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Solvent Hold Tank Sample Results for MCU-14-135/136 and MCU-14-214/215/216: February and March 2014 Monthly Samples

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EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-135-136 in February 2014 and MCU-14-214-216 in March 2014) for analysis. The samples were analyzed for composition. As with the previous solvent sample results, these analyses indicate that the solvent does not require Isopar$^{®}$ L trimming at this time. However, the addition of TiDG (suppressor) to the blended solvent is recommended. Evidence of possible (slight) isomerization of the solvent, probably Isopar®L or TiDG degradation products, was observed.

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LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
ESS	Extraction, Scrub, and Strip
FID	Flame Ionization Detector
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
ORNL	Oak Ridge National Laboratory
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 and removed some of the solvent from the SHT. In turn, facility personel added a non-radioactive "cocktail" solvent containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. The resulting MCU-NGS solvent blends down the BobCalix. In February 2014, Operations personnel delivered two samples from the SHT (MCU-14-135 and MCU-14-136) for analysis. Later in March 2014, Operations personnel sent an additional three samples from the SHT (MCU-14-214, MCU-14-215, and MCU-14-216) 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. A TTQAP has been developed to verify that the performance of the solvent prepared in MCU matches the performance measured in the lab with real waste and simulant solutions.[3] 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. Once taken into the Shielded Cells, the 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).

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 five p-nut vials (two from MCU-14-135-136 and three from MCU-14-214-216) contained a single phase, 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 February and March samples, respectively.

Density measurements of the samples gave results of 0.831 g/mL (0.24% RSD) (or 0.8302 g/mL at 25 °C when corrected for temperature) for MCU-14-135-136 and 0.8245 g/mL for MCU-14-214-216 (or 0.8237 g/mL when corrected for temperature) at 24 °C. The calculated densities (0.8302 g/mL and 0.8237 g/mL at 25 °C) for MCU-14-135-136 and MCU-14-214-216 are lower than the calculated density obtained from the standard sample (0.8352 g/mL for the NGS-MCU blend made in the laboratory)[2]. This is expected since the current solvent has experienced mass transfer via intentional additions and evaporation. Using the density as a starting point, Isopar® L is expected to be higher than nominal and the other components should be slightly lower than nominal. This confirms the excess Isopar® L in MCU-14-135-136 and MCU-14-214-216 samples.

The analytical data for the composite samples from February and March 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 indicate that the solvent has an Isopar® L concentration slightly higher than nominal, and modifier lower than nominal. The total mass sum of the "average" results listed in Table 3-1 and 3-2 add up to 0.823 ± 0.018 g/mL and 0.812 ± 0.018 g/mL respectively which compares well with the measured mass concentration (densities) of 0.83 and 0.824 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. However, the 20% analytical uncertainty of the SVOA measurement gives limited utility to this analytical method. Given the large "acceptable" value the SVOA and the availability of alternate methods, consideration should be given to no longer relying on SVOA. However, SVOA should still be used to examine samples for trace organic impurities on a quarterly basis

Both the MaxCalix and BobCalix concentrations were slightly below the expected value in both samples. The concentration of both extractants decreased by ~8% in the February sample and almost 20% in the March sample. If this trend continues, decontamination and concentration factor performance will not be met and further investigation may be warrant determining if a new depletion mechanism of the extractant is at play. It is recommended that MaxCalix is added to the solvent at nearest opportunity. The suppressor (TiDG*HCl) concentration is well below (~50%) the expected value (1.55 E3 mg/L) for the most recent sample (MCU-14-214-216). The TiDG concentration dropped significantly between the February and March samples. For the February sample (MCU-14-135-136), the TiDG concentration was ~68% of the nominal value. 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 slightly below its nominal value.

This level of TiDG is believed to be sufficient to prevent anionic impurities from pairing with cesium, preventing cesium stripping, and increasing the activity level in the solvent. However, SRNL recommends adding a TiDG trim to the solvent. 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, which could be a result of time and/or volume of waste processed. Further work is necessary to refine the lowest TiDG concentration level the solvent can have while maintaining optimal performance. Unpublished data from ORNL and conversations with a NGS chemistry expert (Dr. Bruce Moyer of ORNL) indicate the TiDG level in the solvent should never drop below 1 mM and that the optimal TiDG level should be 2 mM (a level that reduces the amount of degradation products sent upstream of MCU while above the minimum level of 1 mM). This may require frequent TiDG trimmings to the solvent during the lifecycle of MCU. When compared to the initial target density of 0.829 g/mL for solvent at start up, there is no need to add an Isopar®L trim.[♣]

