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Solvent Hold Tank Sample Results for MCU-15-129-130-131: January 2015 Monthly Sample

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Savannah River National Laboratory™

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EXECUTIVE SUMMARY

SRNL received one set of SHT samples (MCU-15-129, MCU-15-130, and MCU-15-131), pulled on 01/25/2015 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-129-130-131 indicated low concentrations of the suppressor (TiDG), of the extractant (MaxCalix), and of the modifier (CS-7SB) in the solvent relative to their nominal values. This analysis confirms a downward trend of these components. No impurities were found in this solvent. The laboratory will continue to monitor the quality of the solvent in particular for any new impurity or degradation of the solvent components.

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BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
FTIR	Fourier transform infra-red spectroscopy
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

1.0 Introduction

In late FY13, 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 Solvent Hold Tank (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 Savannah River National Laboratory (SRNL) to examine solvent composition changes over time.[1] On January 25, 2015, Operations personnel delivered three samples from the SHT (MCU-15-129, MCU-15-130, and MCU-15-131) 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 (November 29, 2014) 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 studied is shown in Table 2-1.

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

Event	Date
22 gallons of Isopar™L trim added to MCU	December 19, 2014
17 gallons of Isopar™L trim added to MCU	January 24, 2015
SHT sample MCU-15-129-130-131 January 25	January 26, 2015

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-15-129, MCU-15-130, and MCU-15-131 were composited before use. Aliquots of the composited sample were removed to perform analysis by density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, and Fourier-Transform Hydrogen Nuclear Magnetic Resonance (FT-HNMR). The Fourier-Transform Infra-Red spectroscopy (FTIR) instrument was not available at the time. Results from analytical measurements were compared with the theoretical values shown in Table 2-2.

Table 1-2. 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

The p-nut vials from MCU-15-129, MCU-15-130, and MCU-15-131 were examined and found to contain a single phase liquid with no apparent solids contamination or cloudiness. 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-15-129-130-131). Table 3-1 contains the results for the MCU-15-129-130-131 sample.

Isopar™ L and Modifier Levels

Density measurement of the sample gave a result of 0.822 g/mL (0.1% RSD) (or 0.820 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-129-130-131 at 21.5 °C. The calculated density (0.820 g/mL) for MCU-15-129-130-131 is 1.2% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory)[1]. Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be higher than its nominal value.

MCU-15-129 **MCU-15-130** **MCU-15-131**

Figure 1. Typical appearance of the three vials MCU-15-129, MCU-15-130, and MCU-15-131

An examination of Table 3-1 shows that the Isopar™ L concentration is higher than its nominal value while the modifier concentration is correspondingly lower than its nominal value. The NMR analysis reported higher values than the density and chromatography methods. 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 MUC was on January 24, 2015.

All measurements indicate the Isopar™ L level is above its nominal value while the modifier concentration level is below its nominal value. The low modifier concentration and high Isopar™L concentration explains the low solvent density. The accuracy of the different measurements were within expectation as reflected in the total mass sum of the "average" results listed in Table 3-2, which add up to 0.814 ± 0.019 g/mL. This is consistent with the measured and temperature corrected (to 25 ºC) value of 0.820 g/mL, but it is below the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL).

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[1] A second standard was prepared on September 29, 2014

