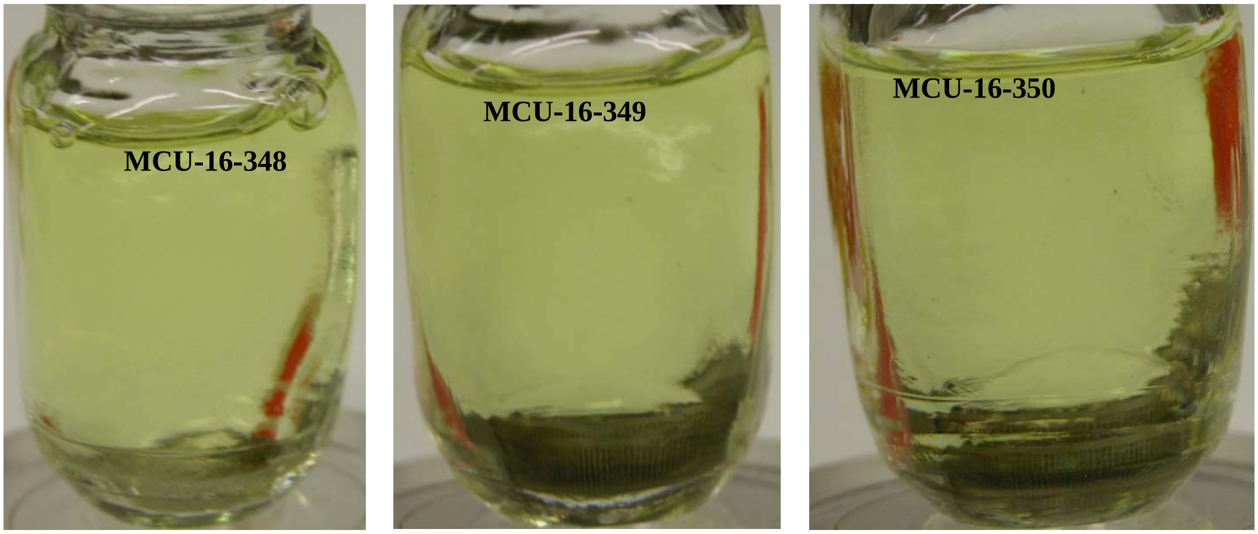

Figure 1. Typical appearance of the three MCU-16-348, MCU-16-349, and MCU-16-350

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 (9% 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 Isopar™L trim addition to MCU was on December 21, 2015.

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). Please note that the HPLC method reported a modifier concentration near its nominal level. We believe the current HPLC reported value is slightly biased high. Looking at Fig.2, the modifier level appears to trend up and down possibly reflecting randomness in 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 0.831 ± 0.019 g/mL. Their sum is consistent with the measured and temperature corrected (to 25 ºC) value of 0.827 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-16-348-349-350

Analysis	Method	LW-AD-Proj-160412-4	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.29E+05	6.23E+05	101
Isopar® L	FT-IR	NA	6.30E+05		101
Isopar® L	Density	NA	6.30E+05		101
Average[$]	All	NA	6.30E+05	6.23E+05	101
Modifier	HPLC	715	1.65E+05	1.69E+05	98
Modifier	FT-HNMR	NA	1.59E+05		94
Modifier	FT-IR	NA	1.55E+05		92
Modifier	Density	NA	1.51E+05		90
Average[$]	All	NA	1.53E+05	1.69E+05	91
TiDG[♠]	Titration	NA	6.42E+02	1.44E+03	45
Average[$]	All	NA	6.42E+02	1.44E+03	45
trioctylamine	Titration	NA	2.70E+02	5.30E+02	51
Average[$]	All	NA	2.70E+02	5.30E+02	51
MaxCalix	HPLC	715	4.42E+04	4.44E+04	100
MaxCalix	FT-HNMR	NA	4.66E+04		105
Average[$]	All	NA	4.50E+04	4.44E+04	101
BOBCalixC6	HPLC	715	2.92E+03	4.03E+03	72
Average[$]	All	NA	2.92E+03	4.03E+03	72
Density (g/mL)	Direct Measurement	NA	0.8269	0.835	99

[#] 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™ 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.

