Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Solvent Hold Tank Sample Results for MCU-14-913 and MCU-14-986/987 : October 2014 Monthly Samples

F. F. Fondeur

K. M. L. Taylor-Pashow

January 2015

SRNL-STI-2014-00623, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2014-00623
Revision 0

Keywords: *MCU, ARP, ISDP, NGS*

Retention: *Permanent*

Solvent Hold Tank Sample Results for MCU-14-914 and MCU-14-986/987 : October 2014 Monthly Samples

F. F. Fondeur
K. M. L. Taylor-Pashow

January 2015

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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

EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-913, pulled 10/7/2014 and MCU-14-986/987, pulled on 10/27/2014) for analysis. The samples were analyzed for composition. Analysis of sample MCU-14-913 indicated low concentrations of the suppressor (TiDG) and of the modifier (CS-7SB) in the solvent. The addition of suppressor and modifier to the solvent on October 26, 2014 restored the concentration of these components to nominal levels as confirmed with the analysis of sample MCU-14-986/987. The laboratory will continue to monitor the quality of the solvent in particular for any new impurity or degradation of the solvent components.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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 October 8, 2014, Operations personnel delivered one sample from the SHT (MCU-14-913) for analysis. Later, on November 3, 2014, Operations personnel sent an additional two samples from the SHT (MCU-14-986 and MCU-14-987) for analysis. The latter samples were sent to verify the trim addition that included TiDG, Isopar™ L, MaxCalix, and modifier made to the solvent on October 26, 2014. 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
Sample from SHT (MCU-14-913)	October 7, 2014
TiDG/MaxCalix trim added to MCU	October 26, 2014
Sample from SHT(MCU-14-986/987)	October 27, 2014
Isopar™L trim added to MCU	November 25, 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, analyzed for pH. In the case of the MCU-14-986 and -987, the two samples were composited before use. Aliquots of these 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). HPLC and SVOA were performed only on the MCU-14-986/987 composite. 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

Component	mg/L	Molar
MaxCalix	~ 44,400	~ 0.0465
BOBCalixC6*	< 4,030	< 0.0035
TOA*	< 530	< 0.003
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

The p-nut vial from MCU-14-913 and each of the two p-nut vials from MCU-14-986/987 contained a single phase liquid with no apparent solids contamination or cloudiness. All samples had a pH value of 5.5. Because of the limited amount of sample volume in MCU-14-913, no chromatography or gamma analysis was conducted. Chromatography analysis (HPLC and SVOA) was conducted on MCU-14-986/987. Table 3-1 contains the results for the MCU-14-913 sample. Table 3-2 contains the results of the analyses for the MCU-986/987 composite.

Density measurements of the samples gave results of 0.833 g/mL (0.15% RSD) (or 0.831g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-14-913 at 22 °C and 0.835 g/mL (0.19% RSD) for MCU-14-986/987 (or 0.832 g/mL when corrected for temperature) at 21.8 °C. The calculated densities (0.831 g/mL) for MCU-14-913 and (0.832 g/mL) for MCU-14-986/987 are similar to the calculated density for the standard sample (0.835 g/mL at 25 °C for the NGS-MCU blend made in the laboratory)[1]. Although the measurements appear similar, there is a slight difference with respect to the standard density measurement that may indicate excess Isopar™ L evaporation since the last trim addition made to MCU was on September 25, 2014. That last trim included Isopar™L, modifier, MaxCalix, and TiDG.[3] Using the density as a starting point, we know that the concentration level of the Isopar™L component in the samples should be similar to their nominal values.

