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Solvent Hold Tank Sample Results for MCU-14-395/396 and MCU-14-497/498: June and July 2014 Monthly Samples

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EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-395/396, pulled 6/27/2014, on July 15, 2014 and MCU-14-497/498, pulled on 7/22/2014, on July 27, 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. Since an addition of TiDG and MaxCalix to the SHT occured in early July 2014, the solvent does not require TiDG addition at this time. The current TiDG level (1.9 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 late 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-radioactive, NGS "cocktail" containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. The resulting "blend" solvent is essentially NGS with residual amounts of BOBCalix and TOA. On July 17, 2014, Operations personnel delivered two samples from the SHT (MCU-14-395 and MCU-14-396) for analysis. Later on July 27, 2014, Operations personnel sent an additional two samples from the SHT (MCU-14-497 and MCU-14-498) 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 and used for comparison and evaluation. The results from the analyses are presented in this document.

2.0 Experimental Procedure

2.1 <u>Experimental Procedure</u>

Samples were received in p-nut vials containing ~10 mL each (see Fig 2-1). Once taken into a radioactive hood, the samples were visually inspected, analyzed for pH, a single month of samples were 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).

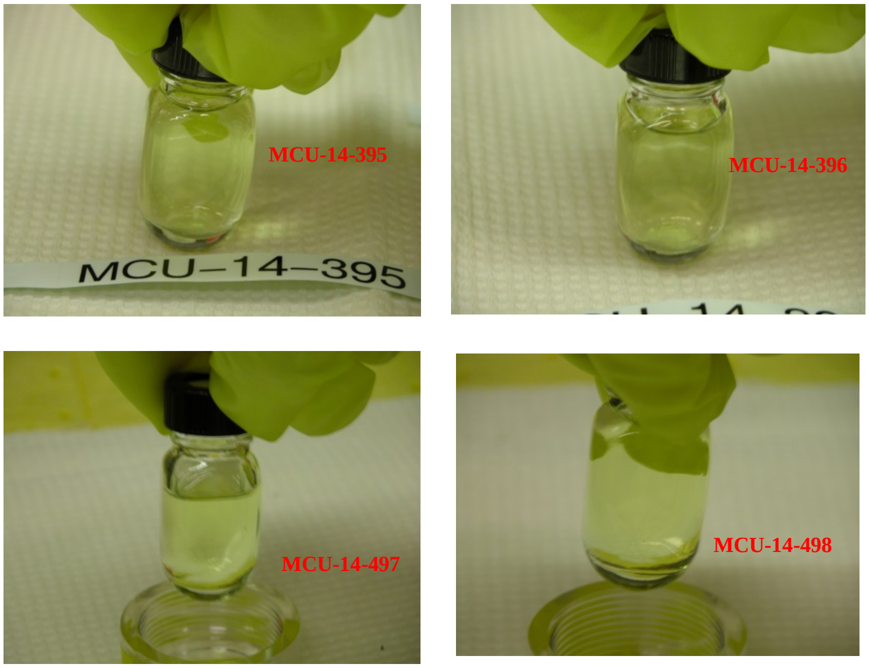

Figure 2-1. Typical appearance of the four vials from MCU-14-395/396 and MCU-14-497/498.

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 four p-nut vials (MCU-14-395/396 and MCU-14-497/498) contained a single phase liquid with no apparent solids contamination or cloudiness. All samples had a pH value of 5.5. Tables 3-1 and 3-2 contain the results of the analyses for the combined June and July samples, respectively.

Density measurements of the samples gave results of 0.8318 g/mL (0.38% RSD) (or 0.8305 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-14-395/396 at 23.5 °C and 0.830 g/mL (0.06% RSD) for MCU-14-497/498 (or 0.8283 g/mL when corrected for temperature) at 23 °C. The calculated densities (0.8305 g/mL and 0.8283 g/mL at 25 °C) for MCU-14-395/396 and MCU-14-497/498 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-14-395/396 and MCU-14-497/498 samples.

