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Solvent Hold Tank Sample Results for MCU-16-1488-1493 (December 2016), MCU-17-86-88 (January 2017), and MCU-17-119-121 (February 2017): Quarterly Report

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July 2017
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EXECUTIVE SUMMARY

A trend summary of three Solvent Hold Tank (SHT) monthly samples; MCU-16-1488-1493 (December 2016), MCU-17-86-88 (January 2017), and MCU-17-119-121 (February 2017) are reported. Analyses indicate that the modifier (CS-7SB) and the extractant (MaxCalix) concentrations are at their nominal recommended levels (169,000 mg/L and 46,300 mg/L respectively). The suppressor (TiDG) level has decreased to a steady state level of 673 mg/L well above the minimum recommended level (479 mg/L).

This analysis confirms the Isopar™ addition to the solvent in January 18, 2017. This analysis also indicates the solvent did not require further additions. 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). Another impurity observed in the samples was mercury. Up to 38 ± 8 micrograms of mercury per mL of solvent was detected in these samples (the average of the CV-AA 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 8 and 9 (Tank 49H) or mixing of previously undisturbed areas of high mercury concentration in Tank 49H.

The gamma level (0.21E5 dpm/mL) measured in the February SHT sample was one order of magnitude lower than the gamma levels observed in the December and January SHT samples. The February gamma level is consistent with the solvent being idle (since January 10, 2017). The gamma levels observed in the December and January SHT samples were consistent with previous monthly measurements where the process operated normally.

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, NGS
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) 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 BOBCalixC6 and trioctylamine (TOA). SHT samples are sent to SRNL to examine solvent composition changes over time.[1] With the exception of Isopar™L which is added to the SHT approximately on a monthly basis due to its high vapor pressure, this report shows the cumulative chemical composition data, including impurities like mercury, of three different SHT samples: MCU-16-1488-1493 (6 p-nuts vials) [December 2016 sample], MCU-17-86-87-88 (January 2017 sample), and MCU-17-119-120-121 (February 2017 sample). A summary report for each of the SHT sample was issued earlier.[2,3,4] MCU-17-119-120-121 was collected after MCU halted operations (January 10, 2017).

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[5] and heel solvent) was prepared in the lab (July 2016) 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 January 2017, an isopar™L addition was made to MCU.[6]

Table 2-1 Log of recent trims to the MCU solvent and SHT sampling dates

Event	Date
20 gallons solvent trim added to MCU	November 8, 2016
11 gallons Isopar™L added to MCU	November 12, 2016
SHT sample MCU-16-1363-1364-1365	November 15, 2016
SHT sample MCU-16-1488-1493 (6 p-nut vials)	December 4, 2016
51 gallons solvent trim added to MCU	December 14, 2016
15 gallons Isopar™L added to MCU	December 27, 2016
SHT sample MCU-17-86-87-88	January 9, 2017
18 gallons of Isopar™L added to MCU	January 18, 2017
SHT sample MCU-17-119-120-121	February 21, 2017

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. The p-nut vials for each monthly sample (SHT) 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[5]~~[2]~~

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	~1440	~ 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 a NGS-CSSX blend formulation.

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 (and its corresponding p-nut vial) was visually examined. No immiscible phases or floating debris or foam were observed (see Fig. 1). However, a film of consisting of water droplets and modifier was observed on the walls of all p-nut vials (see Fig. 1). Due to equipment malfunction no pictures of MCU-17-119-120-121 are shown. 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.

Modifier Levels and Density Measurements

Triplicate density measurements (by gravimetric and vibrating a filled tube method) of the three MCU monthly samples (Dec16, Jan17, and Feb17) gave arithmetic averages slightly less than 1% lower than the baseline solvent at 25 °C when corrected for temperature using the CSSX temperature correction formula[7] (see Fig. 2) but the measurement error intervals include the baseline solvent density value (The calculated density for the baseline solvent is 0.830 g/mL at 25 °C); therefore, it cannot be concluded that the measurements are different from the baseline sample measurement .[2,4] A similar observation and conclusion can be made for the modifier concentration data in Fig. 2. The recommended modifier level (1.69E05 mg/L) in Fig. 2 is well within the error intervals of the three MCU samples reported in this report. Both the density data and the modifier concentration correlate with each other as expected; the solvent density is a concentration-weighed linear combination of the modifier and Isopar™L pure densities.

