Solvent Hold Tank Sample Results for MCU-14-259/260/261 and MCU-14-315/316/317: April and May 2014 Monthly Samples

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Savannah River National Laboratory™
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EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-259/260/261 in April 2014 and MCU-14-315/316/317 in May 2014) for analysis. The samples were analyzed for composition. Both samples have similar chemical composition. As with the previous solvent sample results, these analyses indicate that the solvent does not require Isopar® L trimming at this time. Since an addition of TiDG and MaxCalix to the SHT was added in early July 2014, the solvent does not require TiDG addition at this time. The current TiDG level (1.5 mM) is above the minimum recommended operating level of 1 mM.

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LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
CDT	Contactor Drain Tank (TK-306)
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-Bix(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

Solvent Hold Tank (SHT) samples are sent to Savannah River National Laboratory (SRNL) to examine solvent composition changes over time.[1] In FY13, MCU entered a planned outage to switch to the Next Generation Solvent (NGS) flow sheet. Facility personnel implemented the switch by adding a non-radiative, NGS "cocktail" containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. The resulting MCU-NGS solvent blends down the BobCalix. In April 2014, Operations personnel delivered three samples from the SHT (MCU-14-259, MCU-14-260, and MCU-14-261) for analysis. Later in May 2014, Operations personnel sent an additional three samples from the SHT (MCU-14-315, MCU-14-316, and MCU-14-317) for analysis. These samples are intended to verify that the solvent is within the specified composition range. A baseline "scratch" solvent (a blend of cocktail[2] and heel solvent) was prepared in the lab and used for comparison and evaluation. The results from the analyses are presented in this document.

2.0 Experimental Procedure

2.1 Experimental Procedure

Samples were received in p-nut vials containing ~10 mL each (see Fig 2-1). Once taken into a radioactive hood, the three monthly samples were visually inspected, analyzed for pH, combined and mixed. Samples were removed for analysis by density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, Fourier-Transform Hydrogen Nuclear Magnetic Resonance (FT-HNMR) and Fourier-Transform Infra-Red spectroscopy (FTIR).

Figure 2-1. Typical appearance of the three vials from MCU-14-315/316/317. Samples MCU-14-259/260/261 had a similar appearance.

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 of the six p-nut vials (MCU-14-259/260/261 and MCU-14-315/316/317) contained a single phase liquid with no apparent solids contamination or cloudiness. All samples had a pH value of 5. Tables 3-1 and 3-2 contain the results of the analyses for the combined April and May samples, respectively.

Density measurements of the samples gave results of 0.8212 g/mL (0.24% RSD) (or 0.8187 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-14-259/260/261 and 0.8211 g/mL for MCU-14-315/316/317 (or 0.8186 g/mL when corrected for temperature) at 21 °C. The calculated densities (0.8187 g/mL and 0.8186 g/mL at 25 °C) for MCU-14-259/260/261 and MCU-14-315/316/317 are lower than the calculated density obtained from the standard sample (0.8352 g/mL for the NGS-MCU blend made in the laboratory at 25 °C)[2]. This is expected since the current solvent has experienced mass transfer via intentional additions. Using the density as a starting point, we know that the Isopar® L should be higher than nominal and the other components should be slightly lower than nominal. This confirms the excess Isopar® L in MCU-14-259/260/261 and MCU-14-315/316/317 samples.

The analytical data for the composite samples from April and May are shown in Tables 3-1 and 3-2, respectively. Of all the methods listed, density has the lowest uncertainty. An examination of Tables 3-1 and 3-2 shows consistent results between the different analyses. All measurements, with the exception of SVOA, indicate that the solvent has an Isopar® L concentration slightly higher than nominal, and modifier lower than nominal. The modifier concentration derived from the density measurement in the April and May is slightly lower than measured by other analytical methods. The density measurements currently uses parameters previously obtained with the CSSX solvent to estimate the Isopar® L and modifier concentrations in the NGS-CSSX solvent. Further work is needed to re-estimate these parameters such as the thermal dependency of the NGS solvent density to improve the prediction accuracy of the density measurement. The total mass sum of the "average" results listed in Table 3-1 and 3-2 add up to 0.809 ± 0.019 g/mL and 0.8095 ± 0.019 g/mL respectively which compares well with the measured and corrected to 25 °C mass concentration (densities) of 0.8187 and 0.8186 g/mL, respectively. As indicated in Table 3-1 and Table 3-2, the modifier and Isopar® L concentrations are consistent within the noise of sample handling and method uncertainties.