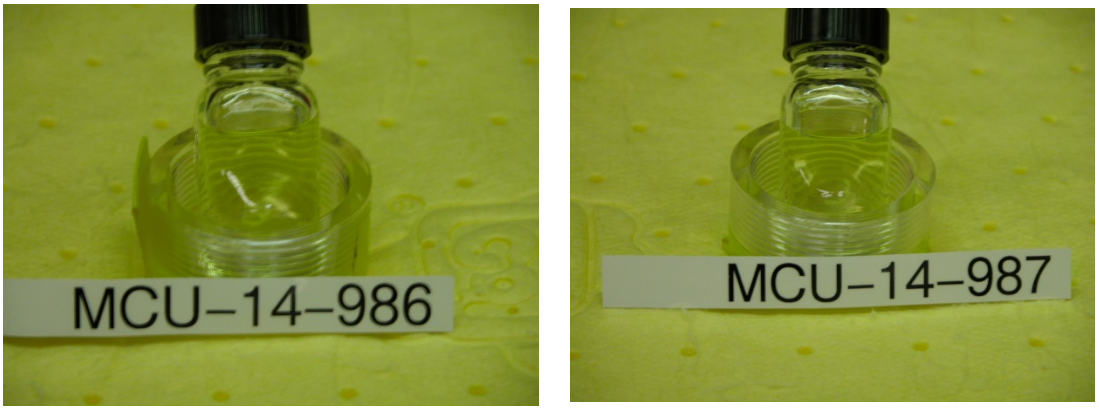

Figure 1. Typical appearance of the two vials from MCU-14-986/987 (Camera malfunctioned while capturing the MCU-14-913 vial image but that vial looked the same as the MCU-14-986/987 vials).

Of all the methods listed, density has the lowest uncertainty. An examination of Tables 3-1 and 3-2 shows that the Isopar™ L and modifier concentrations in MCU-14-913 and MCU-14-986/987 as derived from the density measurements are closer to the nominal than the values obtained from the spectroscopic methods (FT-IR and FT-HNMR). Since the spectroscopic methods are noisier than the gravimetric method, the results from the density measurements are primarily used here. Despite the slight discrepancy, the modifier concentration is slightly lower than nominal in these samples (MCU-14-913 and MCU-14-986/987). However, the addition of TiDG-modifier-Isopar™ L trim to the solvent on

---

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

October 26, 2014 raised the levels of the modifier and TiDG closer to their nominal (recommended) levels.

All measurements indicate that the solvent has nominal levels of Isopar™ L, modifier, TiDG, and MaxCalix. 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 and 3-2 add up to 0.826 ± 0.019 g/mL (excluding BOBCalixC6) and 0.829 ± 0.019 g/mL respectively which compares well with the measured and corrected to 25 °C mass concentration (densities) of 0.833 and 0.832 g/mL, respectively. As indicated in Table 3-1 and Table 3-2, these calculated densities are similar to that of the standard (0.835 g/mL).

As stated earlier, the October 26, 2014 trim to the solvent raised its TiDG level closer to the nominal level (~ 1210 mg/L TiDG or 1301 mg/L TiDG•HCl) as shown in Fig. 2. The TOA concentration slightly dropped to 300 mg/L possibly due to the dilution effect from the October 26 trim. The trim also slowly returned the Max Calix concentration to the expected value (47.8E3 mg/L) as shown in Fig. 3. The rate of rise of the MaxCalix concentration in the solvent is indicative of the mixing effectiveness in the MCU operation in the absence of any destructive or depletion mechanism of the MaxCalix. The MaxCalix's trend level appears to have reached a steady state value (plateau). The BOBCalixC6 concentration has remained steady at 3,000 mg/L level.

The lower modifier level reported by the spectroscopic methods (FTIR and FT-HNMR) may be due to their higher noise level compared to the gravimetric method. The density results are believed to provide the more accurate result.

Gamma measurements of MCU-14-986/987, shown in Fig. 4, indicate the solvent's gamma activity level reached the tens of thousands level (3.44E05 dpm/mL in the MCU-14-986/987 sample: ADS LIMS #300314797). This reading indicates the solvent may not strip properly (compared to the previous three batches) as MCU is processing real radioactive supernate. The reason for the high gamma level in the solvent during the month of October 2014 is not known at this time.

No impurities were detected by the SVOA method (ADS # 300314797). No significant impurities were observed in the H-NMR spectrum of these samples.

