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Solvent Hold Tank Sample Results for MCU-14-667-672 and MCU-14-846-847: August and September 2014 Monthly Samples

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EXECUTIVE SUMMARY

SRNL received two sets of SHT samples (MCU-14-667-672, pulled 8/27/2014 and MCU-14-846-847, pulled on 9/22/2014) for analysis. The samples were analyzed for composition. It is recommended that the solvent receives Isopar® L and TiDG trimming at this time. Analysis of sample MCU-14-846-847 indicates the solvent has evaporated Isopar®L and has lost TiDG to a level below the recommended minimum 1 mM level. Since the addition of MaxCalix to the SHT in early July 2014, the MaxCalix concentration in the solvent has reached nominal values. 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-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 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 is essentially NGS with residual amounts of BOBCalix and TOA. On August 27, 2014, Operations personnel delivered six samples from the SHT (MCU-14-667, MCU-14-668, MCU-14-669, MCU-14-670, MCU-14-671, and MCU-14-672) for analysis. Later, on September 22, 2014, Operations personnel sent an additional two samples from the SHT (MCU-14-846 and MCU-14-847) 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

Samples 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, 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).

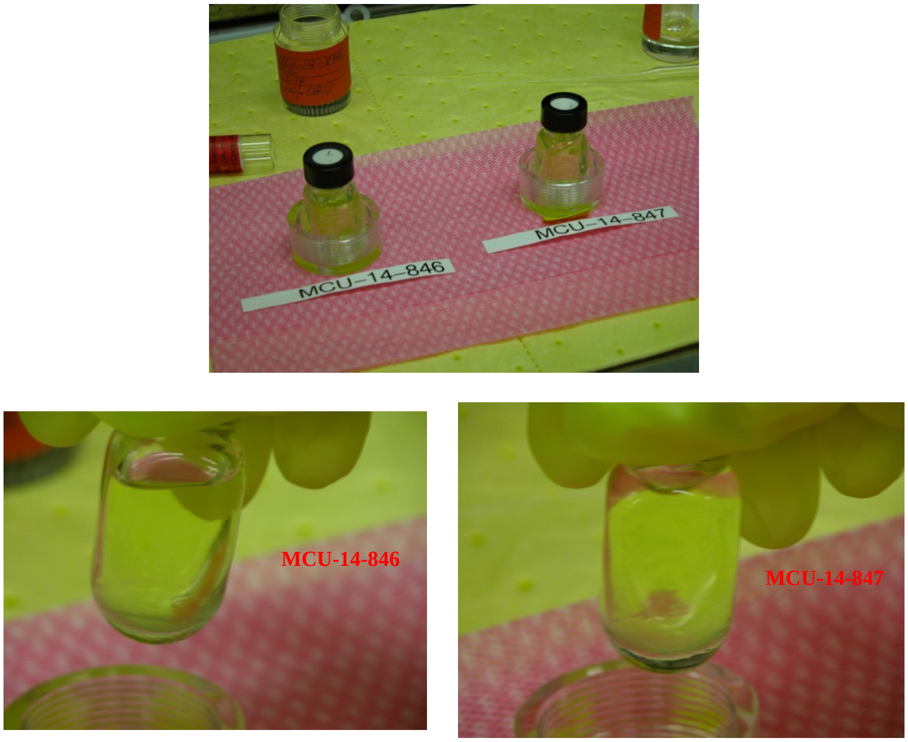

Figure 1. Typical appearance of the two vials from MCU-14-846-847 (Camera malfunctioned while capturing the MCU-14-667-672 vials images but these vials looked the same as the MCU-14-846-847 vials).

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 eight p-nut vials (six from MCU-14-667-672 and two from MCU-14-846-847) 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 August and September samples, respectively.