Both the MaxCalix and BobCalix concentrations were slightly below the expected value in both samples. The concentration of MaxCalix and BobCalix decreased by 15% and 10% respectively in the April sample and by 17% and 15% in the May sample relative to the laboratory standard sample. These levels will return to nominal values once the excess Isopar® L evaporates. On the other hand, the suppressor (based on the TiDG*HCl compound) concentration is well below (~50%) the expected value (1.55 E3 mg/L) for the most recent sample (MCU-14-315/316/317). Since the last characterization report, MCU engineering issued on July 02, 2014 a report recommending adding 420 g of TiDG and 2980 grams of MaxCalix to the SHT.[3] Based on the TiDG concentration of these samples, the TiDG level remained the same from the April to May samples. No addition was made during this time; therefore both SHT samples are chemically similar. In addition, no evidence of TiDG depletion mechanism was observed in these samples. The reason for this lower value is unknown at this time, but a possible decomposition reaction and phase transfer (to aqueous streams) may all have contributed to the lower value. The other suppressor, TOA, concentration was also below its nominal value although it plays no significant role.

This level of TiDG is believed to be sufficient to prevent anionic impurities from pairing with extractant-bounded cesium, preventing cesium stripping, and increasing the activity level in the solvent. Solvent evaporation of Isopar® L will only increase the current TiDG levels to approximately 1000 mg/L (~1.9 mM). From the last solvent characterization report,[4] the recommended operating TiDG level should be at least 2 mM and the minimum suppressor level should not be less than 1 mM. Based on this criteria, there is no need to add TiDG at this time. There is no risk of third phase formation associated with low suppressor concentration. Figure 3-1 shows the TiDG concentration in the solvent since November 2013 as measured by titration. Figure 3-1 shows a steady decrease in the TiDG concentration over time and/or volume of waste processed. However, the TiDG levels slightly increased to 768 mg/L in the last sample. Since engineering personnel recently added TiDG and MaxCalix in a modifier solution to the SHT in early July 2014, the next sets of SHT samples are expected to contain nominal levels of TiDG. Further work is necessary to determine the lowest TiDG concentration level the solvent can have while maintaining optimal performance.

When compared to the initial target density of 0.829 g/mL for solvent start up, there is no need to add an Isopar® L trim.[♣]

Gamma measurements of MCU-14-259/260/261 and MCU-14-315/316/317, shown in Table 3-3, indicate the solvent gained significant gamma activity (1E06 dpm/mL) relative to February/March samples (see Fig. 3-2). These readings are consistent with the mixing of the solvent with radioactive supernatant (April sample was pulled after MCU processed 856 gallons of supernate). The processing of supernatant appeared to have added impurities in the solvent as shown in HNMR spectrum of the April and May samples (see Fig. 3-3). The location of the impurity peaks in the HNMR appears to be associated with 4-sec-butylphenol at the 21 ppm level (estimate). No 4-sec-butylphenol beyond 100 ppm was observed by HPLC. The FTIR analysis did not detect the same level impurities (isomerization) as observed in the March sample. No impurities were detected by the SVOA method.