[$] Reported value for a MCU component is the weighted average of the values reported by the techniques that measured that component.

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

[♠] No TiDG value was estimated by FT-HNMR due to an aged (questionable) standard.

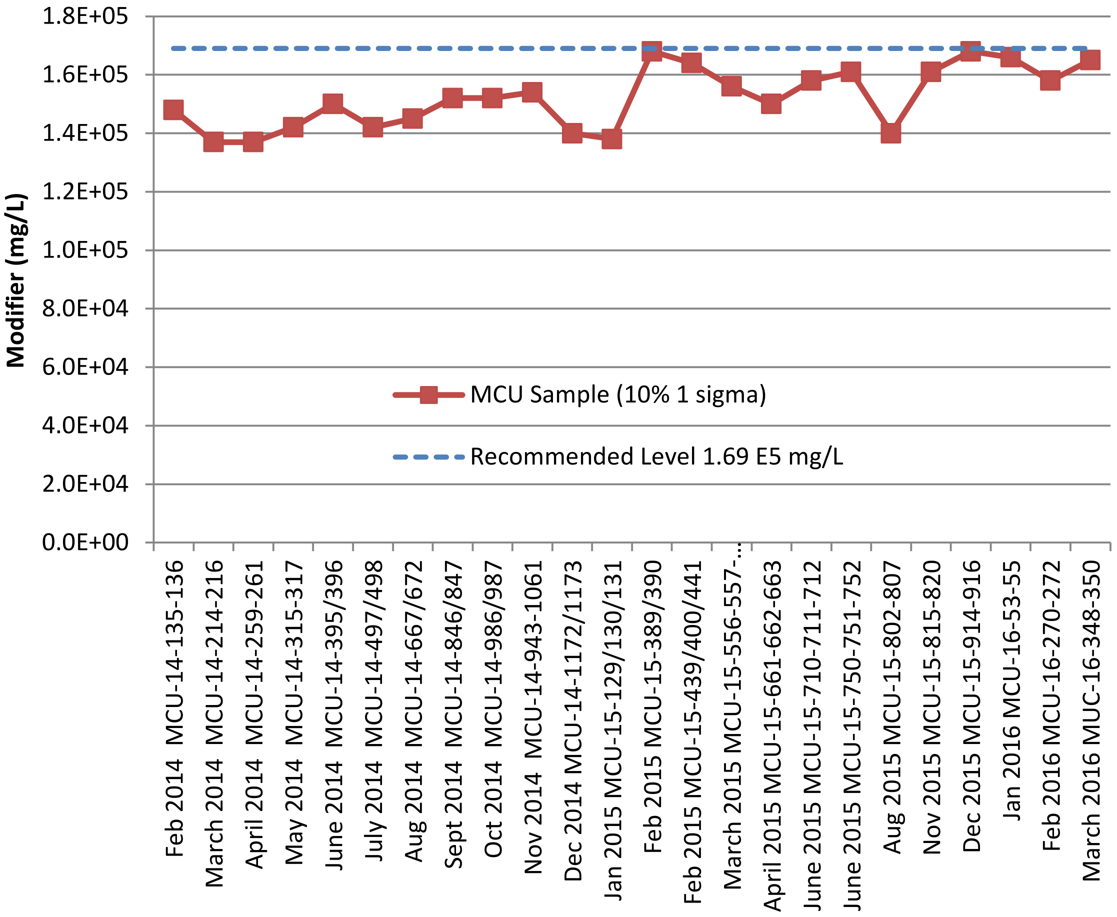

Figure 2 Modifier level in the solvent as measured by HPLC (one sigma is 10%).