A further evaluation of the FTIR data from this solvent revealed the evidence of possible isomerization (C=C formation) of the solvent at the 17 ppm level. The difference spectrum, shown in Fig. 3-2, is typical of irradiated oil but it can also be the break down fragments of the TiDG molecules (an infrared library of these fragments is needed for future analysis and more confident assignments). This residual infrared spectrum has not been seen in the past with CSSX. Solvent isomerization could be the result of higher cesium level and might possibly be accelerating the solvent degradation. An independent detection and identification of this residue may require method development. However, this is only one data point that requires further future sample analysis to be valid. Therefore, at this time the FTIR observation should be not seen as an eminent risk. The SVOA/VOA data revealed no new additional impurities beyond those observed in the CSSX solvent system. No sec-butyl phenol was detected by the HPLC method. The laboratory will continue to examine the solvent quality of future samples to verify the claim made above.

Gamma measurements of MCU-14-135-136 and MCU-14-214-216, shown in Table 3-3, indicate the solvent has received extensive stripping and washing. The gamma readings are one order of magnitude

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[♣] 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.

lower than seen in previous samples as shown in Fig. 3-3. This may be due to the higher extraction and stripping efficiency of the new NGS solvent over that of the CSSX solvent. The lower gamma reading confirms the higher extraction and higher concentration factor of NGS.

Table 3-1. Sample Results for MCU-14-135 and MCU-14-136 Composite

Analysis	**Method**	**LIMS #**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar® L	SVOA	300309984	6.20E+05	6.16E+05	101
Isopar® L	FT-HNMR	NA	6.18E+05	6.16E+05	100
Isopar® L	FTIR	NA	6.18E+05	6.16E+05	100
Isopar® L	Density[*]	NA	6.22E+05	6.16E+05	101
Average[$]	All	NA	6.22E+05	6.16E+05	101
Modifier	HPLC	300309984	1.48E+05	1.69E+05	88
Modifier	SVOA	300309984	1.80E+05	1.69E+05	106
Modifier	FT-HNMR	NA	1.45E+05	1.69E+05	86
Modifier	FTIR	NA	1.62E+05	1.69E+05	96
Modifier	Density[*]	NA	1.58E+05	1.69E+05	93
Average[$]	All	NA	1.57E+05	1.69E+05	93
TiDG (HCl)	Titration	NA	1.01E+03	1.55E+03	65
TiDG (HCl)	FT-HNMR	NA	1.21E+03	1.55E+03	78
Average[$]	All	NA	1.05E+03	1.55E+03	67
trioctylamine	SVOA	300309984	3.0E+02	5.5+02	55
trioctylamine	Titration	NA	4.58E+02	5.5+02	86
Average[$]	All	NA	3.63E+02	5.5+02	75
MaxCalix	HPLC	300309984	39E+03	44E+03	89
MaxCalix	FT-HNMR	NA	40E+03	44E+03	91
Average[$]	All	NA	39E+03	44E+03	89
BobCalix	HPLC	300309984	3.6E+03	4.0E+03	90
Density (g/mL)	Direct Measurement	NA	0.830	0.835	99

[#] 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.

[*] 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.

NA = Not Applicable

Table 3-2. Sample Results for MCU-14-214, MCU-14-215, and MCU-14-216 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300310170	6.00E+05	6.16E+05	97
Isopar® L	FT-HNMR	NA	6.30E+05	6.16E+05	102
Isopar® L	FTIR	NA	6.15E+05	6.16E+05	100
Isopar® L	Density[*]	NA	6.30E+05	6.16E+05	102
Average[$]	All	NA	6.29E+05	6.16E+05	102
Modifier	HPLC	300310170	1.37E+05	1.69E+05	81
Modifier	SVOA	300310170	1.60E+05	1.69E+05	95
Modifier	FT-HNMR	NA	1.37E+05	1.69E+05	81
Modifier	FTIR	NA	1.40E+05	1.69E+05	83
Modifier	Density[*]	NA	1.43E+05	1.69E+05	85
Average[$]	All	NA	1.42E+05	1.69E+05	84
TiDG (HCl)	Titration	NA	7.50E+02	1.55E+03	48
TiDG (HCl)	FT-HNMR	NA	8.93E+02	1.55E+03	58
Average[$]	All	NA	7.71E+02	1.55E+03	50
trioctylamine	SVOA	300310170	2.70E+02	5.50E+02	49
trioctylamine	Titration	NA	4.38E+02	5.50E+02	80
Average[$]	All	NA	3.33E+02	5.50E+02	60
MaxCalix	HPLC	300310170	35E+03	44E+03	80
MaxCalix	FT-HNMR	NA	37E+03	44E+03	84
Average[$]	All	NA	36E+03	44E+03	82
BobCalix	HPLC	300310170	3.3E+03	4.0E+03	83
Density (g/mL)	Direct Measurement	NA	0.8237	0.835	99

