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Solvent Hold Tank Sample Results for MCU-16-53-54-55: January 2016 Monthly Sample

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March 2016

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-16-53-54-55), pulled on 01/25/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-53-54-55 indicated the Isopar™L, and MaxCalix are at nominal levels. The modifier and TiDG concentrations are 3% and 23 % below their nominal concentrations. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent on November 28, 2015. 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, the Fourier transform infra-red spectroscopy (FTIR) method detected trace levels (a few ppm) of amides (a possible degradation product of TiDG). In addition, up to 21 ± 4 micrograms of mercury per gram of solvent (or 17.5 µg/mL) was detected in this sample. There appears to be a possible correlation between the mercury level and the TiDG concentration in the solvent.

The current gamma level (9.16 E4 dpm/mL) confirmed that the gamma concentration has returned to previous level 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)
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 January 26, 2016, Operations personnel pulled and delivered three samples from the SHT (MCU-16-53, MCU-16-54, and MCU-16-55) 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-15-556-557-558	March 16, 2015
SHT sample MCU-15-661-662-663	April 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

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-16-53, MCU-16-54, and MCU-16-55 were composited before use. Aliquots of the composited sample were removed to perform the following analysis: Density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, cold vapor atomic adsorption spectrometry (CVAA), X-ray fluorescence (XRF), and Fourier-Transformed Hydrogen Nuclear Magnetic Resonance (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[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-16-53, MCU-16-54, and MCU-16-55) was visually examined. MCU-16-55 was found to contain a single phase liquid with no apparent solids contamination or cloudiness while minute aqueous droplets were found on the walls of the p-nut vials from sample MCU-16-53 and MCU-16-54. Also a large water droplet was found in MCU-16-53 and it was removed. The water droplets on the walls of the p-nut vials (MCU-16-53 and MCU-16-54) were not considered to compromise the quality of the solvent since these droplets were immiscible in the solvent and remained on the walls after the emptying the p-nuts vial. 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-16-53-54-55). Table 3-1 contains the results for the MCU-16-53-54-55 composite sample.

Isopar™ L and Modifier Levels

A density measurement of the sample gave a result of 0.8348 g/mL (0.03% RSD) (or 0.8327 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-16-53-54-55 at 21 °C. The calculated density (0. 8327 g/mL) for MCU-16-53-54-55 is less than 1% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory)[i]. 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.

