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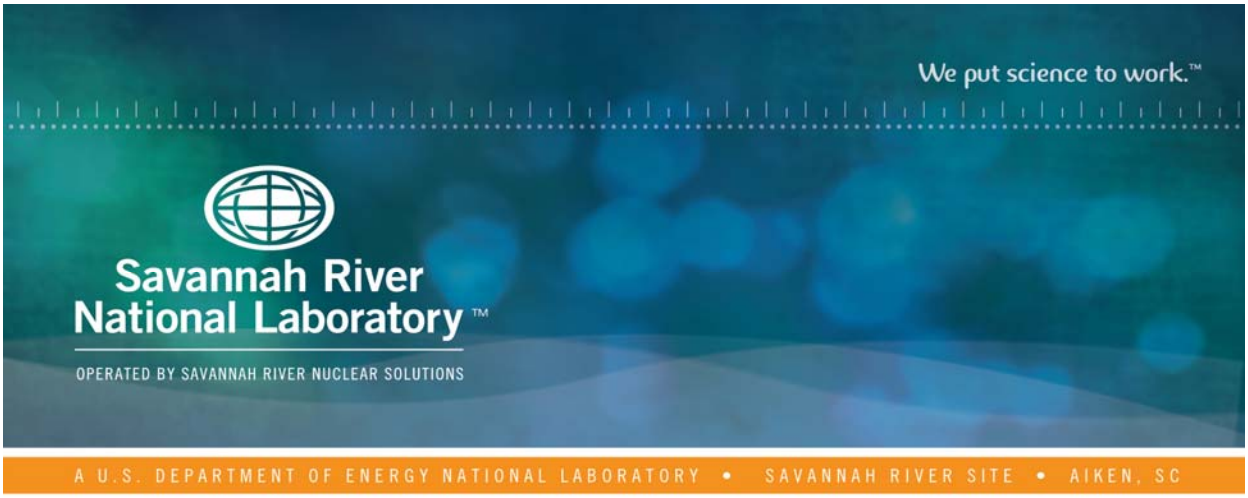

Solvent Hold Tank Sample Results for MCU-14-943 and MCU-14-1061 : November 2014 Monthly Samples

F. F. Fondeur

K. M. L. Taylor-Pashow

February 2015

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REVIEWS AND APPROVALS

AUTHORS:

F. F. Fondeur, Separations and Actinide Science Programs Date

K. M. L. Taylor-Pashow, Separations and Actinide Science Programs Date

TECHNICAL REVIEW:

T. B. Peters, Advanced Characterization and Processing Date

APPROVAL:

F. M. Pennebaker, Manager Date
Advanced Characterization and Processing

S. L. Marra, Manager Date
E&CPT Research Programs

E. A. Brass, Manager Date
MCU & Salt/Sludge Processing

EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-943, pulled 11/28/2014 and MCU-14-1061, pulled on 12/03/2014) for analysis. The samples were combined and analyzed for composition. Analysis of the combined sample (MCU-14-943-1061) indicated low concentrations of the suppressor (TiDG) and modifier (CS-7SB) despite the addition of TiDG to the solvent in October 26, 2014. However, the TiDG level in this sample is within recommended operating parameters. The solvent's density is at nominal value despite the low modifier level. No impurities were observed in the solvent 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.

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LIST OF ABBREVIATIONS

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 November 28, 2014, Operations personnel delivered one sample from the SHT (MCU-14-943) for analysis. Later, on December 3, 2014, Operations personnel sent an additional sample from the SHT (MCU-14-1061) for analysis. The latter sample was sent to increase the sample volume 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 (September 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. Estimated 29,918 gallons of salt solution and dilution stream was processed at MCU between the sampling dates of November 28 and December 3, 2014.

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

Event	Date
TiDG/MaxCalix trim added to MCU[3]	October 26, 2014
22 Gal of Isopar™ L trim added to MCU[3]	November 25, 2014
SHT sampled MCU-14-943	November 28, 2014
SHT sampled MCU-14-1061	December 3, 2014

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 were combined and placed in a 30 mL Teflon bottle. The combined sample is referred to as MCU-14-943-1061 in the rest of this document. Aliquots of this sample were removed for 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) (Fourier-Transform Infra-Red spectroscopy or FTIR was not operational at this time). 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[4]

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 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

Samples, MCU-14-943 and 1061 contained a single phase liquid with no apparent solids contamination or cloudiness. Both samples had a pH value of 5.5. Table 3-1 contains the results for the combined MCU-14-943-1061 sample. The two samples were composited to provide enough volume for analysis.