Table 3-1. Sample Results for MCU-14-259/260/261 Composite

Analysis	**Method**	**LIMS #**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar® L	SVOA	300311584	5.20E+05	6.16E+05	84
Isopar® L	FT-HNMR	NA	6.22E+05	6.16E+05	101
Isopar® L	FTIR	NA	6.23E+05	6.16E+05	101
Isopar® L	Density[*]	NA	6.37E+05	6.16E+05	103
Average[$]	All	NA	6.32E+05	6.16E+05	103
Modifier	HPLC	300311584	1.37E+05	1.69E+05	81
Modifier	SVOA	300311584	1.50E+05	1.69E+05	89
Modifier	FT-HNMR	NA	1.45E+05	1.69E+05	86
Modifier	FTIR	NA	1.47E+05	1.69E+05	87
Modifier	Density[*]	NA	1.33E+05	1.69E+05	78
Average[$]	All	NA	1.35E+05	1.69E+05	80
TiDG (HCl)	Titration	NA	7.87E+02	1.55E+03	51
TiDG (HCl)	FT-HNMR	NA	6.53E+02	1.55E+03	42
Average[$]	All	NA	7.51E+02	1.55E+03	48
trioctylamine	SVOA	300311584	3.40E+02	5.50E+02	62
trioctylamine	Titration	NA	4.12E+02	5.50E+02	75
Average[$]	All	NA	3.77E+02	5.50E+02	69
MaxCalix	HPLC	300311584	3.87E+04	4.40E+04	88
MaxCalix	FT-HNMR	NA	3.60E+04	4.40E+04	82
Average[$]	All	NA	3.76E+04	4.40E+04	85
BobCalix	HPLC	300311584	3.6E+03	4.00E+03	90
Density (g/mL)	Direct Measurement	NA	0.8187	0.835	98

[♣] Note that while freshly prepared blend solvent has a target density of 0.835 g/mL, the MCU facility targets to maintain the solvent inventory at lower densities (0.829 g/mL) to allow longer operating periods before correcting for evaporation.

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar® L and 10% for Modifier. 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 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.

Table 3-2. Sample Results for MCU-14-315/316/317 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300311736	5.60E+05	6.16E+05	91
Isopar® L	FT-HNMR	NA	6.23E+05	6.16E+05	101
Isopar® L	FTIR	NA	6.30E+05	6.16E+05	102
Isopar® L	Density[*]	NA	6.37E+05	6.16E+05	103
Average[$]	All	NA	6.34E+05	6.16E+05	103
Modifier	HPLC	300311736	1.42E+05	1.69E+05	84
Modifier	SVOA	300311736	1.60E+05	1.69E+05	95
Modifier	FT-HNMR	NA	1.44E+05	1.69E+05	85
Modifier	FTIR	NA	1.39E+05	1.69E+05	82
Modifier	Density[*]	NA	1.32E+05	1.69E+05	78
Average[$]	All	NA	1.34E+05	1.69E+05	80
TiDG (HCl)	Titration	NA	8.12E+02	1.55E+03	52
TiDG (HCl)	FT-HNMR	NA	6.53E+02	1.55E+03	42
Average[$]	All	NA	7.68E+02	1.55E+03	50
trioctylamine	SVOA	300311736	3.40E+02	5.50E+02	62
trioctylamine	Titration	NA	4.13E+02	5.50E+02	75
Average[$]	All	NA	3.78E+02	5.50E+02	69
MaxCalix	HPLC	300311736	3.68E+04	4.40E+04	84
MaxCalix	FT-HNMR	NA	3.64E+04	4.40E+04	83
Average[$]	All	NA	3.67E+04	4.40E+04	83
BobCalix	HPLC	300311736	3.40E+03	4.00E+03	85
Density (g/mL)	Direct Measurement	NA	0.8186	0.835	98

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar® L and 10% for Modifier. 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 MaxCalix, 14% for Isopar® L, and 20% for TiDG. NA = 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.

Table 3-3. ^{137}Cs in the NGS-CSSX Solvent

Solvent Sample	Result (dpm/mL)	LIMS #
MCU-14-259/260/261	1.32E+06	300311584
MCU-14-314/315/316	1.22E+06	300311736