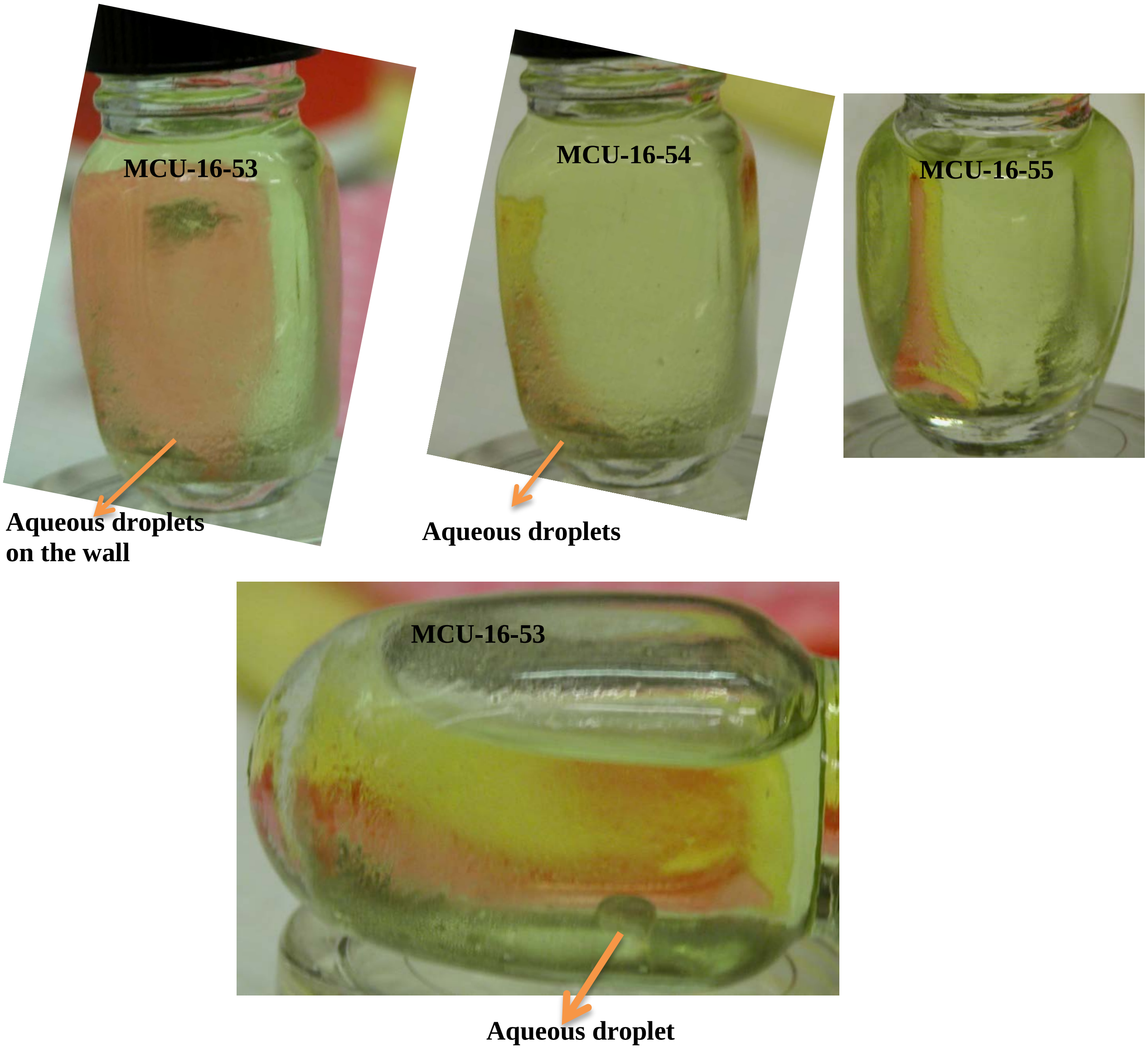

Figure 1. Typical appearance of the three MCU-16-53, MCU-16-54, and MCU-16-55

An examination of Table 3-1 shows that the Isopar™ L concentration is at its nominal value while the modifier concentration is correspondingly slightly lower (3% 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 in December 2015.

All measurements indicate the Isopar™ L level is at its nominal value while the modifier concentration level is below its nominal value (see Fig. 2 for recent modifier concentrations from HPLC measurements). 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 0.835 ± 0.019 g/mL. Their sum is consistent with the measured and temperature corrected (to 25 °C) value of 0.832 g/mL, and also with the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL).

Table 3-1 Sample Results for MCU-16-53-54-55

Analysis	Method	LIMS #	Result (mg/L)[#,Δ]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.31E+05	6.23E+05	101
Isopar® L	Density	NA	6.20E+05		100
Average[$]	All	NA	6.21E+05	6.23E+05	100
Modifier	HPLC	300320724	1.66E+05	1.69E+05	98
Modifier	FT-HNMR	NA	1.60E+05		95
Modifier	Density	NA	1.64E+05		97
Average[$]	All	NA	1.64E+05	1.69E+05	97
TiDG[♠]	Titration	NA	1.11E+03	1.44E+03	77
Average[$]	All	NA	1.11E+03	1.44E+03	77
trioctylamine	Titration	NA	2.91E+02	5.30E+02	55
Average[$]	All	NA	2.91E+02	5.30E+02	55
MaxCalix	FT-HNMR	NA	4.44E+04	4.44E+04	100
MaxCalix	HPLC	300320724	4.63E+04		104
Average[$]	All	NA	4.56E+04	4.44E+04	103
BOBCalixC6	HPLC	300320724	3.00E+03	4.03E+03	74
Average[$]	All	NA	3.00E+03	4.03E+03	74
Density (g/mL)	Direct Measurement	NA	0.8327	0.835	100

[#] 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%.

