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Solvent Hold Tank Sample Results for MCU-15-661-662-663: April 2015 Monthly Sample

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EXECUTIVE SUMMARY

The Savannah River National Lab (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-15-661, MCU-15-662, and MCU-15-663 pulled on April 2, 2015) for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-661-662-663 indicated a low concentration (~ 63% of nominal) of the suppressor (TiDG) and a slightly below the nominal concentration (~ 10% below nominal) of the extractant (MaxCalix). The modifier (CS-7SB) level was also 10% below its nominal value while the Isopar™ L level was slightly above its nominal value. This analysis confirms the addition of Isopar™L to the solvent on March 6, 2015. Despite that the values are below target component levels, the current levels of TiDG, CS-7SB and MaxCalix are sufficient for continuing operation without adding a trim at this time until the next monthly sample.

No impurities above the 1000 ppm level were found in this solvent. However, the sample was found to contain approximately 18.4 $ug/g_{solvent}$ mercury.

The gamma level increased to 8 E5 $dpm/mL_{solvent}$ and it represents an order of magnitude increase relative to previous solvent samples. The increase means less cesium is being stripped from the solvent. Further analysis is needed to determine if the recent spike in the gamma measurement is due to external factors such as algae or other material that may impede stripping

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)
CV-AA	Cold-Vapor Deposited Atomic Adsorption
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 CY13, Modular Caustic-Side Solvent Extraction Unit (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 SHT heel. The resulting "blend" solvent ("NGS Blend solvent") is essentially Next Generation Solvent (NGS) with residual amounts of BOBCalixC6 and trioctylamine (TOA). SHT samples are sent to SRNL to examine solvent composition changes over time.[1] The facility added Isopar™L to the solvent on March 6, 2015. On April 6, 2015, operations personnel delivered three samples from the SHT (MCU-15-661, MCU-15-662, and MCU-15-663) 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 (May 14, 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 being studied is shown in Table 2-1. On March 6, 20 gallons of Isopar™L was added to MCU.

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

Event	Date
Isopar™L added to MCU*	March 6, 2015
SHT sample MCU-15-661-662-663	April 2, 2015

*T. E. Smith, "Engineering Evaluation of MCU Solvent and Recommended Isopar™L Additions to Maintain Specifications", X-ESR-H-00764, June 2015

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. MCU-15-661, MCU-15-662, and MCU-15-663 were composited before use. Aliquots of the composited samples were removed to perform analysis by density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, Fourier-Transformed Infra-Red Spectroscopy (FTIR), and Fourier-Transformed Hydrogen Nuclear Magnetic Resonance (FT-HNMR). Results from analytical measurements were compared with the theoretical values shown in Table 2-2. A portion of the composite sample was digested (Parr bomb) and the liquid analyzed for mercury by Cold-Vapor Deposition Atomic Absorption (CV-AA).

Table 2-2 Nominal concentrations of the relevant components in NGS Blend[2]

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 or refurbished in MCU

[#] The total sum is approximately 0.842 g/mL which is more than 0.835 g/mL (standard density at 25 °C)

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

Physical Appearance

The p-nut vials from MCU-15-661, MCU-15-662, and MCU-15-663 were examined and found to contain a single phase liquid with no apparent solids contamination or cloudiness. All samples had a pH value of 5.5. No unusual reactions, solids, foaming, or immiscible layers were observed after compositing the samples (MCU-15-661-662-663). Table 3-1 contains the results for the MCU-15-661-662-663 sample.

Isopar™ L and Modifier Levels

Density measurement of this sample gave a result of 0.829 g/mL (0.2% RSD) (or 0.8271 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-15-661-662-663 at 22.3 °C. The temperature-adjusted density (0.827 g/mL) for MCU-15-661-662-663 is 1% below the temperature adjusted density of the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory)[1]. Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be slightly above the nominal value.