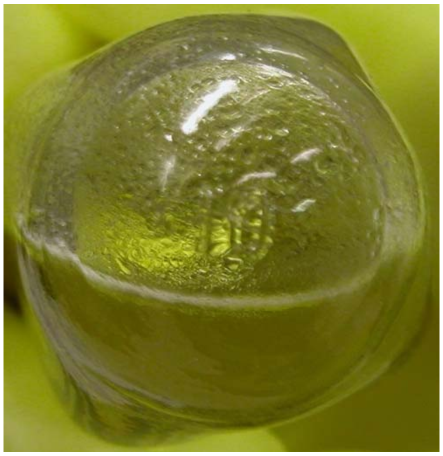
Typical picture of MCU-16-1488-1493 (6 p-nut vials)	**All p-nut vials showed caustic water droplets**
	
A typical picture of MCU-17-86-87-88	**All p-nut vials showed water droplets and modifier**
	

Figure 1 A picture of sample MCU-17-1488-1493 (top) and MCU-17-86-88. A picture of MCU-17-119-121 was not available due to equipment malfunction

All measurements indicate the Isopar™L level is at its nominal value while the modifier concentration level is slightly below its nominal value (see Fig. 2 for recent modifier concentrations from HPLC measurements). Looking at Fig. 2, the modifier level appears to return to its nominal level observed right after the trim addition to the solvent on November 8, 2016. The trend in the modifier level correlates with the trend in the density measurements as expected (see Fig. 2).[8]