Density measurements of the samples gave results of 0.8235 g/mL (0.30% RSD) (or 0.8214 g/mL at 25 °C when corrected for temperature using the CSSX temperature correction formula) for MCU-14-667-672 at 22.5 °C and 0.8423 g/mL (0.15% RSD) for MCU-14-846-847 (or 0.8382 g/mL when corrected for temperature) at 19.5 °C. The calculated densities (0.8214 g/mL) for MCU-14-667-672 and for MCU-14-846-847 (0.8382 g/mL) bound the calculated density for the standard sample (0.8283 g/mL at 25 °C for the NGS-MCU blende made in the laboratory)[2]. The low density observed in the MCU-14-667-672 sample is consistent with the trim addition made to MCU in early July 2014 that included Isopar®L, modifier, MaxCalix, and TiDG.[3] On the other hand, the calculated density of MCU-14-846-847 is consistent with the laboratory standard sample density. 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 for the MCU-14-667-672 sample while nominal concentration values are expected for the MCU-14/846-847 sample.

The analytical data for the composite samples from August and September 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 shows that the Isopar®L and modifier concentrations in MCU-14-667-672 as derived from the spectroscopic methods (FT-IR and FT-HNMR) are closer to nominal than the values obtained from the density measurements. Since the spectroscopic methods are noisier than the gravimetric method, the results from the density measurements provide the more reliable answer. A slight discrepancy in the modifier's results was obtained from the FT-HNMR relative to the FTIR and density measurements in the MCU-14-846-847 sample. However, the modifier concentration is slightly higher than nominal in this sample. This is consistent with the inevitable Isopar®L mass transfer in the solvent.

All measurements indicate that the solvent has an Isopar® L concentration slightly higher than nominal, and modifier lower than nominal in the MCU-14-667-672 sample. In the MCU-14-846-847sample, all measurements indicate the solvent has evaporated some Isopar®L, and it may require a trim at the earliest convenience. Please note 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 be inaccurate. However, the FT-HNMR and FT-IR measurements have corroborated the density measurements in previous samples. Therefore, if more accurate results are desired, then further work may be 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 0.816 ± 0.019 g/mL and 0.836 ± 0.019 g/mL respectively which compares well with the measured and corrected to 25 °C mass concentration (densities) of 0.8214 and 0.8382 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.

Also noted in Table 3-1 is the drop in the TiDG level to 1.2 mM in the MCU-14-667-672 sample and later to 0.87 mM in the MCU-14-846-847 sample as shown in Table 3-2. Figure 2 shows the rapid TiDG level decline below the recommended minimum operating level of 1 mM.[3] The rate of TiDG level decline appears to be the fastest observed thus far. Since early July and short before the addition of TiDG , MCU has processed more than 366 thousand gallons of supernate (see Table 3-3 for the volume of processed supernate between the samples). Between the MCU-14-497/498[4] and MCU-14-668/672 samples, approximately 380 mg/$L_{solvent}$ of TiDG was lost (or 0.7 µg/($L_{solvent}$*$L_{supernate}$) . Similarly, between sample MCU-14-667-672 and MCU-14-846-847, the solvent lost TiDG at a rate of 0.3 µg/($L_{solvent}$*$L_{supernate}$) of TiDG per liter of supernate processed.

The current level of TiDG may be insufficient 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 418 mg/L (~0.8 mM) is well below the recommended operating TiDG level of 2 mM,[5] (the minimum recommended operating TiDG level should not be less than 1 mM). Based on this criteria, there is a need to add TiDG at the earliest convenient time. However, there is negligible risk of third phase formation associated with low suppressor concentration

The MaxCalix concentrations slowly returned 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.

When compared to the initial target density of 0.829 g/mL for solvent start up, addition of an Isopar® L trim is prudent.[♣]

Gamma measurements of MCU-14-667-672 and MCU-14-846-847, shown in Table 3-4 and also shown in Fig. 4, indicate the solvent's gamma activity level continues to be in the tens of thousands level (3.61E04 dpm/mL in the MCU-14-667-672 sample and 4.02E04 dpm/mL in the MCU-14-846-847 sample). This reading indicates the solvent is being stripped properly as MCU is processing real radioactive supernate. This data correlates with the high DF achieved at MCU during this time frame (30,000 to 40,000).