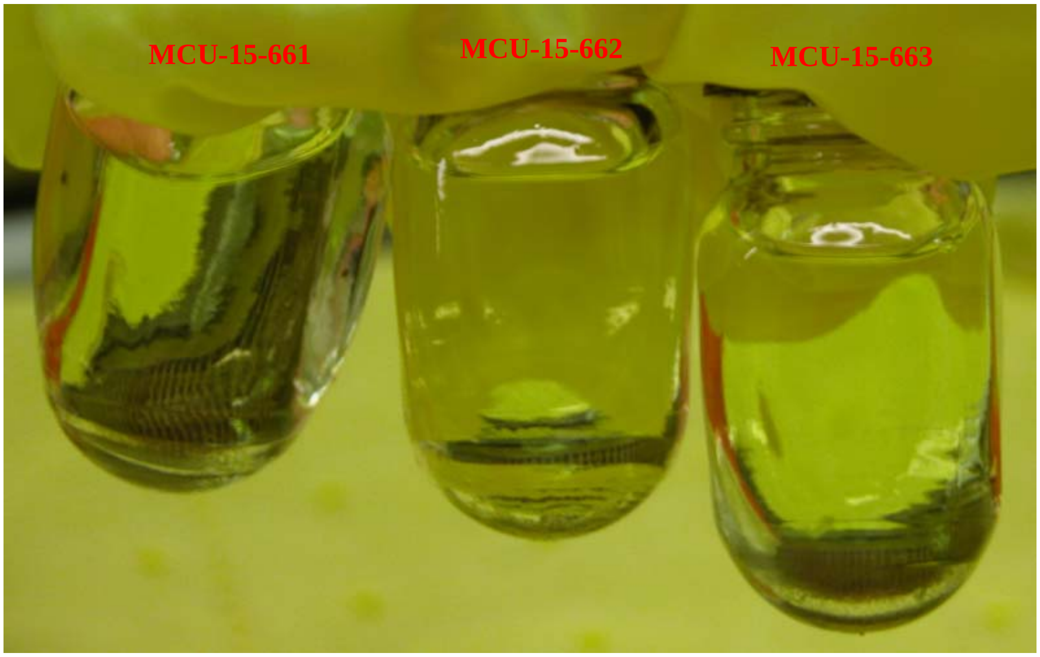

Figure 1. Typical appearance of the three vials MCU-15-661, MCU-15-662, and MCU-15-663

An examination of Table 3-1 shows that the Isopar™ L is slightly above its nominal value while the modifier concentration is 10% below its nominal value. This observation confirms the Isopar™L trim addition made to the solvent on March 6, 2015. The modifier level continues to trend downward indicating modifier is being lost to the aqueous streams at MCU (more likely than decomposition). Of all

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[1] A second standard was prepared on December 12, 2014

the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement.

All measurements indicate the Isopar™ L level and the modifier concentration level are at their nominal value. This explains why the temperature adjusted density is similar to the standard sample density. The accuracies of the different measurements were within expectation as reflected in the total mass sum of the "average" results listed in Table 3-1, which added up to 0.821 ± 0.020 g/mL. This value is reasonably close to the measured and corrected to 25 °C mass concentration (density) of the sample (0.827 g/mL) and indicates an absence of biased estimates in the analytical results.

Table 3-1. Sample Results for MCU-15-661-662-663

Analysis	**Method**	**LIMS #**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar® L	FT-HNMR	NA	6.31E+05	6.23E+05	101
Isopar® L	FTIR	NA	6.22E+05		100
Isopar® L	Density[*]	NA	6.26E+05		101
Average[$]	All	NA	6.26E+05	6.23E+05	101
Modifier	HPLC	300316685	1.50E+05	1.69E+05	89
Modifier	FT-HNMR	NA	1.49E+05		88
Modifier	FTIR	NA	1.52E+05		90
Modifier	Density[*]	NA	1.51E+05		89
Average[$]	All	NA	1.51E+05	1.69E+05	89
TiDG	Titration	NA	0.92E+03	1.44E+03	64
TiDG	FT-HNMR	NA	0.87E+03		60
Average[$]	All	NA	0.91E+03	1.44E+03	63
trioctylamine	Titration	NA	2.82E+02	5.30E+02	53
Average[$]	All	NA	2.82E+02	5.30E+02	53
MaxCalix	FT-HNMR	NA	4.00E+04	4.44E+04	90
MaxCalix	HPLC	300316685	3.95E+04		89
Average[$]	All	NA	3.98E+04	4.44E+04	90
BOBCalixC6	HPLC	300316685	2.88E+03	4.03E+03	71
Average[$]	All	NA	2.88E+03	4.03E+03	71
Density (g/mL)	Direct Measurement	NA	0.8271	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.