Table 3-1 Sample Results for MCU-15-129-130-131

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.17E+05	6.23E+05	99
Isopar® L	Density[*]	NA	6.36E+05	6.23E+05	102
Average[$]	All	NA	6.35E+05	6.23E+05	102
Modifier	HPLC	300315699	1.38E+05	1.69E+05	82
Modifier	FT-HNMR	NA	1.60E+05	1.69E+05	95
Modifier	Density[*]	NA	1.34E+05	1.69E+05	79
Average[$]	All	NA	1.35E+05	1.69E+05	80
TiDG	Titration	NA	4.94E+02	1.44E+03	34
TiDG	FT-HNMR	NA	7.57E+02	1.44E+03	53
Average[$]	All	NA	5.19E+02	1.44E+03	36
trioctylamine	Titration	NA	3.53E+02	5.30E+02	67
Average[$]	All	NA	3.53E+02	5.30E+02	67
MaxCalix	FT-HNMR	NA	4.62E+04	4.44E+04	104
MaxCalix	HPLC	300315699	3.80E+04	4.44E+04	86
Average[$]	All	NA	4.04E+04	4.44E+04	91
BOBCalixC6	HPLC	300315699	2.78E+03	4.03E+03	69
Average[$]	All	NA	2.78E+03	4.03E+03	69
Density (g/mL)	Direct Measurement	NA	0.820	0.835	98

[#] Analytical uncertainty is 20% for SVOA and 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, 14% for Isopar™ L, and 20% for TiDG. N/A = Not Applicable.

[*] 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.

Suppressors Levels

The TiDG concentration level (519 mg/L) is at 36 % of its nominal value of 1440 mg/L. This level is at the minimum recommended level (480 mg/L) and it is recommended that additional TiDG is added to the solvent. This data point also confirms the persistent downward trend in the TiDG concentration that was detected in the November and December SHT samples as shown in Fig. 2. The TOA concentration appears to reach a steady state concentration at 353 mg/L (in the previous month the TOA level was 348 mg/L). These numbers are within analytical error. In addition, the TOA concentration appears not to correlate with the Isopar™ L concentration which in this case is above its nominal value. Since MCU no longer adds TOA, the reason for this increase is unknown at this time. However, a simple correlation analysis between TiDG as determined by titration and HNMR and TOA as determined by titration appears to indicate a strong negative correlation between TiDG and TOA as determined by titration. The correlation is perhaps due to TiDG degradation to form 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 equivalence points coincide.[4] Prior to the December sample analysis, there was a strong positive correlation (0.78) between TiDG and TOA based on titration analysis (both components decreased with time). After the correlation has become strongly negative (see Table 3-2).

Table 2-2. Correlation coefficient between TiDG and TOA as determined by Titration and HNMR since the NGS-CSSX implementation. HNMR does not adequately measure TOA.

	TiDG titration	*TOA titration*	*TiDG HNMR*
TiDG Titration	1		
TOA Titration	**-0.78**	1	
TiDG FT-HNMR	0.76	-0.63	1

Extractant Levels

The MaxCalix concentration continues its downward trend (4.04E4 mg/L) as shown in Fig. 3. The trend appears to be linear with time or volume of processed waste. The BOBCalixC6 concentration remained relatively constant at 2,780 mg/L. MCU no longer adds BOBCalixC6 to the solvent.

Gamma Level

The gamma measurement of MCU-15-129-130-131 is shown in Fig. 4. As can been seen in Fig. 4, the measured gamma level (3.89 E4 dpm/mL, ADS: 300315699) is relatively the same as the December 2014 sample and it is also consistent with previous gamma level measurements of the solvent when there was not known processing issues at MCU. This indicates the solvent is extracting and stripping as intended.

Impurities

No impurities were detected by the SVOA method (ADS # 300315699) above the 1000 ppm level. No significant impurities were observed in the H-NMR spectrum of these samples.