Table 3-1. Sample Results for MCU-14-913

Analysis	**Method**	**LIMS #**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar™ L	FT-HNMR	NA	6.51E+05	6.23E+05	104
Isopar™ L	FTIR	NA	6.38E+05	6.23E+05	102
Isopar™ L	Density[*]	NA	6.19E+05	6.23E+05	99
Average[$]	All	NA	6.21E+05	6.23E+05	100
Modifier	FT-HNMR	NA	1.45E+05	1.69E+05	86
Modifier	FTIR	NA	1.44E+05	1.69E+05	85
Modifier	Density[*]	NA	1.64E+05	1.69E+05	97
Average[$]	All	NA	1.60E+05	1.69E+05	95
TiDG	Titration	NA	3.40E+02	1.44E+03	24
TiDG	FT-HNMR	NA	7.42E+02	1.44E+03	52
Average[$]	All	NA	3.60E+02	1.44E+03	25
trioctylamine	Titration	NA	4.82E+02	5.30E+02	91
Average[$]	All	NA	4.82E+02	5.30E+02	91
MaxCalix	FT-HNMR	NA	4.45E+04	4.44E+04	100
Average[$]	All	NA	4.45E+04	4.44E+04	100
Density (g/mL)	Direct Measurement	NA	0.833	0.835	100

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR uncertainty is 15% for Isopar™ L and 13% for the 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 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.

[$] $x = \frac{\sum_1^i \left(x_i / \delta_i^2 \right)}{\sum_1^i \left(1 / \delta_i^2 \right)}$; x_i stands for the concentration obtained at a given method and δ_i is the corresponding uncertainty.

Table 3-2. Sample Results for MCU-14-986/987 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar™ L	FT-HNMR	NA	6.44E+05	6.23E+05	103
Isopar™ L	FTIR	NA	6.38E+05	6.23E+05	102
Isopar™ L	Density[*]	NA	6.20E+05	6.23E+05	99
Average[$]	All	NA	6.21E+05	6.23E+05	100
Modifier	HPLC	300314797	1.52E+05	1.69E+05	90
Modifier	FT-HNMR	NA	1.50E+05	1.69E+05	88
Modifier	FTIR	NA	1.44E+05	1.69E+05	85
Modifier	Density[*]	NA	1.62E+05	1.69E+05	96
Average[$]	All	NA	1.59E+05	1.69E+05	94
TiDG (HCl)	Titration	NA	1.30E+03	1.44E+03	90
TiDG (HCl)	FT-HNMR	NA	1.65E+03	1.44E+03	114
Average[$]	All	NA	1.35E+03	1.44E+03	94
trioctylamine	Titration	NA	3.01E+02	5.30E+02	57
Average[$]	All	NA	3.01E+02	5.30E+02	57
MaxCalix	HPLC	300314797	4.31E+04	4.44E+04	97
MaxCalix	FT-HNMR	NA	4.72E+04	4.44E+04	106
Average[$]	All	NA	4.44E+04	4.44E+04	100
BOBCalixC6	HPLC	300314797	3.00E+03	4.03E+03	74
Average[$]	All	300314797	3.00E+03	4.03E+03	74
Density (g/mL)	Direct Measurement	NA	0.832	0.835	100

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR uncertainty is 15% for Isopar™ L and 10% for the 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 13% for 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.