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

[$] $x = \frac{\Sigma_1^i \left(x_i / \delta_i^2 \right)}{\Sigma_1^i \left(1 / \delta_i^2 \right)}$; 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.

[Δ] Isopar™L may have evaporated during the sample preparation for FTIR. Thus, FTIR data was excluded from the final results.

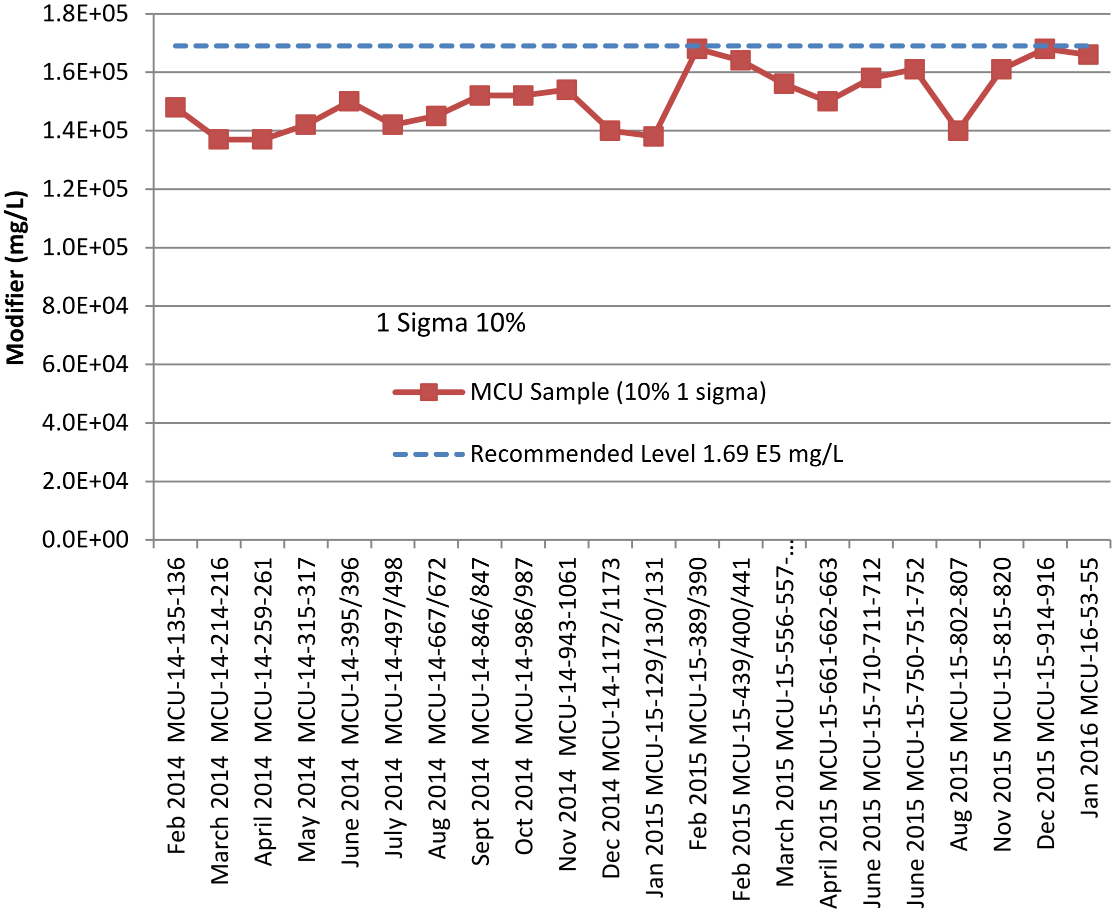

Figure 2 Modifier level in the solvent as measured by HPLC (one sigma is 10%).