The analytical data for the composite samples from June and July 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 density measurements currently use parameters previously obtained with the CSSX solvent to estimate the Isopar® L and modifier concentrations in the NGS-CSSX solvent and therefore it may not be accurate. 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 0.821 ± 0.019 g/mL and 0.819 ± 0.019 g/mL respectively which compares well with the measured and corrected to 25 °C mass concentration (densities) of 0.8305 and 0.8283 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 were low relative to the laboratory standard sample, 18% and 14% respectively in the July 17 sample and by 14% and 17% in the July 27 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 below (~65% of) the expected value (1.55 E3 mg/L) for the most recent sample (MCU-14-497/498). Since the last characterization report, MCU engineering issued on July 02, 2014 a report recommending adding 420 g of TiDG (of which 340g were added but according to the 497/948 sample results only 235 g or 69 % of added TiDG effectively ended up in the SHT) and 2980 g of MaxCalix to the SHT (of which 2,652 g or 89 % of added MaxCalix effectively ended up in the SHT).[3] However, the TiDG concentration of these samples, the TiDG level is above the minimum recommended level for sufficient stripping of 1 mM. 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 and it will be allowed to decline with no further additions.

The current level of TiDG is believed to be sufficient to prevent anionic impurities from pairing with extractant-bound cesium, preventing cesium stripping, and increasing the activity level in the solvent. The current TiDG level of 1000 mg/L (~1.9 mM) is at the recommended operating TiDG level of 2 mM,[4] (the minimum recommended operating TiDG 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 increased to 1000 mg/L in this last sample. This level is consistent with recent addition of TiDG and MaxCalix in a modifier solution to the SHT in early July 2014.

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-14-395/396 and MCU-14-497/498, shown in Table 3-3, indicate the solvent's gamma activity decreased (4.1E04 dpm/mL) relative to the June sample (see Fig. 3-2). This activity level was previously seen in samples MCU-135/136 and MCU-214/216 analyzed early April 2014. This reading indicates the solvent is being stripped properly as MCU is processing real radioactive supernate.

No 4-sec-butylphenol beyond 100 ppm (HPLC method detection limit) was observed by HPLC. No impurities were detected by the SVOA method. No significant impurities were observed in the H-NMR spectrum of these samples.

[♣] 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.

Table 3-1. Sample Results for MCU-14-395/396 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300312860	6.50E+05	6.16E+05	106
Isopar® L	FT-HNMR	NA	6.31E+05	6.16E+05	102
Isopar® L	Density[*]	NA	6.26E+05	6.16E+05	102
Average[$]	All	NA	6.27E+05	6.16E+05	102
Modifier	HPLC	300311584	1.50E+05	1.69E+05	89
Modifier	SVOA	300312860	1.70E+05	1.69E+05	101
Modifier	FT-HNMR	NA	1.44E+05	1.69E+05	85
Modifier	Density[*]	NA	1.54E+05	1.69E+05	91
Average[$]	All	NA	1.53E+05	1.69E+05	91
TiDG (HCl)	Titration	NA	7.14E+02	1.55E+03	46
TiDG (HCl)	FT-HNMR	NA	1.18E+03	1.55E+03	76
Average[$]	All	NA	7.51E+02	1.55E+03	48
trioctylamine	SVOA	300312860	2.70E+02	5.50E+02	49
trioctylamine	Titration	NA	4.23E+02	5.50E+02	77
Average[$]	All	NA	3.30E+02	5.50E+02	60
MaxCalix	HPLC	300312860	3.75E+04	4.40E+04	85
MaxCalix	FT-HNMR	NA	3.40E+04	4.40E+04	77
Average[$]	All	NA	3.60E+04	4.40E+04	82
BobCalix	HPLC	300312860	3.44E+03	4.00E+03	86
Density (g/mL)	Direct Measurement	NA	0.8305	0.835	99