Suppressors Levels

The average TiDG concentration level (6.42 ± 0.6 E2 mg/L) is at 45 % of its nominal value of 1440 mg/L confirming the continued depletion of the trim addition to the solvent done in December 2015 (a noticeable spike in the TiDG concentration level was observed in Fig. 3). 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-16-348-349-350 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 May 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 fluctuate and it is currently at 270 ± 38 mg/L (in the previous sample the TOA level was at 248 mg/L). The difference between this and last month measurement is within analytical error. After the second TiDG addition to the solvent in October 2014, the TOA concentration has fluctuated from 300 to 250 mg/L (see Fig. 3). 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.[4] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.[5]

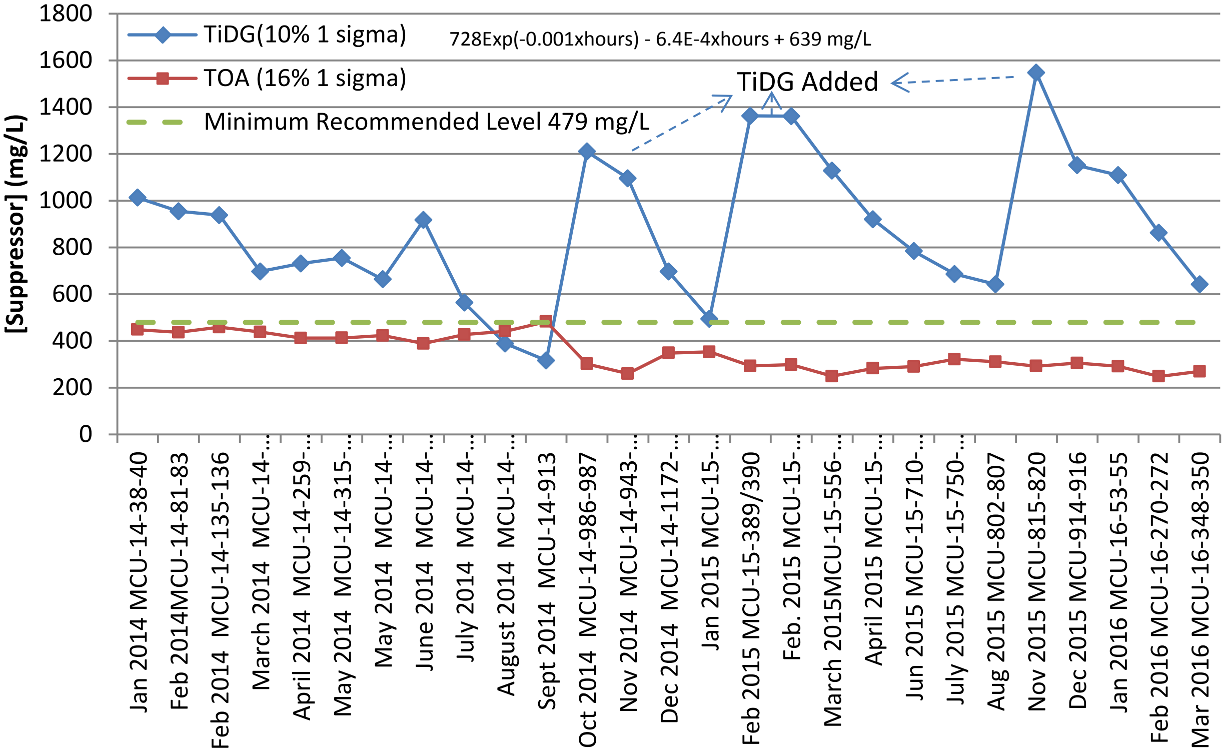

Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.

Extractant Levels

The average calculated MaxCalix level is 4.50E4 mg/L (±10%) and it is at its nominal value. The sudden drop in the MaxCalix concentration in the previous month relative to the current measurement is probably due to analytical variance (see Figure 4). However, the current MaxCalix concentration level is consistent with its historical trend (Fig. 4). The residual concentration of BOBCalixC6 level is currently at 72% 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, it can’t be explained at this time the constancy of the BOBCalixC6 concentration in the solvent.