Suppressors Levels

The average TiDG concentration level (1.11 ± 0.1 E3 mg/L) is at 77 % 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-16-53-54-55 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 auto-decomposition and phase transfer to the aqueous phases (salt solution and boric acid). The TOA concentration appears to have decreased slightly 291 ± 46 mg/L (in the previous sample the TOA level was at 305 mg/L). The difference between this and last month measurement is within analytical error. Looking at the slope of the TOA concentration data, it appears to trend upwards with time after the trim addition (TiDG). The TOA's concentration level trend appears to anti-correlate with the TiDG's concentration level trend (or the disappearance of Isopar™ L due to evaporation). This anti-correlation is believed to be due to the combined effects of titration of TiDG's decomposition products, dilution effects from the trimming, and to the evaporation of Isopar™ L. Since MCU no longer adds TOA, a drop in TOA concentration is expected with time. The drop in the TOA concentration level, right after the trim addition, is possibly due to the dilution effect of the trim (see Fig. 3). Based on previous historical trends the TOA concentration is expected to increase. The increase is perhaps due to TiDG degradation into primary amines, which have previously been identified as degradation products of the suppressor when heated.[3] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.[4]

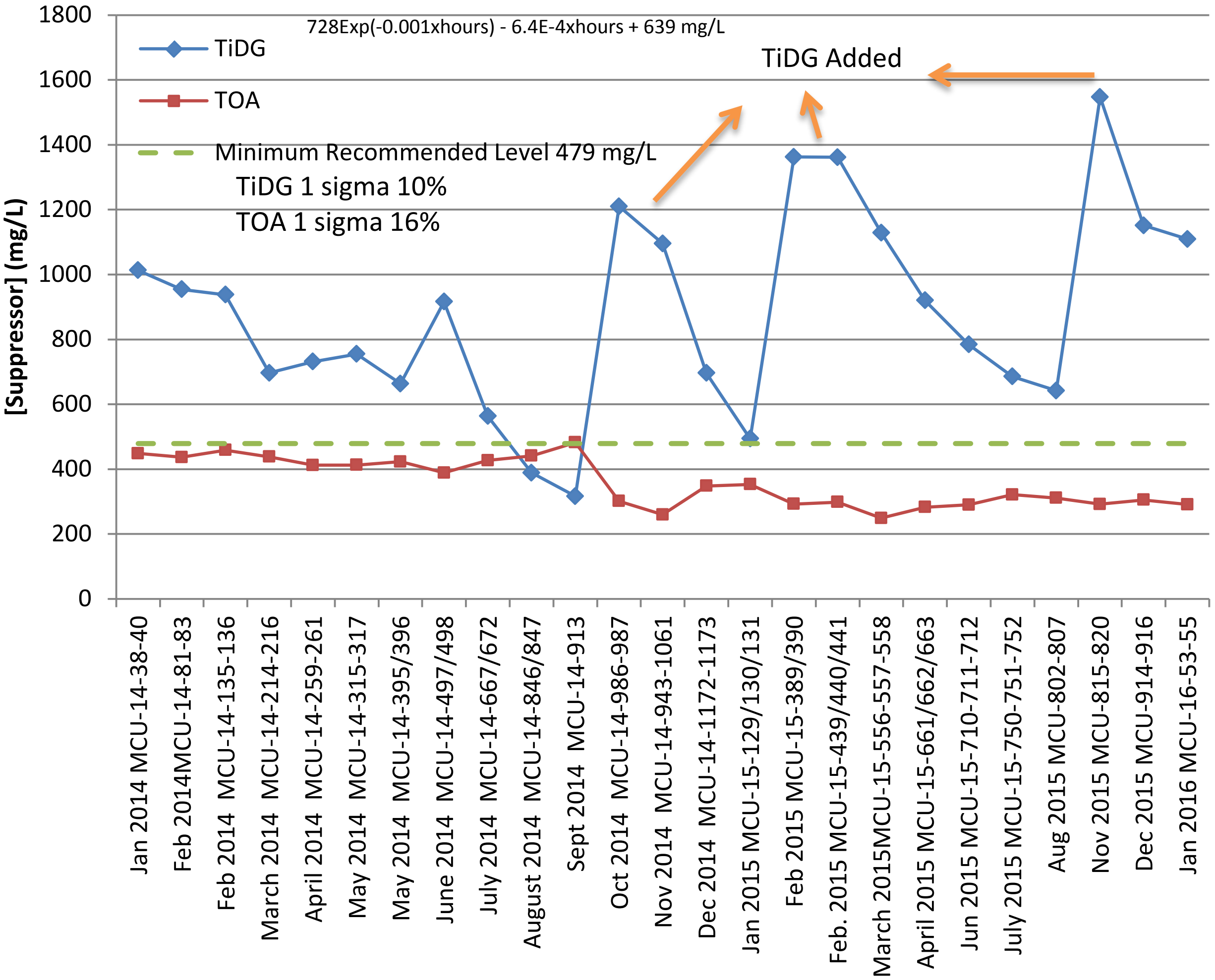

Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.

Extractant Levels

The average MaxCalix level is 4.56E4 mg/L (±10%) and it is 3% above its nominal value. The MaxCalix concentration has remained steady in the past 5 monthly samples (see Figure 4). The residual concentration of BOBCalixC6 level is currently at 74% of the level measured when the NGS was implemented in late FY13. 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.