Suppressors Levels

The TiDG concentration level (0.91E+033 mg/L) for the MCU-15-661-662-663 is 63 % of the nominal value of 1440 mg/L. The suppressor concentration is above the minimum recommended operating level (479 mg/L) and thus, the solvent does not require a TiDG addition at this time. Inferring from past TiDG concentrations level trends and in the absence of new additions or new removal mechanisms, the TiDG concentration is expected to continue to drop as shown in Fig. 2. The TOA concentration is the same within analytical uncertainty, as the March sample. Since MCU no longer adds TOA, a slow decrease in the TOA concentration is expected. However, since TOA is an amine, personnel suspect that TiDG degradation into primary amines and urea, which have previously been identified as degradation products of the suppressor when heated may be a source.[3] The urea (carbamide) may possibly undergo further degradation to form amides.[4]

Extractant Levels

The average MaxCalix level in the MCU-15-661-662-663 sample is 3.98 E+04 mg/L (±13%) which is 10% below the nominal concentration but it is within the 95% confidence level of the analytical measurement (see Figure 3). The BOBCalixC6 concentration level in MCU-15-661-662-663 is 2.88 E+03 mg/L and it continues its downward trend.

Gamma Level

The gamma measurement of MCU-15-661-662-663 is 8.04E5 dpm/mL (±5%). This level represents a spike compared with recent trends (see Fig. 4). Further analysis is needed to determine if the recent spike in the gamma measurement is due to external factors such as bacteria (amide) or other factors that may impede stripping.

Impurities

No impurities were seen at the 1000 ppm level or higher as indicated by the SVOA method. No impurities (oxidation or nitration) products were observed in this sample by FTIR (unlike in sample MCU-15-439-440-441 where secondary liquid solvent droplets were observed to contain modifier and oxidized aliphatic oil). However, the mercury level as measured by the CV-AA method was 18.4 (20% error) ug/g.

Recommendation

The current analysis indicates low modifier and TiDG levels in this solvent relative to the standard. The TiDG level (910 $mg/L_{solvent}$) is below the minimum operating recommended level (958 $mg/L_{solvent}$) but above the minimum recommended level (479 $mg/L_{solvent}$). There is sufficient TiDG in the solvent for continuing operation without adding a trim until the next monthly sample and given the need to minimize the byproducts from TiDG decomposition, we don’t recommend a TiDG trim at this time. Similarly, the modifier level (0.47 M) is well above the minimum modifier level at which the MaxCalix becomes insoluble in the solvent.