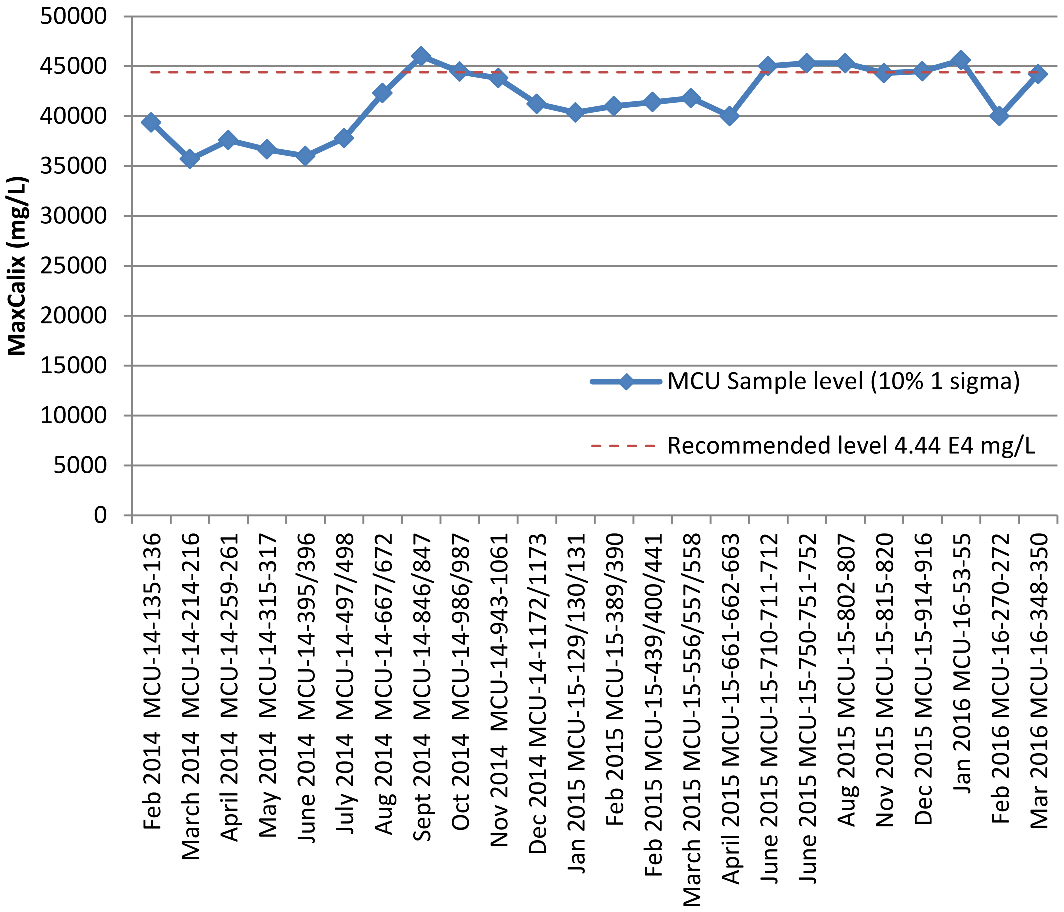

Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

Gamma Level

The gamma measurement of MCU-16-348-349-350 is 1.11E5 dpm/mL (±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 (with the exception of the Gamma counts from the February 2016 sample that is under further re-evaluation). It confirms the steady state trend level observed since June 2015 (see Fig. 5).