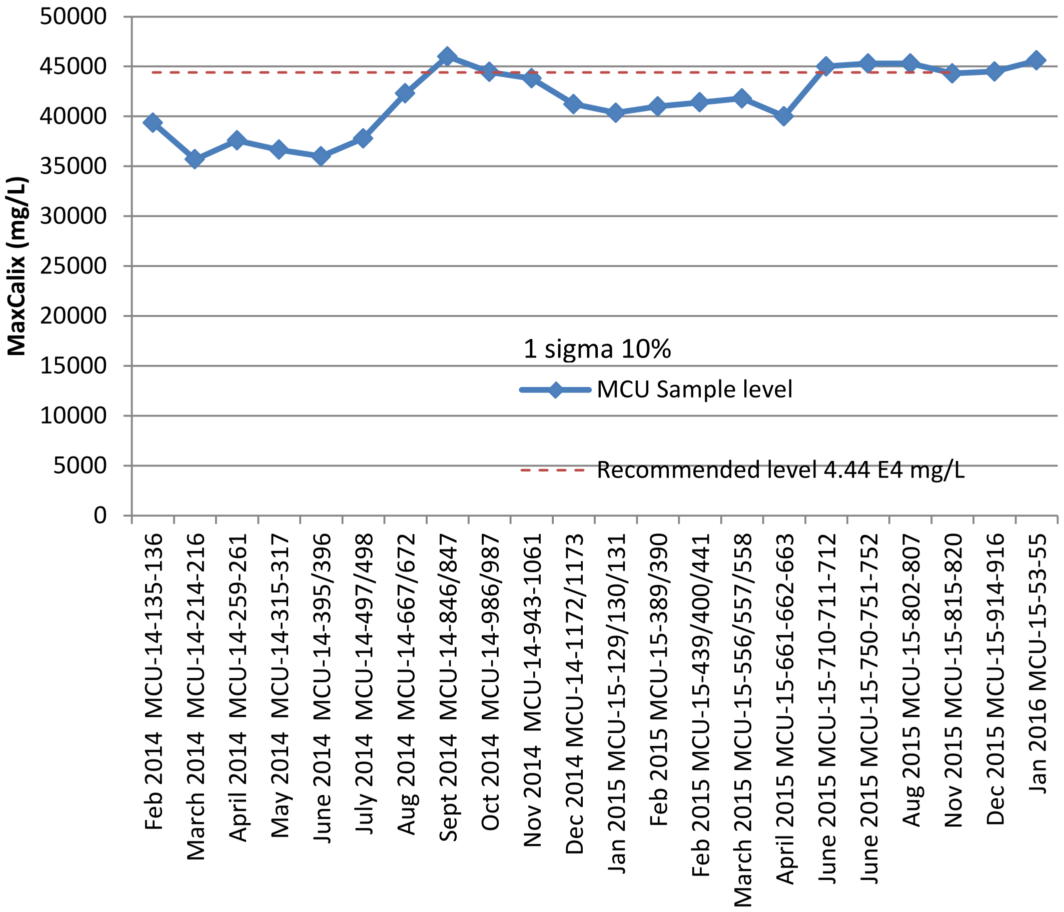

Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

Gamma Level

The gamma measurement of MCU-16-53-54-55 is 9.16E4 dpm/mL (±5%). This level of activity is consistent with the previous gamma levels when the process was operating normally in early 2015. It confirms the end of the upward trend observed in the June through November 2015 samples (see Fig. 5).