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-14-667-672 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	6.28E+05	6.16E+05	102
Isopar® L	FTIR	NA	6.21E+05	6.16E+05	101
Isopar® L	Density[*]	NA	6.33E+05	6.16E+05	103
Average[$]	All	NA	6.33E+05	6.16E+05	103
Modifier	HPLC	300313671	1.45E+05	1.69E+05	86
Modifier	FT-HNMR	NA	1.51E+05	1.69E+05	90
Modifier	FTIR	NA	1.51E+05	1.69E+05	89
Modifier	Density[*]	NA	1.38E+05	1.69E+05	82
Average[$]	All	NA	1.40E+05	1.69E+05	83
TiDG (HCl)	Titration	NA	6.06E+02	1.55E+03	39
TiDG (HCl)	FT-HNMR	NA	6.28E+02	1.55E+03	40
Average[$]	All	NA	6.10E+02	1.55E+03	39
trioctylamine	Titration	NA	4.27E+02	5.50E+02	78
Average[$]	All	NA	4.27E+02	5.50E+02	78
MaxCalix	HPLC	300313671	4.00E+04	4.40E+04	91
MaxCalix	FT-HNMR	NA	4.23E+04	4.40E+04	96
Average[$]	All	NA	4.08E+04	4.40E+04	93
BobCalix	HPLC	300313671	3.42E+03	4.00E+03	86
Density (g/mL)	Direct Measurement	NA	0.8214	0.835	98

[#] 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-14-846-847 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	FT-HNMR	NA	5.94E+05	6.16E+05	96
Isopar® L	FTIR	NA	6.08E+05	6.16E+05	99
Isopar® L	Density[*]	NA	6.12E+05	6.16E+05	99
Average[$]	All	NA	6.11E+05	6.16E+05	99
Modifier	HPLC	300314181	1.52E+05	1.69E+05	90
Modifier	FT-HNMR	NA	1.64E+05	1.69E+05	97
Modifier	FTIR	NA	1.79E+05	1.69E+05	106
Modifier	Density[*]	NA	1.75E+05	1.69E+05	104
Average[$]	All	NA	1.72E+05	1.69E+05	102
TiDG (HCl)	Titration	NA	4.18E+02	1.55E+03	27
TiDG (HCl)	FT-HNMR	NA	7.47E+02	1.55E+03	48
Average[$]	All	NA	4.42E+02	1.55E+03	29
trioctylamine	Titration	NA	4.41E+02	5.50E+02	80
Average[$]	All	NA	4.41E+02	5.50E+02	80
MaxCalix	HPLC	300314181	4.31E+04	4.40E+04	98
MaxCalix	FT-HNMR	NA	4.60E+04	4.40E+04	105
Average[$]	All	NA	4.41E+04	4.40E+04	100
BobCalix	HPLC	300314181	3.73E+03	4.00E+03	93
Density (g/mL)	Direct Measurement	NA	0.8382	0.835	100

[#] 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.

[$] $x = \frac{\Sigma_1^i \left(x_i / \delta_i^2 \right)}{\Sigma_1^i \left(1 / \delta_i^2 \right)}$; x_i stands for the concentration obtained at a given method and δ_i is the corresponding uncertainty.

Table 3-3. The TiDG concentration loss per gallon of supernate processed assuming the TiDG losses are due to contact with the supernate

Samples bracketing the Gallons Processed	**Gallons Processed Between Samples***	**TiDG Concentration Lost (mg/$L_{solvent}$)**
MCU-14395-396 - MCU-14-497-498	65,167	TiDG was added during this run
MCU-14-497-498 - MCU-14-668-672	144,652	380
MCU-14-668-672 - MCU-14-846-847	155,916	188

* T.Smith provided data in this column

Table 3-4. ^{137}Cs in the NGS-CSSX Solvent (±5 uncertainty)

Solvent Sample	**Result (dpm/mL)**	**LIMS #**
MCU-14-667-672	3.61E+04	300313671
MCU-14-846-847	4.02E+04	300314181