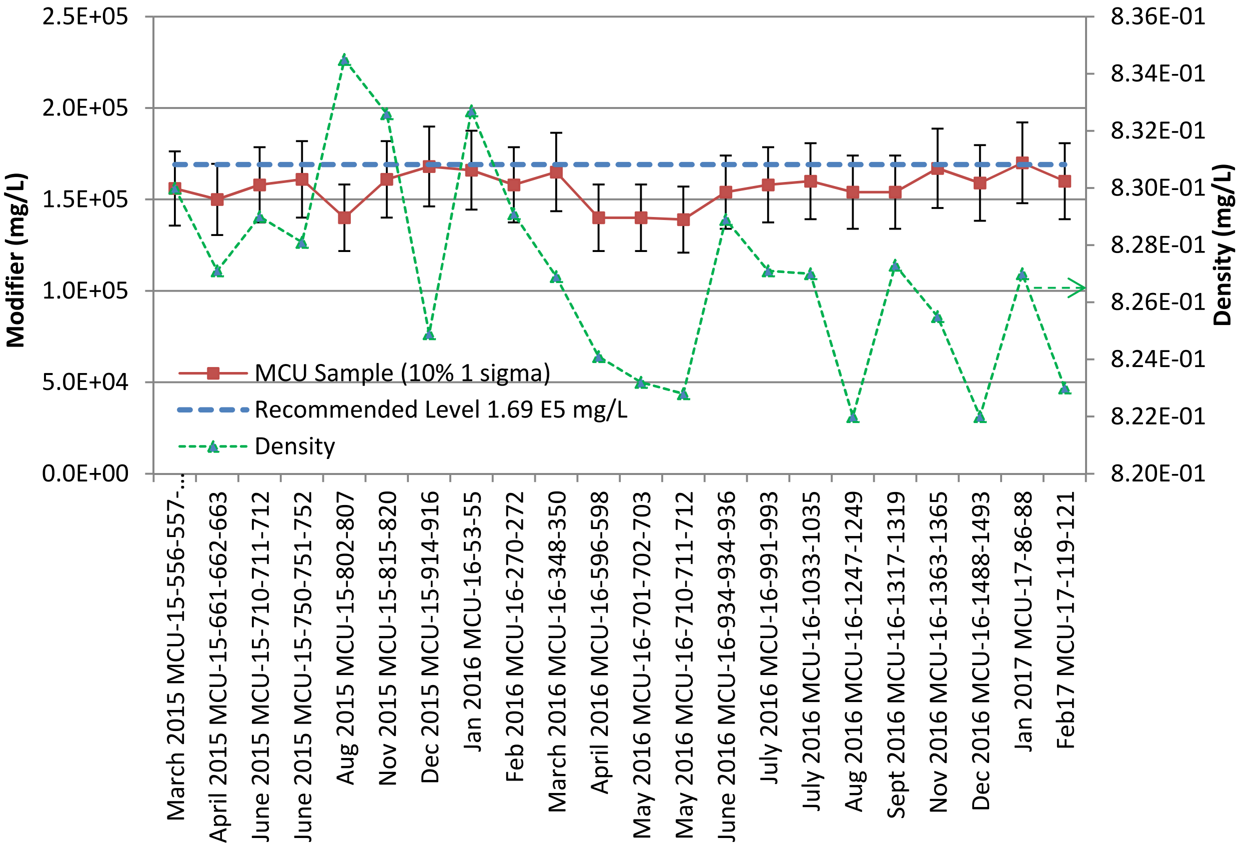


Figure 2. Modifier level in the solvent as measured by HPLC (one sigma is 10%).

Suppressors Levels

The average TiDG concentration levels for MCU-16-1488-1493, MCU-17-86-88, and MCU-17-119-121 are shown in Figure 3. As can be seen in Fig. 3, the TiDG level is steadily decreasing since the trim addition to the SHT in November 2016. The trend level pattern since November 2016 matches previous trends (confirming the “saw tooth” pattern” observed before). Part of that trend (January and February samples) MCU was not processing any aqueous solution (MCU stopped solvent extraction operations on January 10, 2017). Thus, the trend may reflect TiDG degradation under radiolysis and caustic solution conditions alone (without mass transfer losses to aqueous solutions). The February suppressor concentration (673 ± 67mg/L)is above its minimum recommended operating level (479 mg/L). The TOA concentration appears to remain steady and it is currently at 190 ± 30 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 slower than expected degradation rate (or slower transfer rate to aqueous streams during operation) to 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).[9] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide.[10]