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR malfunction due to an electrical outage. 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-14-497/498 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300312937	6.40E+05	6.16E+05	104
Isopar® L	FT-HNMR	NA	6.43E+05	6.16E+05	104
Isopar® L	Density[*]	NA	6.24E+05	6.16E+05	101
Average[$]	All	NA	6.25E+05	6.16E+05	101
Modifier	HPLC	300312937	1.42E+05	1.69E+05	84
Modifier	SVOA	300312937	1.80E+05	1.69E+05	107
Modifier	FT-HNMR	NA	1.45E+05	1.69E+05	86
Modifier	Density[*]	NA	1.53E+05	1.69E+05	91
Average[$]	All	NA	1.52E+05	1.69E+05	90
TiDG (HCl)	Titration	NA	9.86E+02	1.55E+03	64
TiDG (HCl)	FT-HNMR	NA	1.07E+03	1.55E+03	69
Average[$]	All	NA	1.00E+03	1.55E+03	65
trioctylamine	SVOA	300312937	2.70E+02	5.50E+02	49
trioctylamine	Titration	NA	3.89E+02	5.50E+02	71
Average[$]	All	NA	3.21E+02	5.50E+02	58
MaxCalix	HPLC	300311736	3.91E+04	4.40E+04	89
MaxCalix	FT-HNMR	NA	3.60E+04	4.40E+04	82
Average[$]	All	NA	3.78E+04	4.40E+04	86
BobCalix	HPLC	300311736	3.30E+03	4.00E+03	83
Density (g/mL)	Direct Measurement	NA	0.8283	0.835	99

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR unit malfunction due to an unexpected electrical outage. 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.

[$] $x = \frac{\sum_1^i \left(x_i / \delta_i^2 \right)}{\sum_1^i \left(1 / \delta_i^2 \right)}$; 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-14-395/396	1.29E+06	300312860
MCU-14-497/498	4.11E+04	300312937

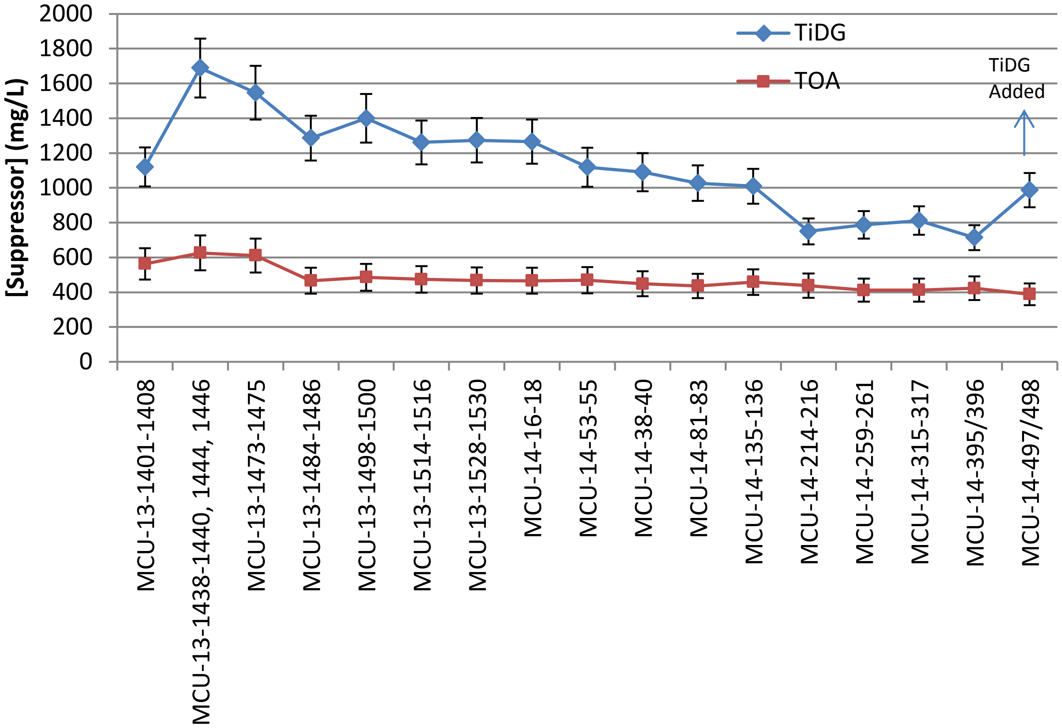

Figure 3-1. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended TiDG level is 517 mg/L.