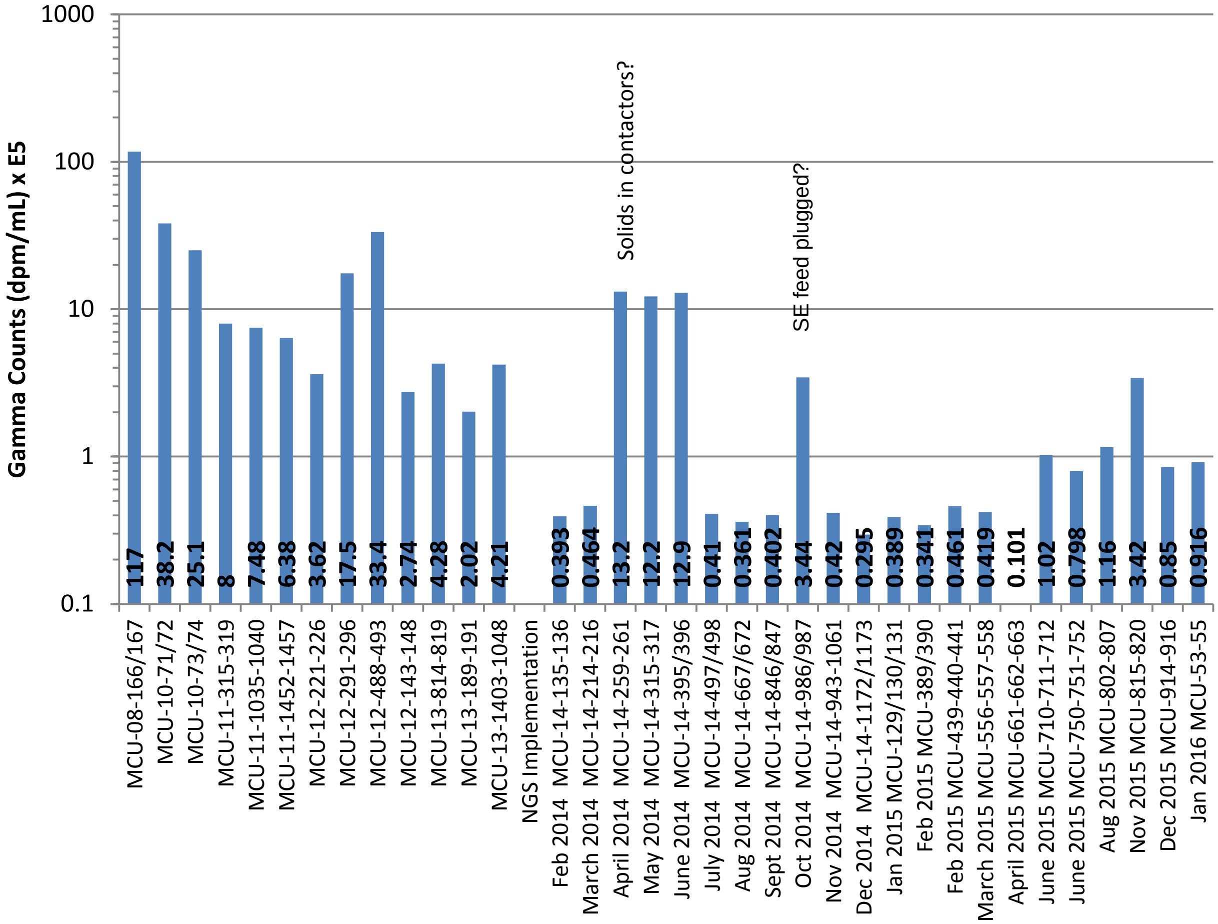

Figure 5. The gamma count of selected SHT samples. One standard deviation is 5%.

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. However, evidence of amides (RCO-NHR) in this sample after subtracting the scratch solvent spectrum (see Fig. 6). The amides may be a degradation byproduct from TiDG. The frequent addition of TiDG (see Fig. 3) is possibly raising the TiDG's decomposition products in the solvent.

A few mL of the blended solvent was digested and analyzed for mercury (by the cold vapor method and the XRF method). The CV-AA method detected 21 ug/$g_{solvent}$ mercury (or 17 ug/$mL_{solvent}$) while the XRF method detected a similar total mercury level of 22.7 µg/$g_{solvent}$ (20% st. dev.) in this solvent. This level of mercury is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm)[5] 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.[6] For 200 gallons of solvent (757.1 L) and assuming a density of 0.8327 g/mL, the solvent could contain a total of 13 ± 3 g of mercury. A comparison of this measurement with previous month data is shown in Fig. 7. Based on the Mercury

XRF data, there appears to be a possible correlation between the concentration of TiDG and the concentration of mercury in the solvent. A negative correlation was observed between the [Hg] and the [TiDG] of the samples starting with MCU-15-815/820 and ending with MCU-15-5/55. The positive trend in the mercury concentration can also be due to an increase in the mercury concentration of salt batch 8 (Tank 49H).