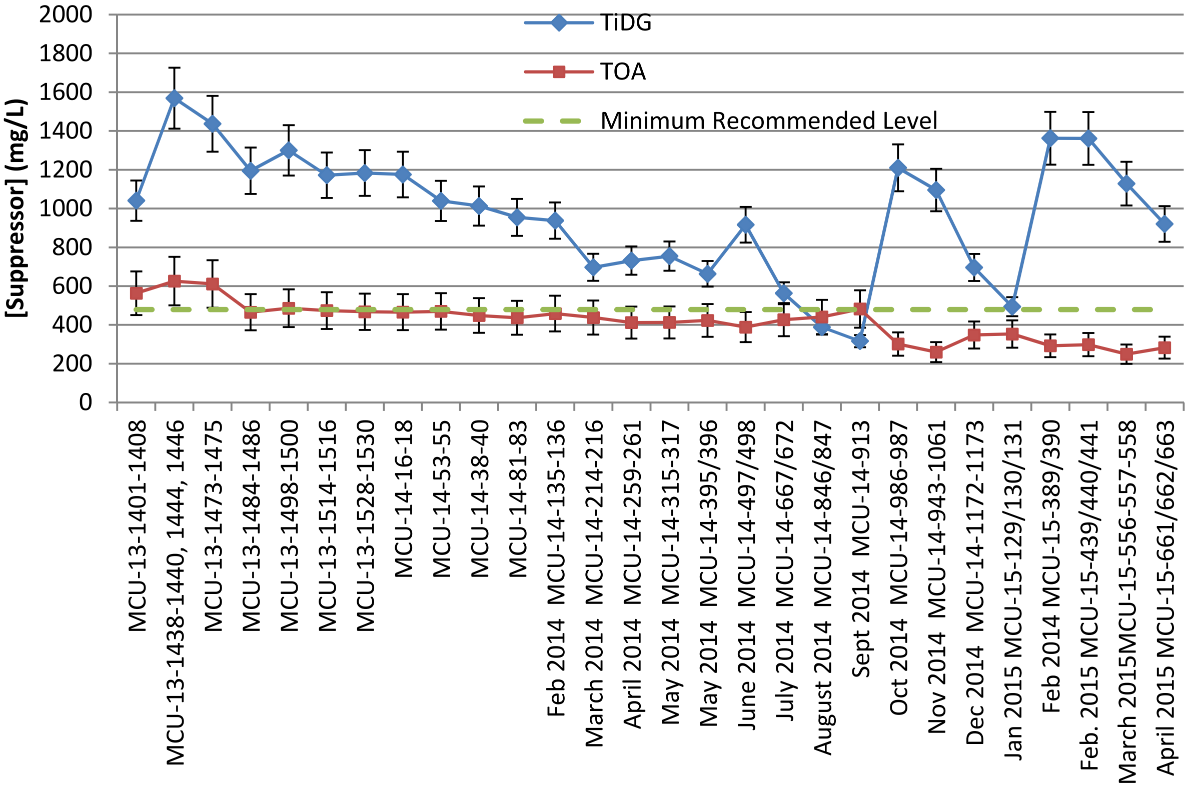

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended is 480 mg/L for TiDG.