Isopar™ L and Modifier Levels

Density measurements of the samples gave results of 0.833 g/mL (0.15% RSD) (or 0.831 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-14-943-1061 at 21.5 °C. The calculated density (0.831 g/mL) for MCU-14-943-1061 is similar to the calculated density for the standard sample (0.832 g/mL at 25 °C for the NGS-CSSX blend made in the laboratory)[1]. The last trim addition, which contained only Isopar™L was added to MCU on November 25, 2014.[3] Using the density as a starting point, it appears that the concentration level of the Isopar™ L component in the sample should be similar to its nominal value.

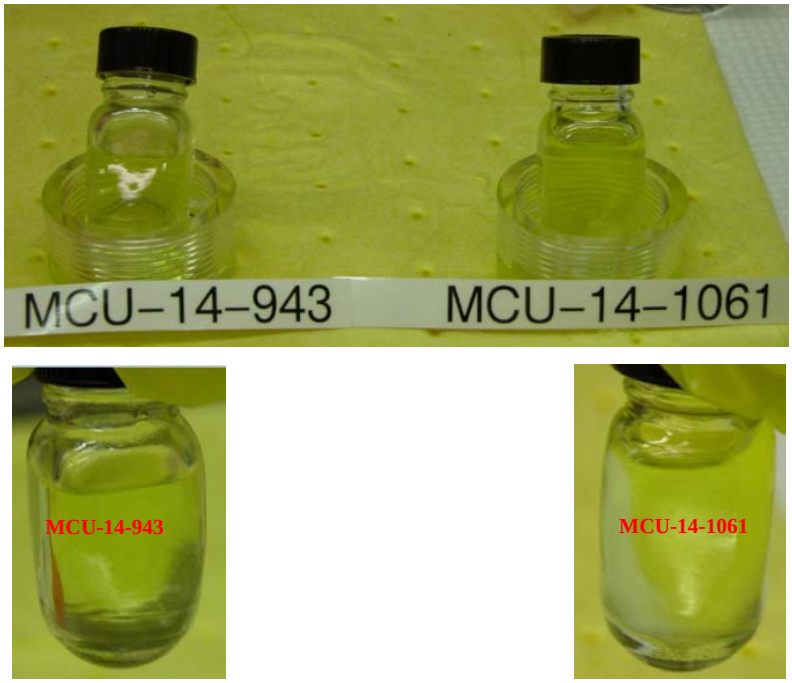

Figure 1. Typical appearance of the two vials from MCU-14-943 and MCU-14-1061.

Of all the methods listed, density has the lowest uncertainty. An examination of Table 3-1 shows that the Isopar™ L as derived from the density measurements is closer to its nominal value while the modifier concentration is slightly less than its nominal values. Since this sample density is similar to the standard density, the two main components, Isopar™ L and the modifier, are close to their nominal values.

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

The accuracy of the different measurement were within expectation as reflected in the total mass sum of the "average" results listed in Table 3-1, which add up to 0.829 ± 0.019 g/mL. This value compares well with the measured and corrected to 25 °C mass concentration (density) of 0.831 g/mL.

Suppressors Levels

As shown in Table 2-1, the October 26, 2014 trim added TiDG•HCl to the solvent and that trim raised the TiDG level to near its nominal level (nominal is ~ 1440 mg/L TiDG).[5] In this sample, the suppressors' concentration levels are below their nominal values. The TiDG and TOA concentration levels in sample MCU-14-943-1061 are 77% and 49% of their nominal values. However, the TiDG level is above the minimum recommended level (479 mg/L).[6] As shown in Fig. 2, the TiDG level appears to trend downward after the October 26, 2014 trim. MCU no longer trims the solvent with TOA.

Extractants Levels

The MaxCalix level is at its nominal value in sample MCU-14-943-1061 after the October 26th trim addition. As shown in Fig. 3, the MaxCalix level is at its nominal value but its trend appears to be downward. Future samples will indicate if the observed downward trend in Fig. 3 is persistent. The BOBCalixC6 level is at 79% of its nominal value. The BOBCalixC6 is also no longer added to MCU.

Gamma Level

The gamma level measurement of MCU-14-943-1061 is shown in Fig. 4. As shown in this figure, the sample (MCU-14-943-1061) gamma level is less than 1E5 dpm/mL (4.15E4 dpm/mL). This level is consistent previous gamma levels (except for the spike observed in the October sample) in the solvent when there were not known issues with extraction or stripping. The spike observed in the October sample seems to coincide with the finding of solids in the strip feed tank.