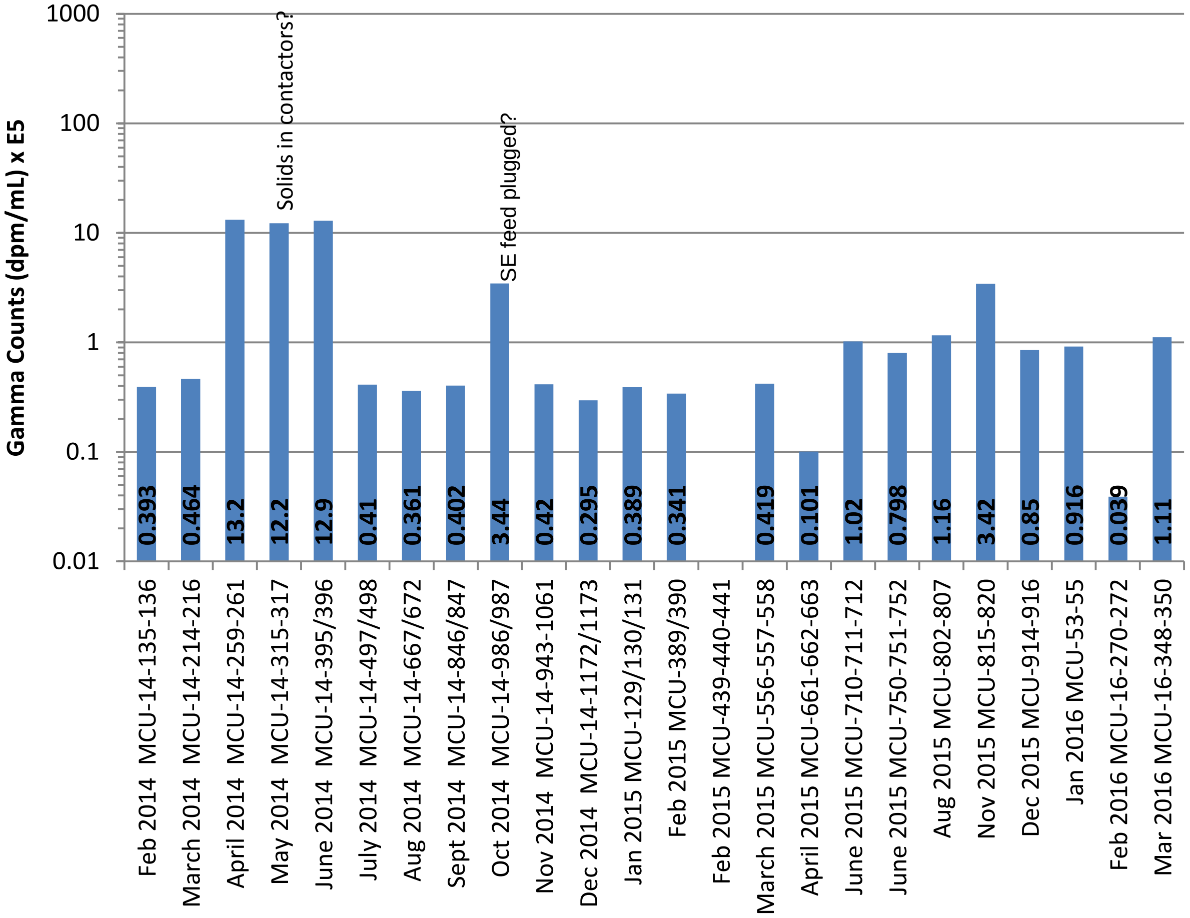

Figure 5. The gamma count of selected SHT samples. One standard deviation is 5%.

Impurities

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

A few mL of MCU-16-348-349-350 was digested and analyzed for total mercury by the CVAA method. The total mercury concentration was 21.6 ± 4.1 ug/g$_{solvent}$ (or 18 ±3.4 ug/mL$_{solvent}$). The XRF method detected 12.1 ± 2.4 ug/g$_{solvent}$ mercury (or 10.0 ug/mL$_{solvent}$ at 25°C) of the undigested MCU-16-348-349-350 sample.

The nature of the discrepancy between the CVAA and XRF results is under further investigation. Regardless of which result is true, this level of mercury is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm)[6] 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.[7] For 200 gallons of solvent (757.1 L) and assuming a density of 0.8291 g/mL, the solvent could contain a total of 14 ± 2 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).