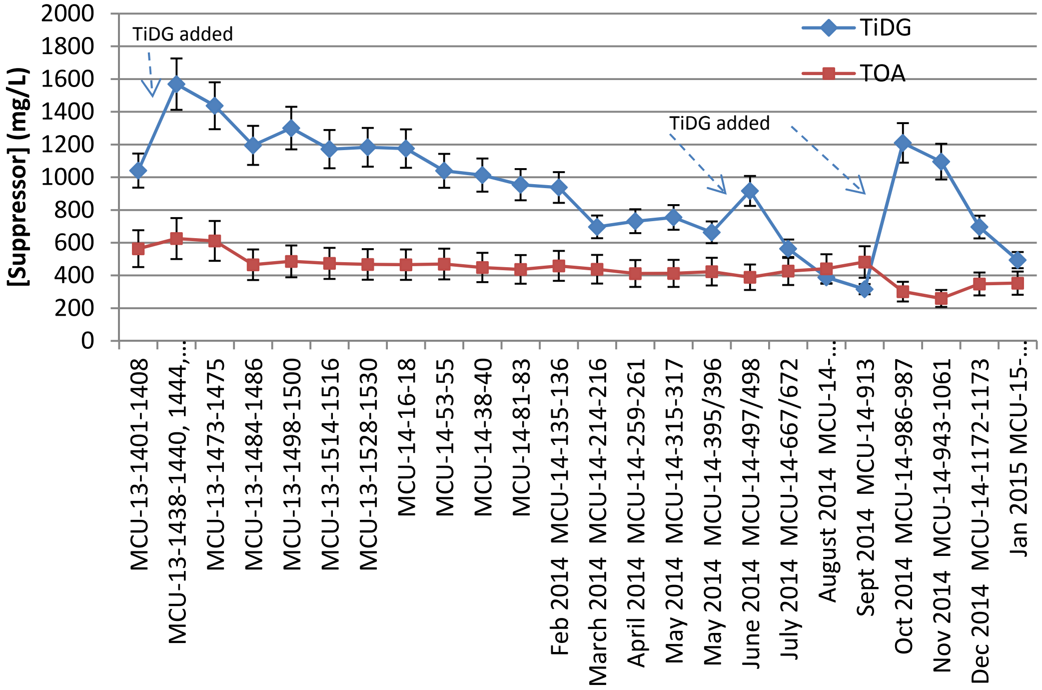

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 480 mg/L for TiDG.