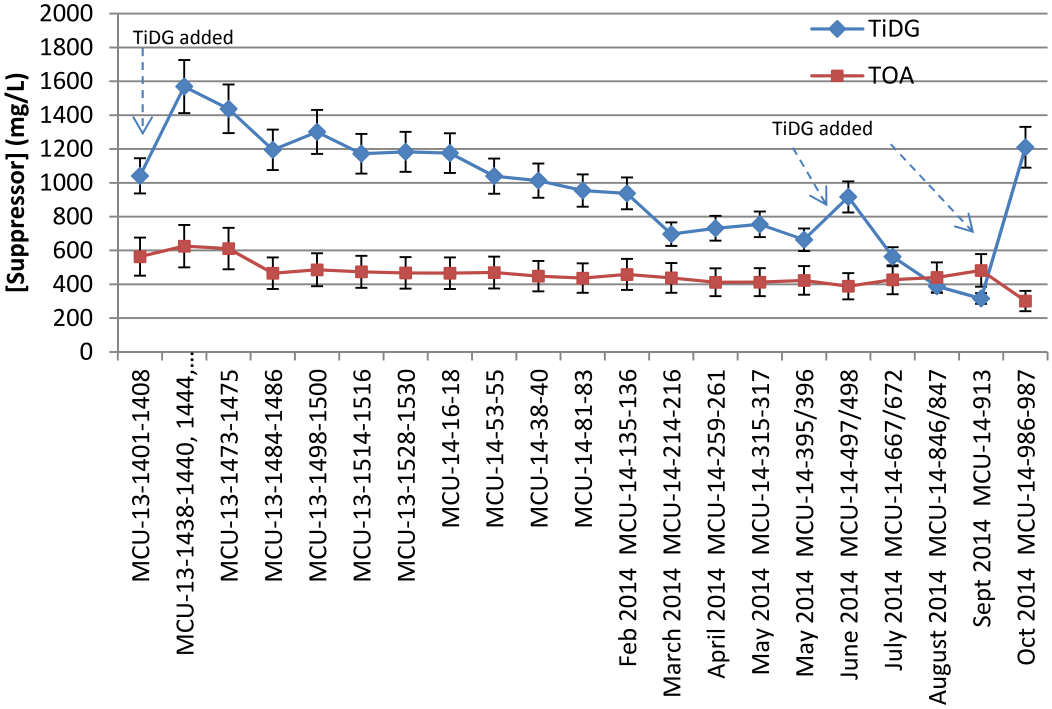

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 480 mg/L for TiDG or 515 mg/L for TiDG*HCl.

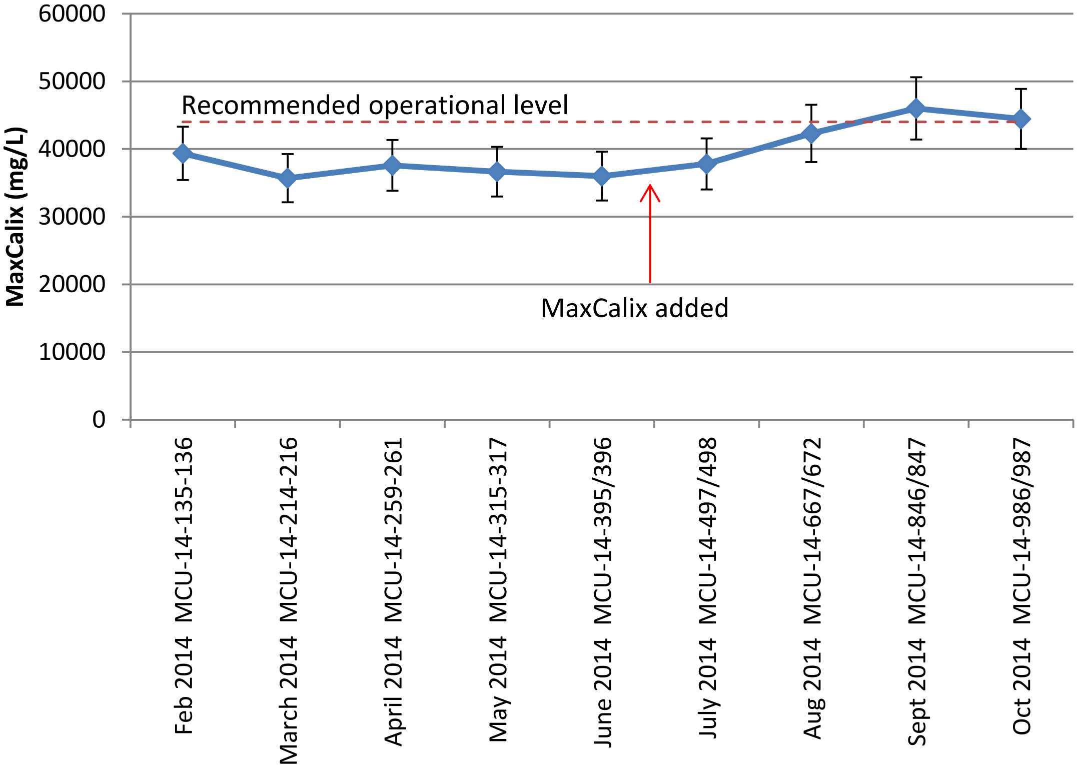

Figure 3. MaxCalix concentration as measured by HPLC (and FT-HNMR) of recent samples since NGS implementation (44,000 mg/L is the nominal concentration).