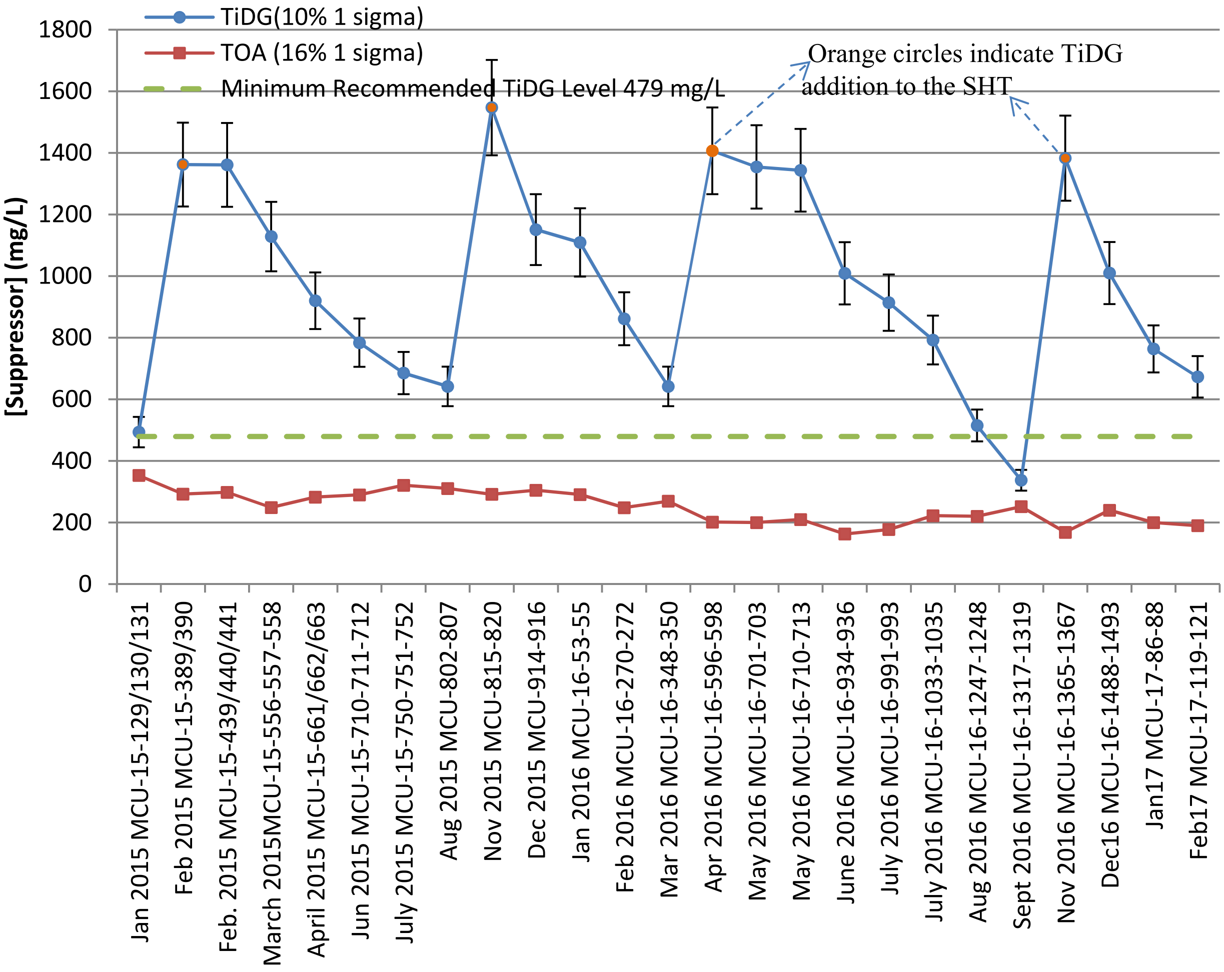


Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.

Extractant Levels

The average calculated MaxCalix levels for the December (4.41E4 mg/L), January (4.82E4 mg/L), and February (4.30E4 mg/l) samples are consistent with previous MaxCalix measurements. Their error intervals include the recommended value (4.63E4 mg/L). Note the current recommended value is the difference between 47,800 mg/L (50 mM MaxCalix) and the current BOBCalixC6 concentration in the SHT (1.50E3 mg/L in the February sample). The recent variations in the MaxCalix concentration seen in Fig. 4 is within the uncertainty range for this measurement. The uncertainty is possibly due to analytical or sampling or process variances since MaxCalix was added to the SHT on November 8, 2016.

The residual concentration of BOBCalixC6 level is currently at 37% of the level measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). This level is approximately the same level 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. Given that no BOBCalixC6 is added to the solvent, the level is expected to decrease with time.