Impurities

No impurities were detected by the SVOA method (ADS # 300315205). No significant impurities were observed in the H-NMR spectrum of these samples.

Table 3-1. Sample Results for MCU-14-943-1061

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	6.22E+05	6.23E+05	100
Average[$]	All	NA	6.21E+05	6.23E+05	100
Modifier	HPLC	300315205	1.54E+05	1.69E+05	91
Modifier	FT-HNMR	NA	1.60E+05	1.69E+05	95
Modifier	Density[*]	NA	1.59E+05	1.69E+05	94
Average[$]	All	NA	1.59E+05	1.69E+05	94
TiDG	Titration	NA	1.10E+03	1.44E+03	76
TiDG	FT-HNMR	NA	1.14E+03	1.44E+03	79
Average[$]	All	NA	1.10E+03	1.44E+03	77
trioctylamine	Titration	NA	2.60E+02	5.30E+02	49
Average[$]	All	NA	2.60E+02	5.30E+02	49
MaxCalix	HPLC	300315205	4.38E+04	4.44E+04	99
MaxCalix	FT-HNMR	NA	4.62E+04	4.44E+04	104
Average[$]	All	NA	4.46E+04	4.40E+04	101
BOBCalix	HPLC	300315205	3.20E+03	4.03E+03	79
Average[$]	All	300315205	3.20E+03	4.03E+03	79
Density at 25ºC (g/mL)	Direct Measurement	NA	0.8306	0.835	99

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR data not available for this sample. 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, 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.

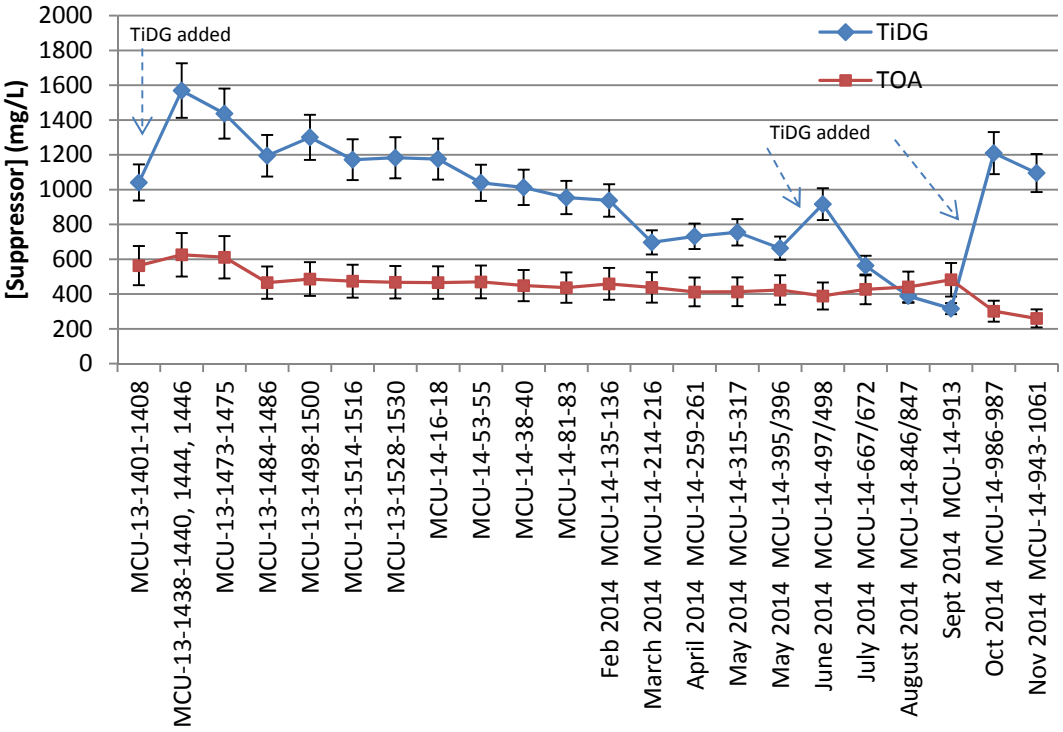

Figure 2. Suppressor concentration (free base form) as measured by titration in SHT samples since NGS implementation. The minimum recommended is 479 mg/L for TiDG or 515 mg/L for TiDG*HCl.