[#] 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.

[*] 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.

NA = Not Applicable

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

Solvent Sample	Result (dpm/mL)	LIMS #
MCU-14-135-136	3.93E+04	300309984
MCU-14-214-216	4.64E+04	300310170

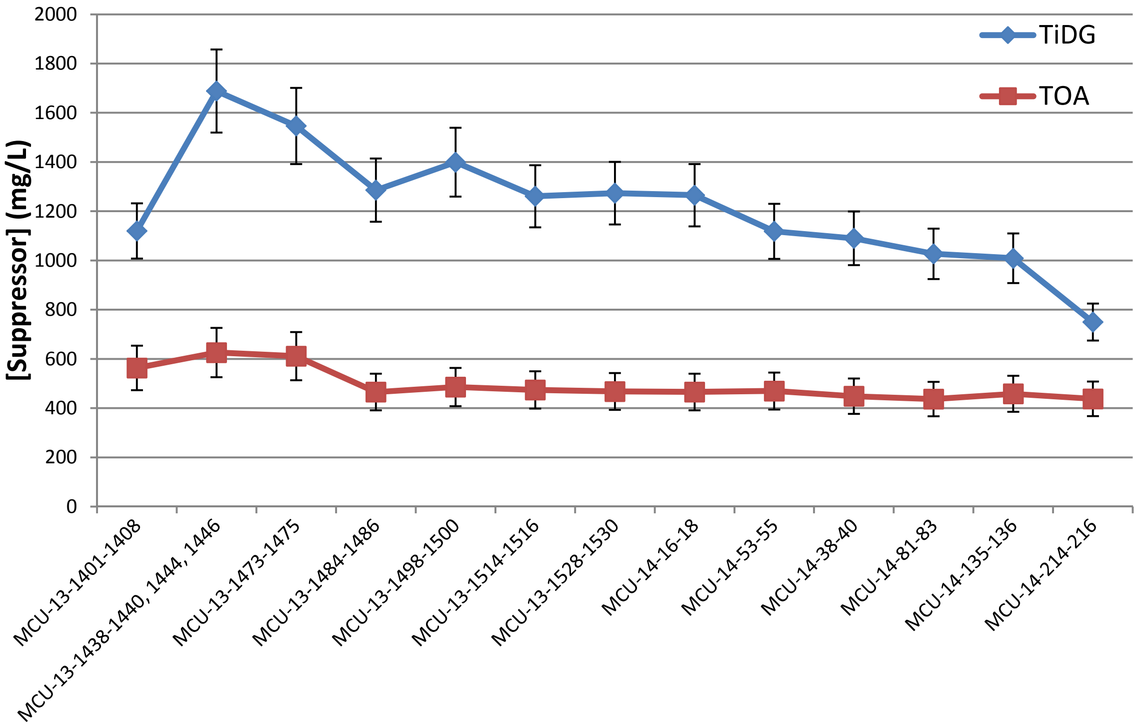

Figure 3-1. Suppressor concentration as measured by titration in SHT samples since NGS implementation (June 2013 to March 2014).