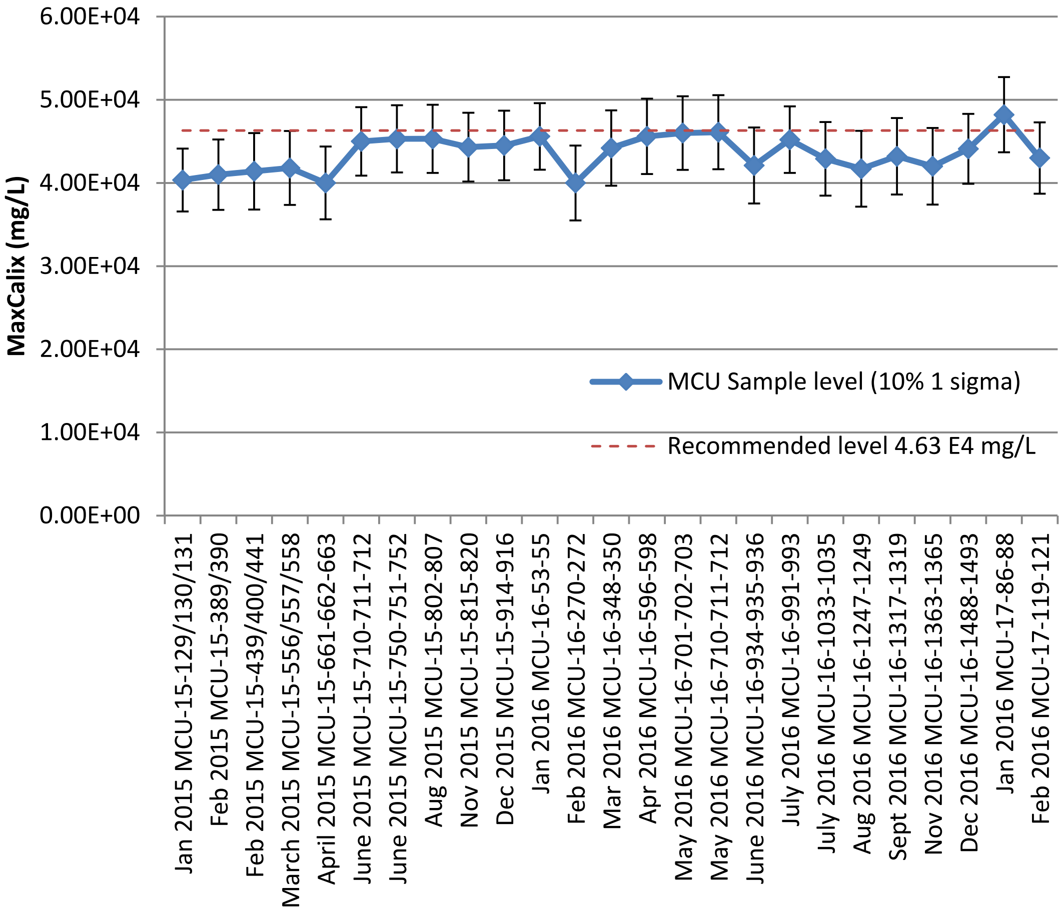


Figure 4. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (46,000 mg/L is the nominal concentration).

Gamma Level

The gamma measurements for the December, January and February samples are in Fig. 5 in relation to past gamma measurements. The gamma measurement for the February sample (MCU-17-119-121) is one order of magnitude lower than the December and January measurements. This low gamma level has been previously observed before but this time is probably due to MCU no processing salt solutions since January 2017. It is possible that the solvent being idle since January, that any radioactive aqueous solution carried over has physically separated.