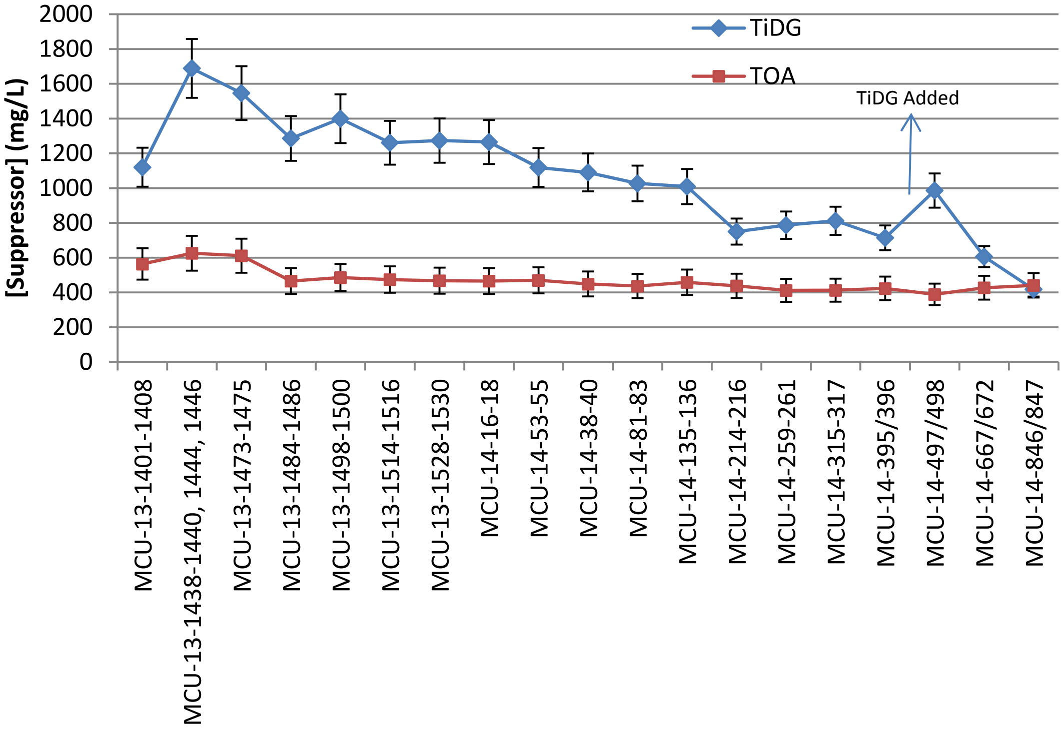

Figure 2. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended TiDG level is 517 mg/L.