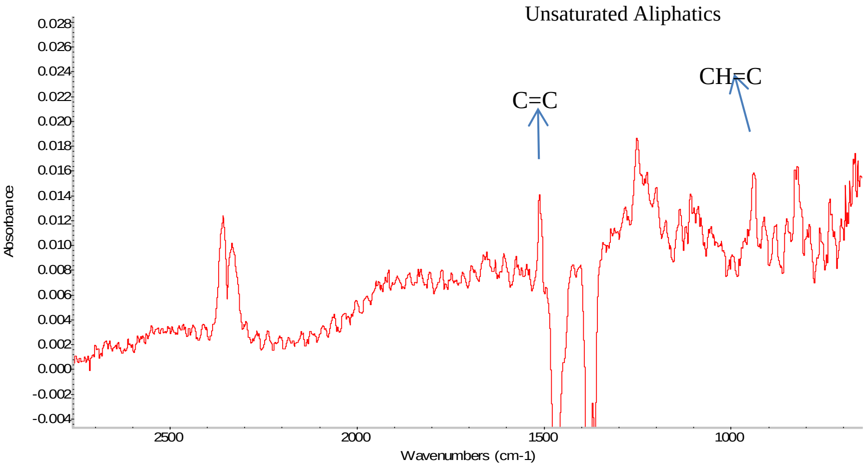

Figure 3-2. FTIR difference spectrum of MCU-14-214-216 showing the presence of unsaturated aliphatic in the solvent (a similar pattern was observed in the FTIR spectrum of MCU-14-134-135).

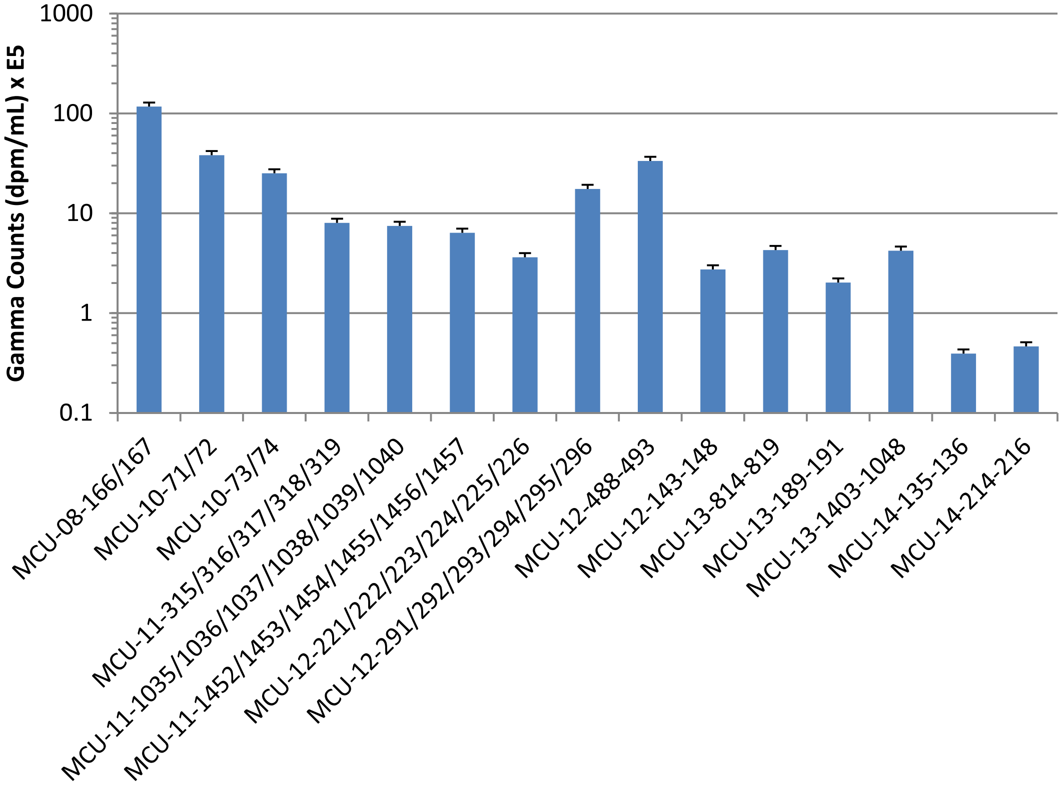

Figure 3-3. The gamma count of selected SHT samples. One standard deviation is 5%.

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. However, the addition of TiDG (suppressor) to the blended solvent is recommended. Evidence of slight isomerization of the solvent was observed.

5.0 Recommendations

Addition of TiDG to the solvent is recommended to restore the TiDG concentration to 1550 mg/L. Also addition of MaxCalix to the solvent is recommended while investigation continues to verify if the extractant depletion is driven by a new mechanism. The laboratory will continue to monitor the quality of the solvent in particular for any new impurity or degradation of the solvent components.

6.0 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] Peters, T.B, Washington, A.L., Fondeur, F.F. “Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU”, SRNL-RP-2013-00536, Rev. 0, September 2013.

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