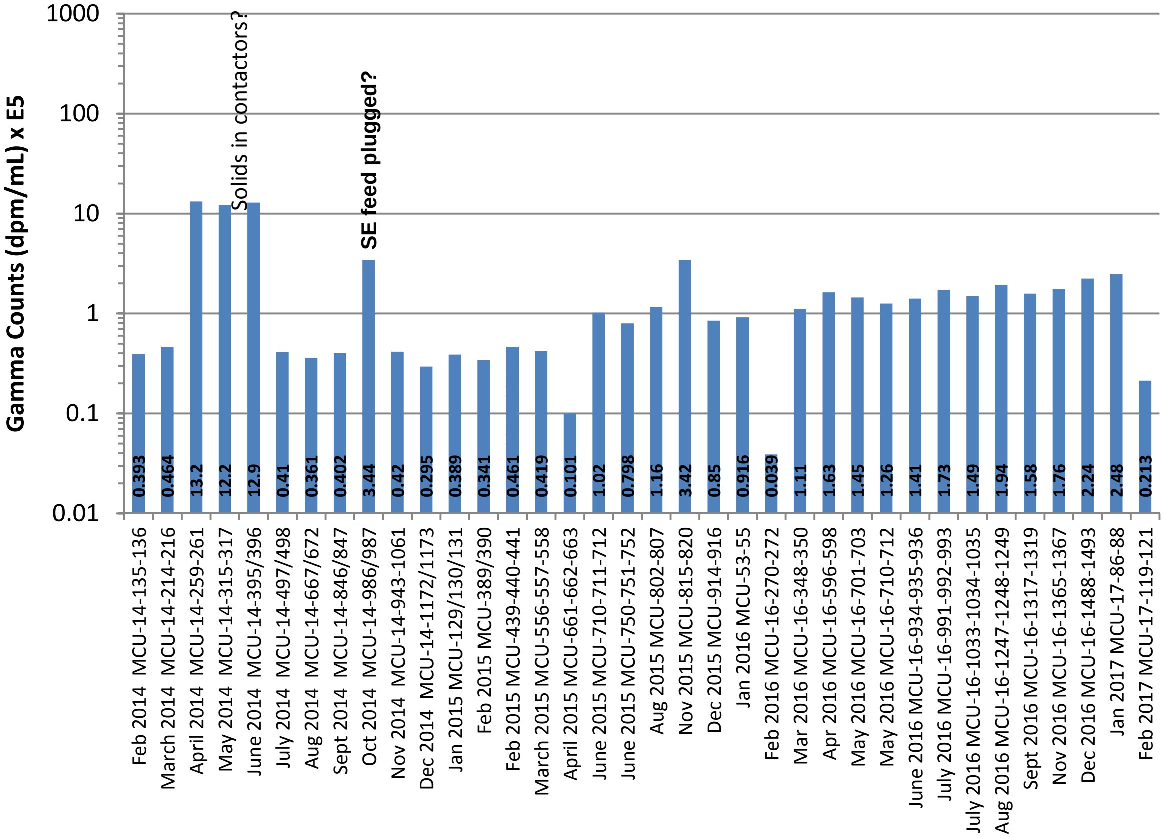


Figure 5. The gamma count of selected SHT samples. One sigma is 5%.

Impurities

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

A few mL of MCU-16-1363-1364-1365 was analyzed by XRF and then digested and analyzed for total mercury by the CVAA method. The average mercury concentration in the December 2016, January 2017 and February 2017 SHT were 36.5 ± 7 mg/L, 31.8 ± 6 mg/L, and 29 ± 6 mg/L respectively. These levels are consistently higher than the levels observed before August 2016.

This level of mercury is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm)[11], 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.[12] For 200 gallons of solvent (757.1 L) and assuming a density of 0.826 g/mL, the solvent could contain a total of 34 ± 7 g of mercury (based on the average of the two measurements). A comparison of this measurement with previous months 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 Batches 8 and 9 (Tank 49H). Also higher levels of total mercury (~109 ppm) were observed in Tank 50H third and fourth quarters surveillance samples.[10]