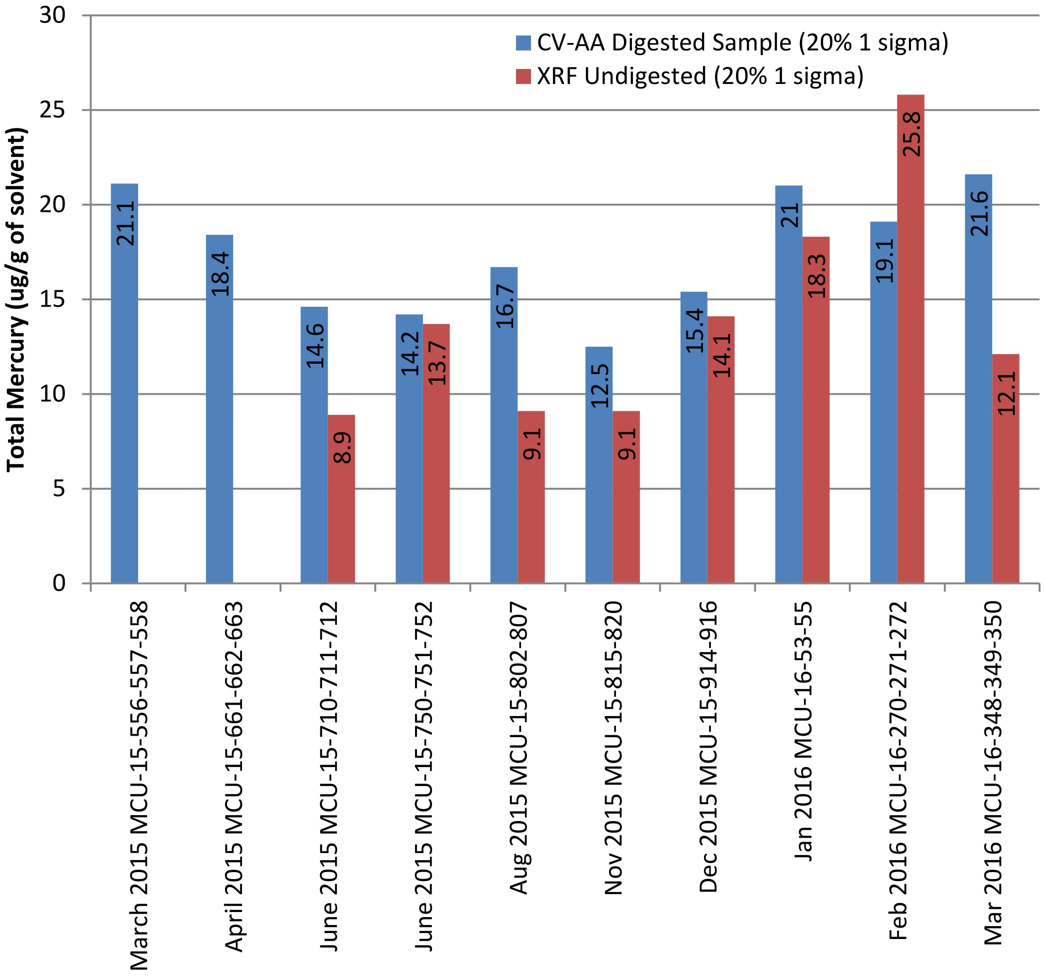

Figure 6. Total mercury in recent SHT samples. One standard deviation is 20%. CVAA = Cold Vapor Atomic Absorption Spectrometry. XRF =X-ray Fluorescence (20% one sigma).

Recommendations

The current analysis indicates the solvent has a lower modifier (91% of its nominal concentration) and TiDG (55%) levels, but it has slightly higher levels of Isopar™L (101%) relative to the standard. The lower MaxCalix concentration observed in the February 2016 sample was due to analytical measurement fluctuations. The TiDG, MaxCalix and Isopar™L levels are expected to trend downward with time. 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 March sample results, there is no need to add MaxCalix to the solvent at this time.

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-16-348-349-350), pulled on 03/30/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-348-349-350 indicated the Isopar™L concentration is above its nominal level (101%). The modifier (CS-7SB) and the TiDG concentrations are 9% and 55 % 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™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 SVOA. No impurities were observed in the HNMR. However, up to 21.6 ± 4 micrograms of mercury per gram of solvent (or 18.3 µg/mL) was detected in this sample (as determined by the CVAA method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in salt batch 8 (Tank 49H).

The current gamma level (1.11E5 dpm/mL) confirmed that the gamma concentration has returned to previous level (about the same gamma counts of the samples from late 2015) 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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