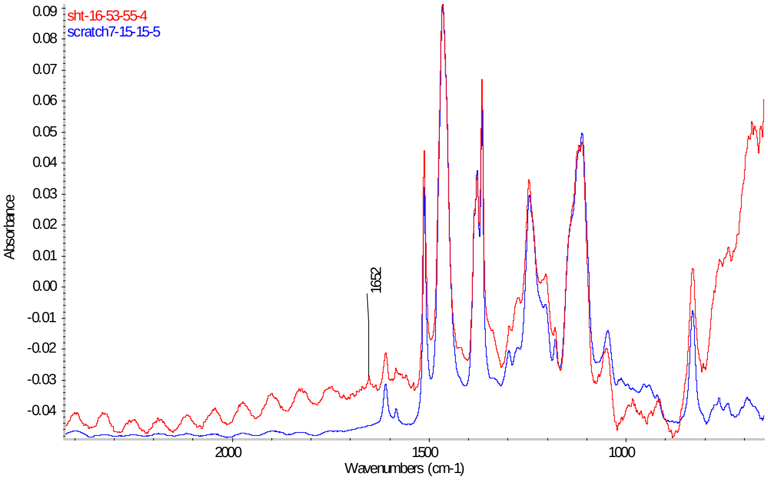

Figure 6. Possible amide presence in the solvent

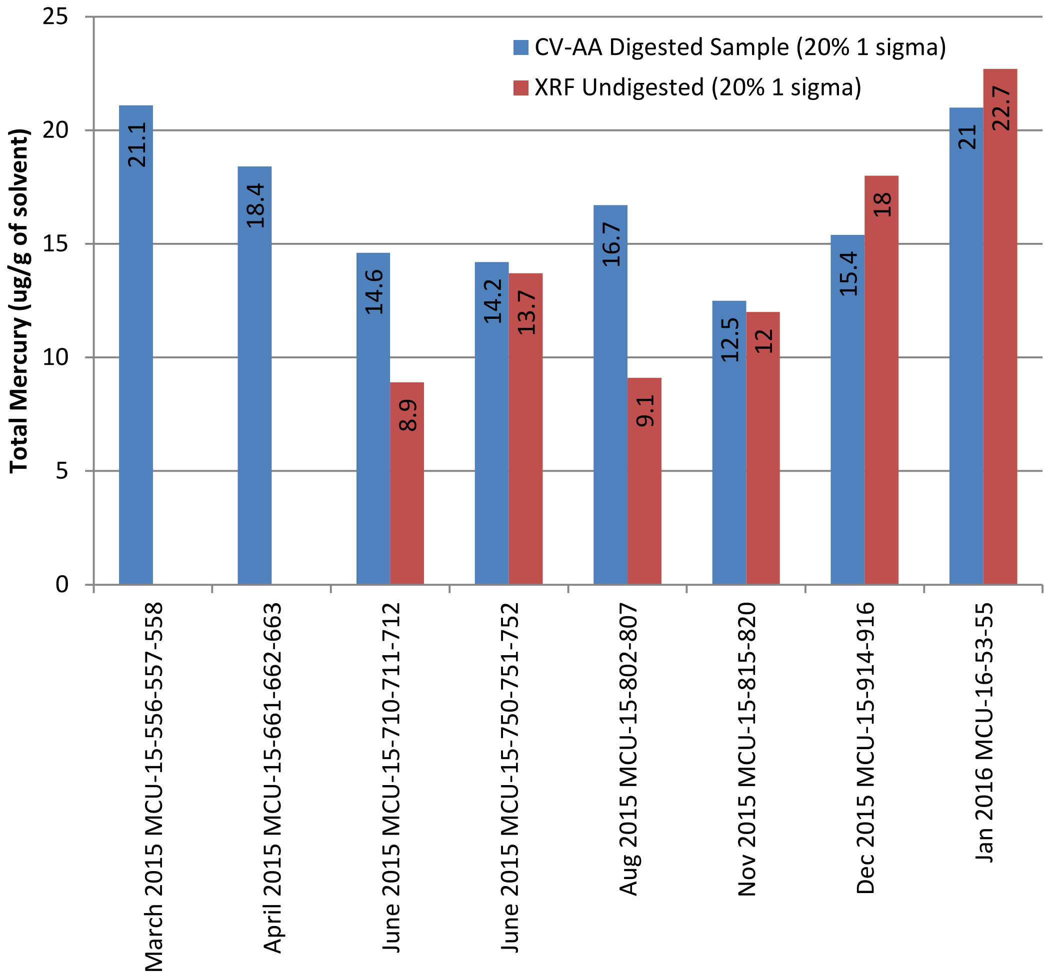

Figure 7. Total mercury in recent SHT samples. One standard deviation is 20%. CVAA = Cold Vapor Atomic Absorption Spectrometry. XRF =X-ray Fluorescence (20% one sigma).

Recommendation

The current analysis indicates the solvent has a slightly lower modifier (3%) and TiDG (23%) levels, but it has nominal levels of Isopar™L and MaxCalix relative to the standard. 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.

4.0 Conclusions

SRNL received one set of SHT samples (MCU-16-53-54-55), pulled on 01/25/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-53-54-55 indicated the Isopar™L, and MaxCalix are at nominal levels. The modifier and TiDG concentrations are 3% and 23 % below their nominal concentrations. This analysis confirms the addition of TiDG, MaxCalix, and modifier to the solvent in November 2015. 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, the FTIR method detected trace levels (a few ppm) of amides (a possible degradation product of TiDG). In addition, up to 21 ± 4 micrograms of mercury per gram of solvent (or 17.5 µg/mL) was detected in this sample (as determined by the CV-AA method). There appears to be a correlation between the mercury level and the TiDG concentration in the solvent.

The current gamma level (9.16 E4 dpm/mL) confirmed that the gamma concentration has returned to previous level 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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