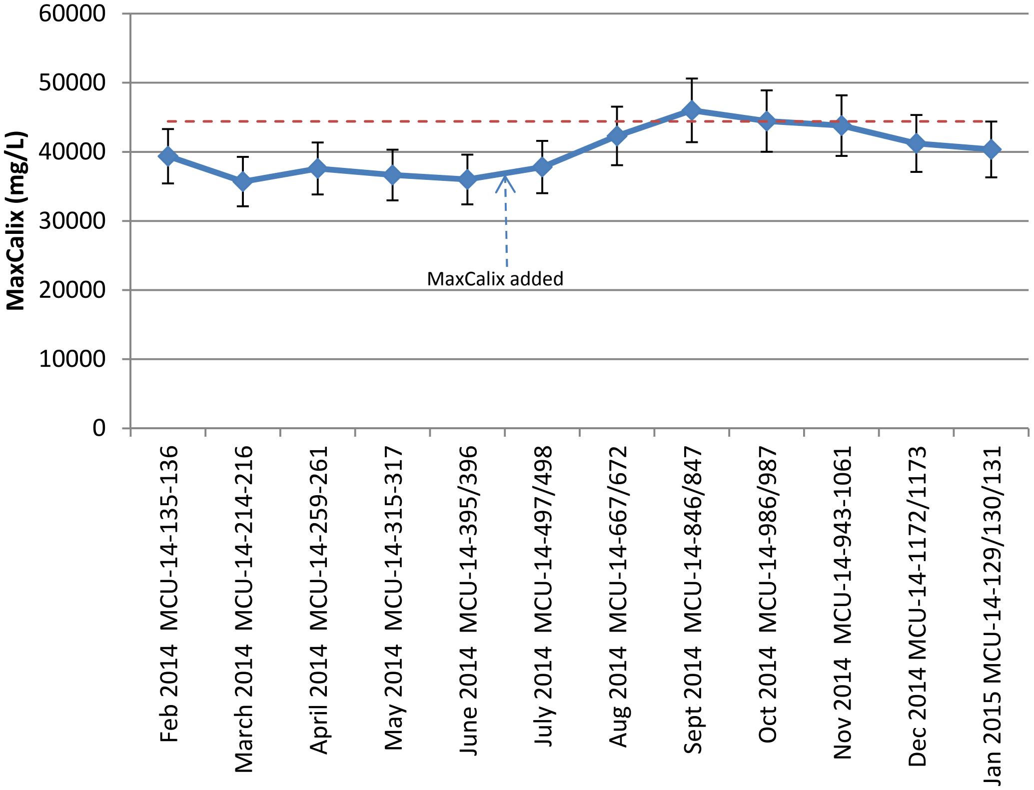

Figure 3. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,000 mg/L is the nominal concentration).

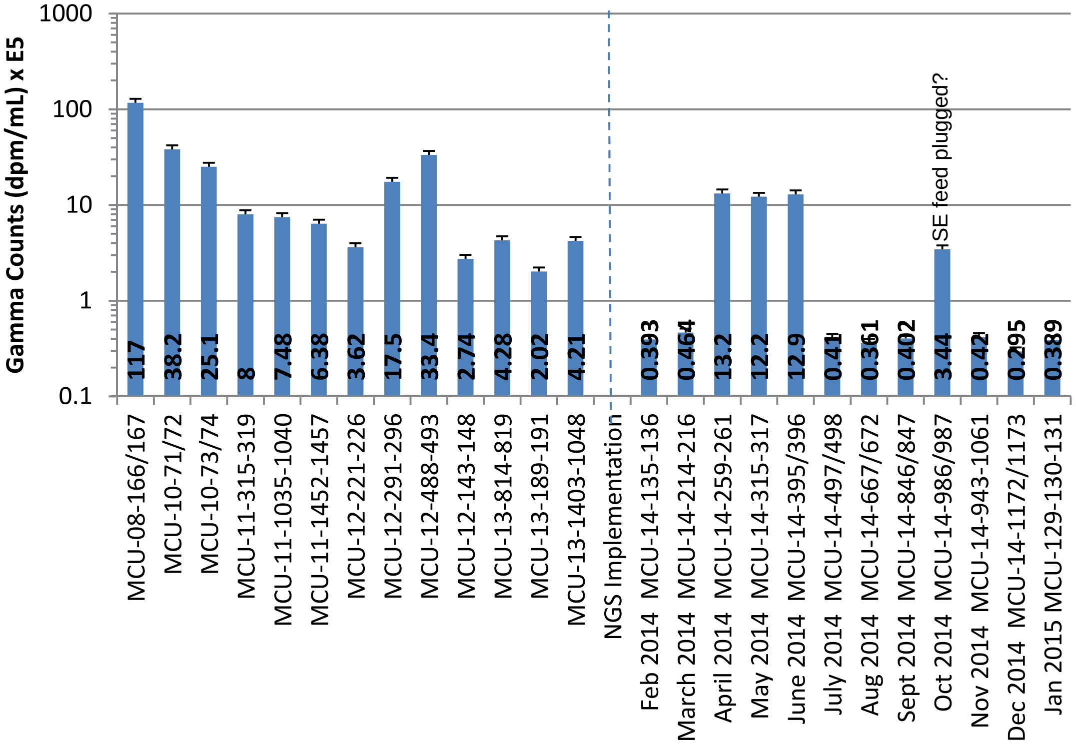

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

SRNL received one set of SHT samples (MCU-15-129, MCU-15-130, and MCU-15-131, pulled on 01/25/2014) for analysis. The sample was analyzed for composition. Analysis of composited sample MCU-15-129-130-131 indicated low concentrations of the suppressor (TiDG), of the extractant (MaxCalix), and of the modifier (CS-7SB) in the solvent relative to their nominal values. This analysis confirms a downward trend of these components. No impurities were found in this solvent. The laboratory will continue to monitor the quality of the solvent in particular for any new impurity or degradation of the solvent components.

5.0 References

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[3] 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.

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