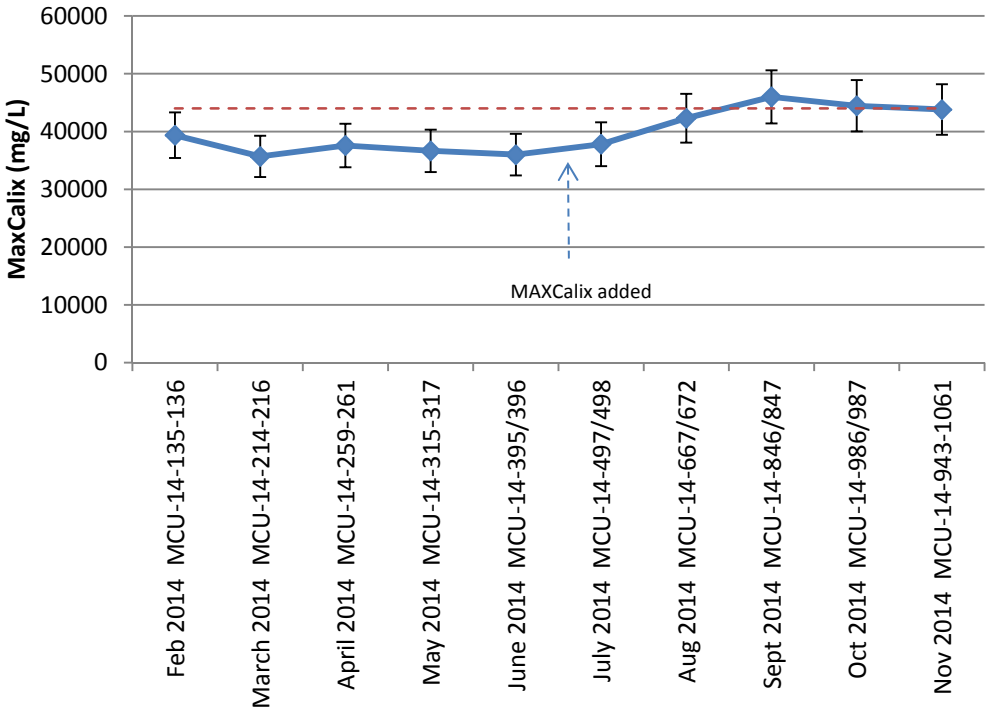

Figure 3. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,000 mg/L is the nominal concentration).

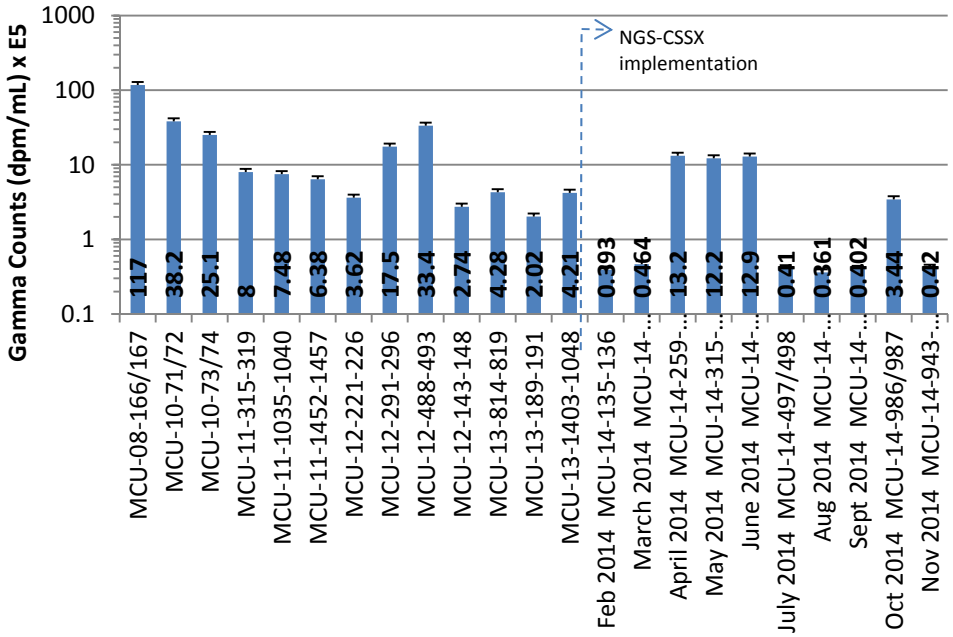

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

SRNL received two sets of SHT samples (MCU-14-943, pulled 11/28/2014 and MCU-14-1061, pulled on 12/03/2014) for analysis. The samples were analyzed for composition. Analysis of the combined sample (MCU-14-943-1061) indicated low concentrations of the suppressor (TiDG) and modifier (CS-7SB) despite the addition of TiDG to the solvent in October 26, 2014. The solvent's density is at nominal value despite the low modifier level. No impurities were observed in the solvent 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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