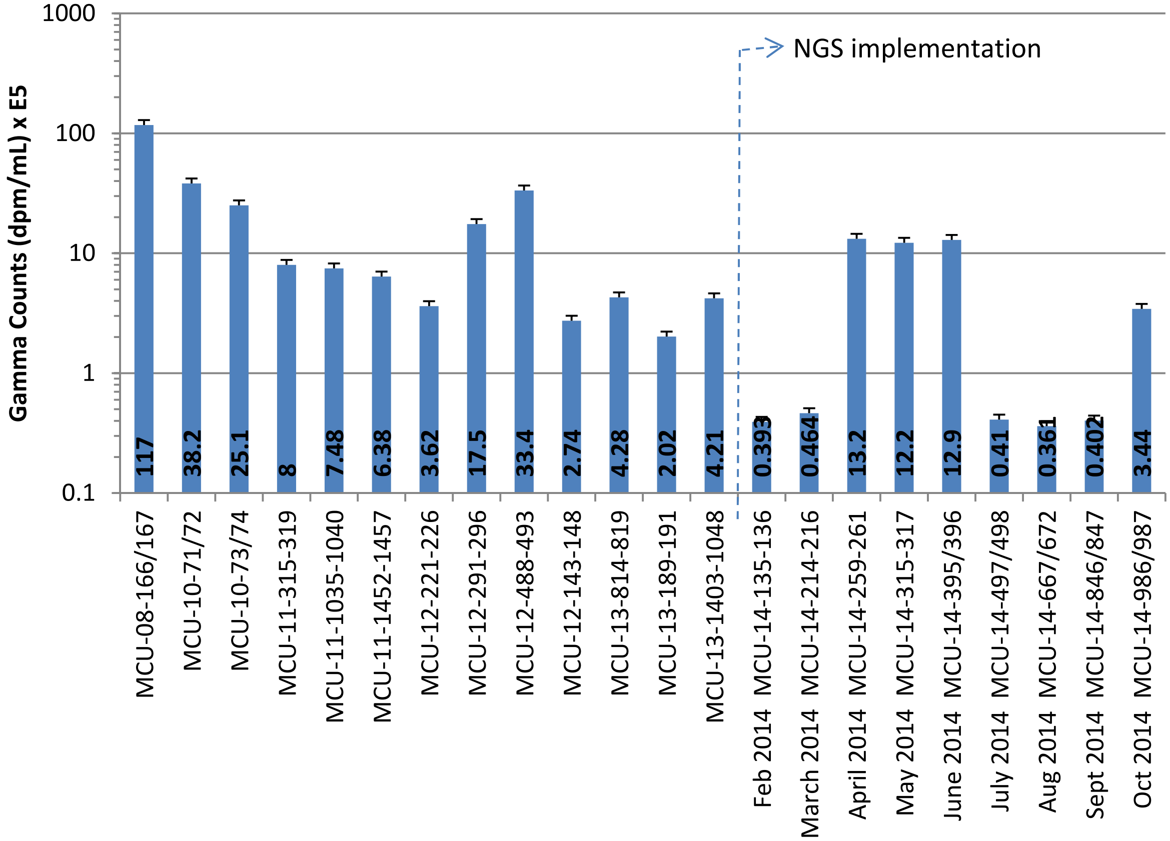

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

SRNL received two sets of SHT samples (MCU-14-913, pulled 10/7/2014 and MCU-14-986/987, pulled on 10/27/2014) for analysis. The samples were analyzed for composition. Analysis of sample MCU-14-913 indicated low concentrations of the suppressor (TiDG) and of the modifier (CS-7SB) in the solvent. The addition of suppressor and modifier to the solvent in October 26, 2014 restored the concentration of these components to nominal levels as confirmed with the analysis of sample MCU-14-986/987. 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

---

[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] T. B. Peters, A. L. Washington II, and S. D. Fink, “Results of Analyses of the Next Generation Solvent for Parsons”, SRNL-STI-2012-00065, rev. 0, February 2012

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

E. A. Brass, 241-121H
C. K. Chiu, 704-27S
E. J. Freed, 704-S
A. G. Garrison, 241-121H
T. E. Smith, 241-152H
R. T. McNew, 241-152H
C. J. Scherman, 241-152H
B. A. Gifford, 704-56H
D. J. Martin, 766-H
A. R. Shafer, 704-27S

P. R. Jackson, DOE-SR, 703-46A

T. B. Peters, 773-42A
C. A. Nash, 773-42A
F. F. Fondeur, 773-A
K. M. L. Taylor-Pashow, 773-A