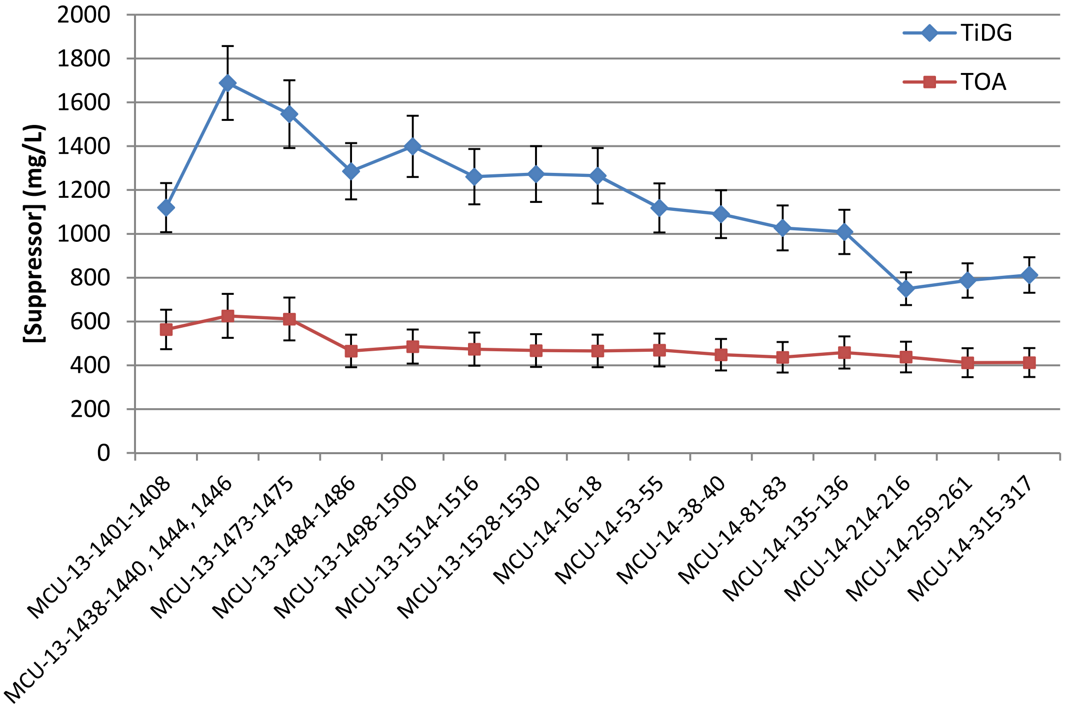

Figure 3-1. Suppressor concentration as measured by titration in SHT samples since NGS implementation.