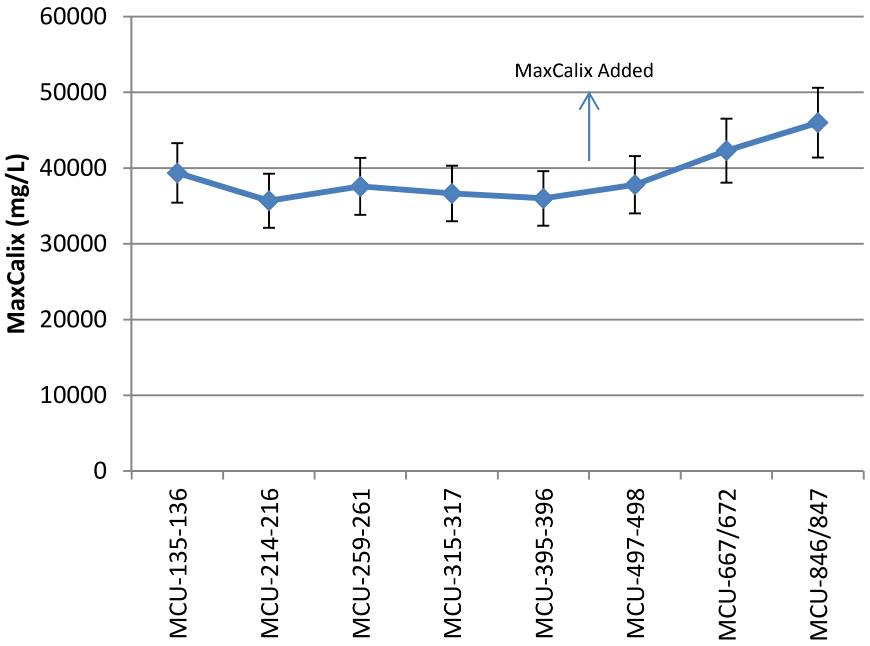

Figure 3. MaxCalix concentration as measured by HPLC (and FT-HNMR) of recent samples since NGS implementation (47,766 mg/L is the nominal concentration).

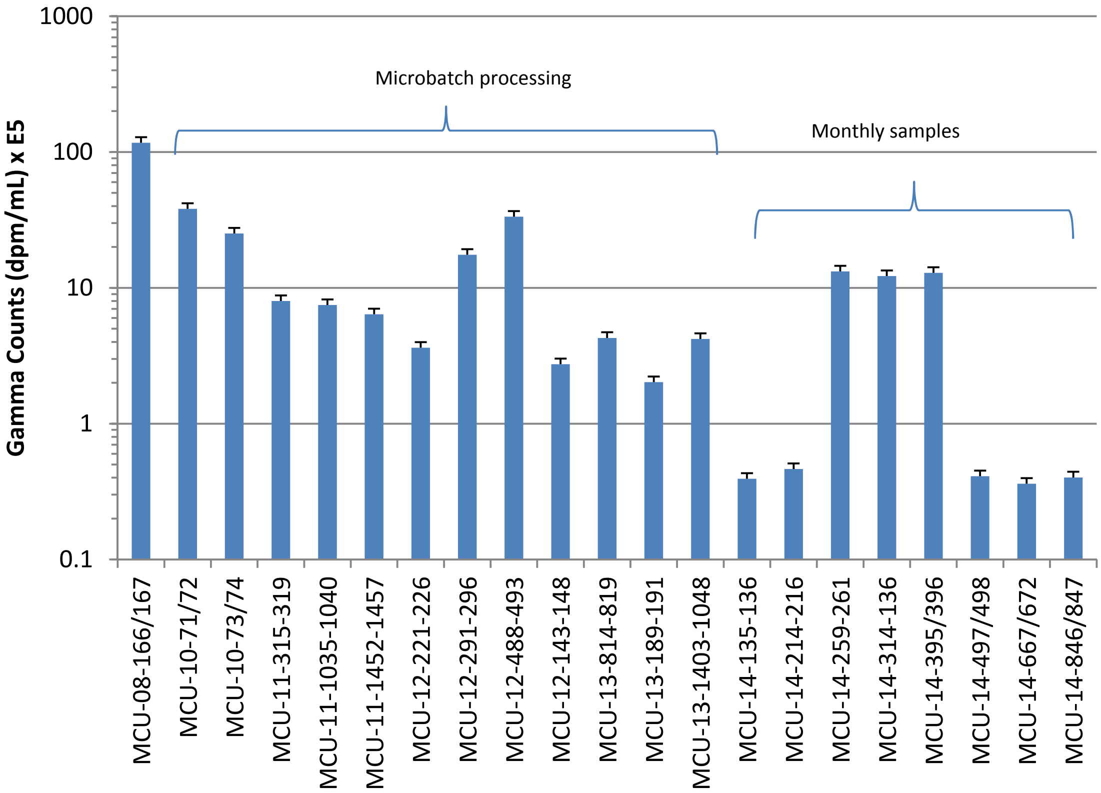

Figure 4. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

It is recommended that the solvent receives an Isopar® L and TiDG trimming at this time. Analysis of sample MCU-14-846-847 indicates the solvent has evaporated Isopar®L and has lost TiDG to a level below the recommended minimum 1 mM level. Since the addition of MaxCalix to the SHT in early July 2014, the MaxCalix concentration in the solvent has reached nominal values. 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.

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[5] 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.

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