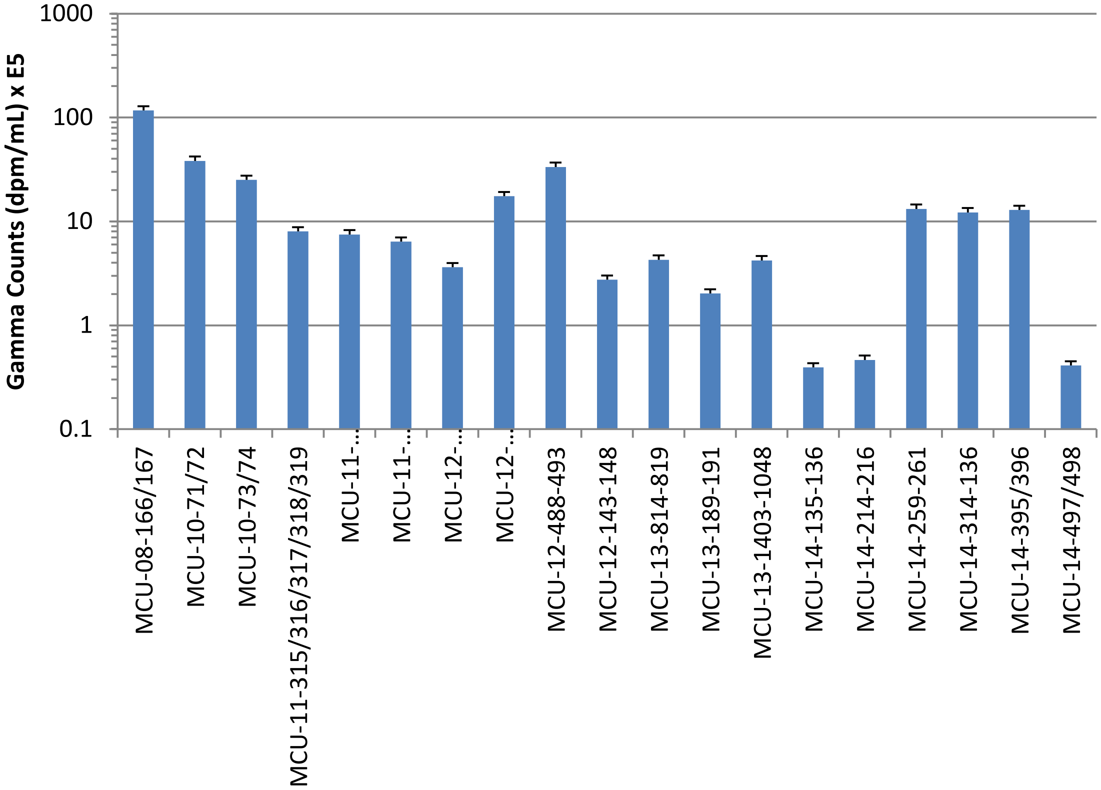

Figure 3-2. The gamma count of selected SHT samples. One standard deviation is 5%.

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. Both samples have similar composition. Since an addition of TiDG and MaxCalix to the SHT occurred in early July 2014, both the MaxCalix and TiDG levels are near nominal values. 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-14-135/136 and MCU-14-214/215/216: February and March 2014 Monthly Samples,” SRNL-STI-2014-00270, Rev. 0, June 2014.

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