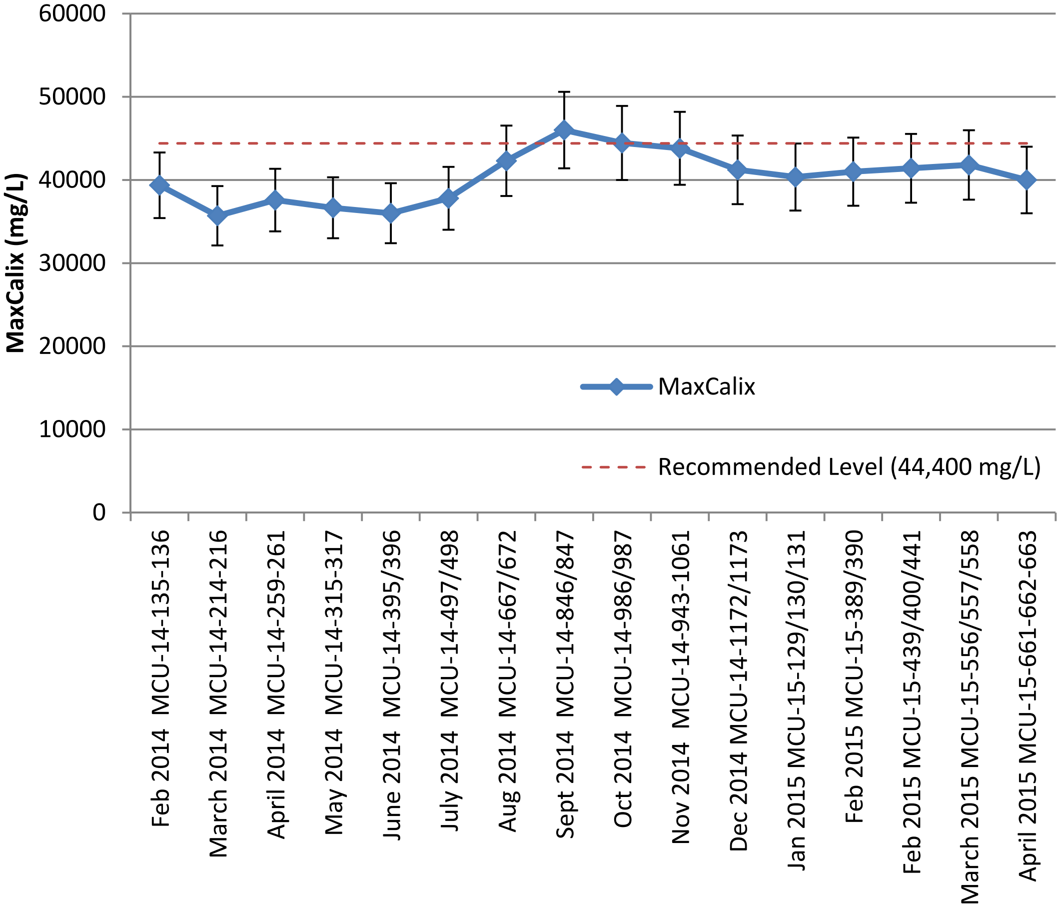

Figure 3. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

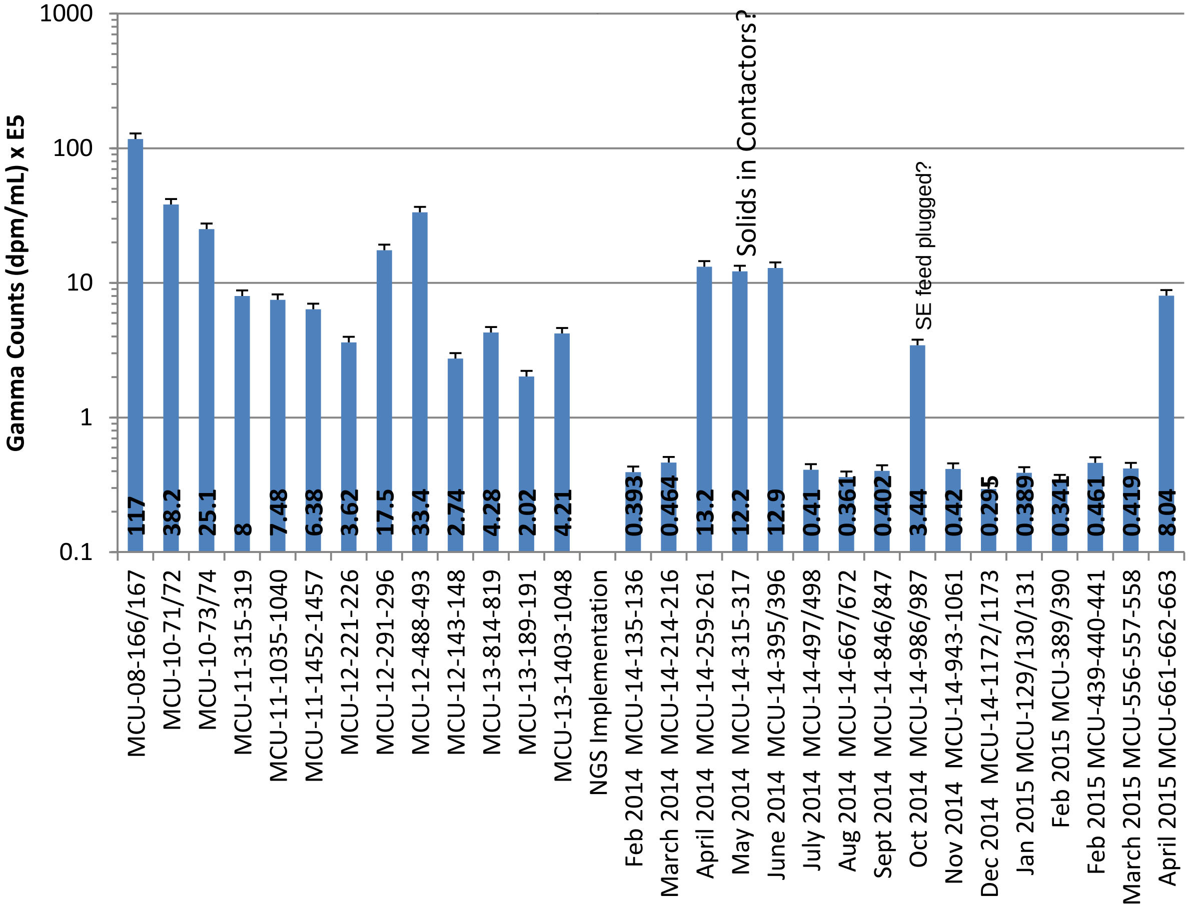

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

SRNL received one set of SHT samples (MCU-15-661, MCU-15-662, and MCU-15-663 pulled on April 2, 2015) for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-15-661-662-663 indicated a low concentration (~ 63% of nominal) of the suppressor (TiDG) and a slightly below the nominal concentration (~ 10% below nominal) of the extractant (MaxCalix). The modifier (CS-7SB) level was also 10% below its nominal value while the Isopar™ L level was slightly above its nominal value. This analysis confirms the addition of Isopar™L to the solvent on March 6, 2015. Despite that the values are below target component levels, the current levels of TiDG, CS-7SB, and MaxCalix are sufficient for continuing operation without adding a trim at this time until the next monthly sample.

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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] B. A Moyer, L. H. Delmau, B. D. Roach, and N. J. Williams, “Thermal Degradation of Next Generation Solvent using Triisodecylguanidine Suppressor: Impacts on Solvent Performance and Organic Content of Aqueous Effluents” ORNL-LTR-NGCSSX-020, Rev. 1, July 2013.

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