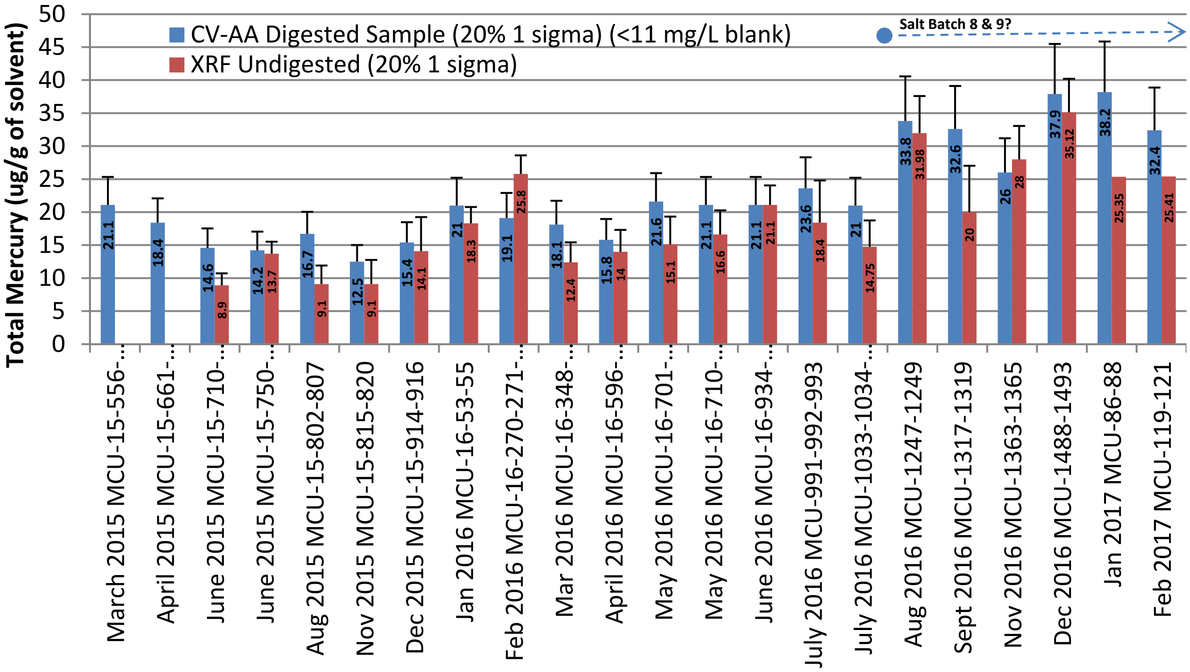


Figure 6. Total mercury in recent SHT samples. One sigma is 20%. CVAA = Cold Vapor Atomic Absorption Spectrometry. XRF =X-ray Fluorescence (20% one sigma).

Recommendations

The current analysis indicates the solvent has 92% of its nominal modifier and 93% of its suppressor (TiDG), but it has a nominal level of Isopar™L (100%) relative to the standard. The MaxCalix concentration is at 92% of its nominal level. The TiDG, MaxCalix, modifier, and Isopar™L amounts are expected to trend downward with time but at different rates. Based on the November sample, the solvent did not require any further trim addition.

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 component concentrations in the solvent.

4.0 Conclusions

A trend summary of three Solvent Hold Tank (SHT) monthly samples; MCU-16-1488-1493 (December 2016), MCU-17-86-88 (January 2017), and MCU-17-119-121 (February 2017) are reported. Analyses indicate that the modifier (CS-7SB) and the extractant (MaxCalix) concentrations are at their nominal recommended levels (169,000 mg/L and 46,300 mg/L respectively). The suppressor (TiDG) level has decreased to a steady state level of 673 mg/L well above the minimum recommended level (479 mg/L).

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5.0 References

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[1] W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.

[2] F. Fondeur, "Solvent Hold Tank Sample Results for MCU-16-1488/1489/1490/1491/1492/1493: December 2016 Monthly Sample", SRNL-L3100-2017-00039 Rev. 1, May 2017.

[3] F. F. Fondeur, 'Solvent Hold Tank Sample Results for MCU-17-86/87/88: January 2017 Monthly Sample" SRNL-L3100-2017-00042, Rev. 0, May 2017.

[4] F. F. Fondeur, "Solvent Hold Tank Sample Results for MCU-17-119/120/121: February 2017 Monthly Sample", SRNL-L3100-2017-00044, Rev. 1, May 2017

[5] M. R. Williams, "Next Generation Solvent Preparation" ITS-0173, July 11, 2013.

[6] K. Marra, "Engineering Evaluation of MCU Solvent and Recommended Trim and Isopar™L Addition to Maintain Specifications", X-ESR-H-00862, December, 2016

[7] L. H. Delmau, J. F. Birdwell, Jr., 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. Sloop, Jr., B. A. Tomkins, "Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent", ORNL/TM-2002/190, October 2002.

[8] 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.

[9] 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, July 2013.

[10] 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, July 2013.

[11] H. L. Clever and M. Iwamoto, "Solubility of Mercury in Normal Alkanes", *Ind. Eng. Chem. Res.* (1987), 26, 336-337.

[12] 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.

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

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