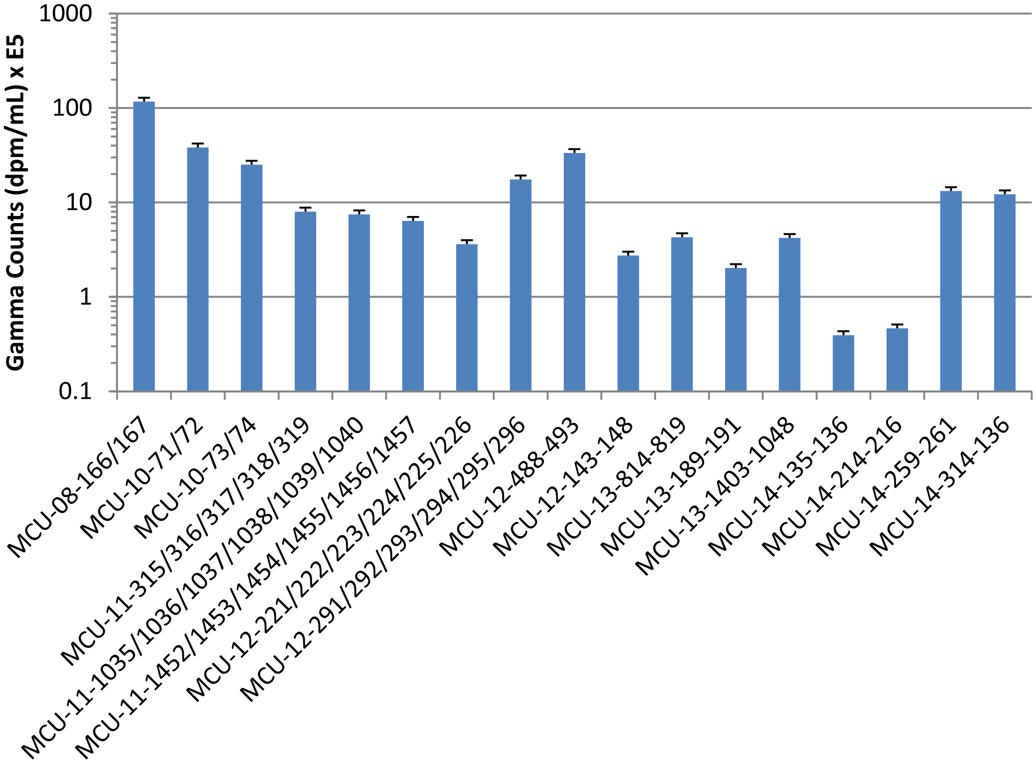

Figure 3-2. The gamma count of selected SHT samples. One standard deviation is 5%.

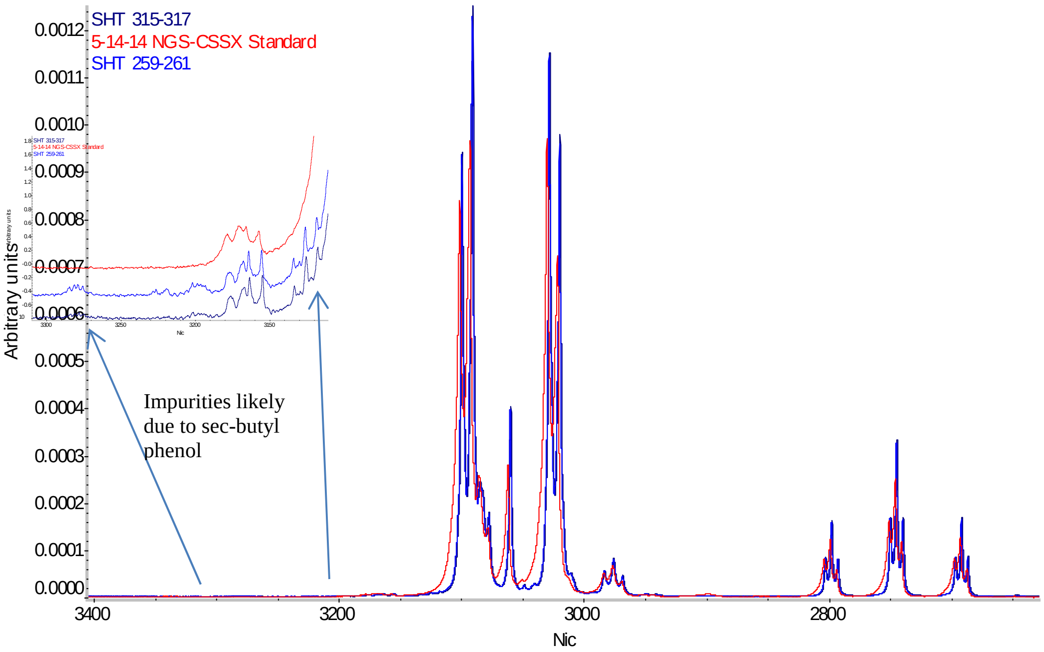

Figure 3-3. The H-NMR spectra of MCU-14-259/260/261, MCU-14-315/316/317, and the lab standard (NGS-CSSX)

4.0 Conclusions

As with the previous solvent sample results, these analyses indicate that the solvent does not require Isopar® L trimming at this time. Both samples have similar composition. Since an addition of TiDG and MaxCalix to the SHT was added early July 2014, it is expected the TiDG concentration (based on the TiDG*HCl) will return to nominal levels. Therefore, the solvent does not require TiDG addition at this time. 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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[1] W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.

[2] T. B. Peters and M. R. Williams, "Results of Analysis of NGS Concentrate Drum Samples" SRNL-STI-2013-00521, September 2013.

[3] T. E. Smith, "Engineering Evaluation of MCU Solvent and Recommended Isopar®L Additions to Maintain Specifications," X-ESR-H-00688, Rev. 0, July 2, 2014.

[4] F. F. Fondeur and K. Taylor-Pashow, "Solvent Hold Tank Sample Results for MCU-14-259/260/261 and MCU-14-315/316/317: April and May 2014 Monthly Samples," SRNL-STI-2014-00270, Rev. 0, May 2014.

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