



Solvent Hold Tank Sample Results for MCU-13-1403/1404/1405/1406/1407/1408: Quarterly Sample from September 2013

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed solvent samples from the Modular Caustic-Side Solvent Extraction Unit (MCU) in support of continuing operations. A quarterly analysis of the solvent is required to maintain solvent composition within specifications. Analytical results of the analyses of Solvent Hold Tank (SHT) samples MCU-13-1403, MCU-13-1404, MCU-13-1405, MCU-13-1406, MCU-13-1407, and MCU-13-1408 received on September 17, 2013 are reported. This sample was taken after the addition of the Next Generation Solvent (NGS) cocktail to produce a NGS-MCU blended solvent.

The results show that the solvent contains a slight excess of Isopar[®] L and a deficit concentration of modifier and TiDG when compared to the target composition. Addition of TiDG trim is recommended.

SRNL also analyzed the SHT sample for ¹³⁷Cs content and determined the measured value is within tolerance and that the value has returned to levels observed in 2011.

In contrast to what was observed in the heel prior to adding the NGS cocktail, no organic impurities were detected in these solvent samples.

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LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(<i>tert</i> -octylbenzo-crown-6)
CSSX	Caustic Side Solvent Extraction
ESS	Extraction, Scrub, and Strip
FID	Flame Ionization Detector
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- <i>alt</i> -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	<i>N,N',N''</i> -tris(3,7-dimethyloctyl)guanidine
TOA	Triethylamine

1.0 Introduction

Solvent Hold Tank (SHT) samples are sent to Savannah River National Laboratory (SRNL) to examine solvent composition changes over time.¹ Recently, MCU entered a planned outage to implement the NGS flowsheet. In turn, facility personnel added a non-radioactive “cocktail” solvent containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. NGS levels within the “cocktail” were such that when added to in equal volume would result in ~50/50 CSSX-NGS solvent blend. On September 17, 2013, Operations personnel delivered six samples from the SHT (MCU-13-1403, MCU-13-1404, MCU-13-1405, MCU-13-1406, MCU-13-1407, and MCU-13-1408) for analysis. These samples are intended to verify that the solvent is within the specified composition range. A baseline “scratch” solvent (a blend of NGS “cocktail”² and CSSX heel solvent³) 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

Samples were received in p-nut vials containing ~10 mL each. Once taken into the Shielded Cells, the samples were visually inspected, analyzed for pH, 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).

2.1 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. Details for the work are contained in a controlled laboratory notebook.⁴

3.0 Results and Discussion

Each of the six p-nut vials contained a single phase, with no apparent solids contamination or cloudiness. All samples had a pH value of 10. Table 1 contains the results of the analyses for the combined sample.

A triplicate density measurement of the organic phase gave a result of 0.826 g/mL (0.24% RSD) at 23 °C (or 0.8243 g/mL at 25 °C when corrected for temperature). The calculated density (0.8243 g/mL) is lower than the calculated density obtained from the Sept 4, 2013 sample.³ This is expected since the current CSSX solvent was blended with a lower density solvent formulation (NGS). The calculated density is lower than the calculated standard density for the 50/50 CSSX-NGS blended solvent (0.8294 g/mL). Using the density as a starting point, we know that the Isopar[®] L should be slightly higher than nominal and the other components should be slightly lower than nominal. This confirms a slight excess of Isopar[®] L in this batch.

The analytical data for the composite sample is shown in Table 1. Of all the methods listed, density has the lowest uncertainty. With the exception of the SVOA data, the

results as a whole are internally consistent between methods for Isopar[®] L and Modifier*. The density result is confirmed by the FTIR and FT-HNMR results which are separate methods. With the exception of the SVOA method, all measurements indicate Isopar[®] L slightly higher than nominal, and Modifier lower than nominal. The total mass sum of the “average” results per liter listed in Table 1 adds up to 8.31 E5 mg/L which compares well with the mass concentration of the standard per liter (8.29 E5 mg/L). As indicated in Table 1, the Modifier and Isopar[®] L concentrations are consistent within the noise of sample handling and method uncertainties. The SVOA method measured a modifier concentration of 120 E3 mg/L. This value is 78% of the value measured by the other methods and therefore, it was not used in Table 1 (the SVOA method has been found to be less reliable for measuring the modifier).

The MaxCalix concentration is slightly above the expected value while the BobCalix concentration is within its nominal value. The suppressor (TiDG*HCl or in the chloride form) concentration is well below (~67%) the expected value (1.55 E3 mg/L). The reason for this lower value is unknown at this time but improper mixing, inadequate TiDG addition, dilution (due to excess Isopar[®] L), and/or TiDG decomposition may have contributed to the lower value. The other suppressor, TOA, concentration was within its nominal value.

Reduced levels of TOA and/or TiDG will not lead to third formation (see Appendix A). The current level of TiDG may be insufficient to prevent anionic impurities from pairing with cesium, preventing cesium stripping, and increasing the activity level in the solvent. It is prudent to add a TiDG trim to the solvent.

When compared to target density of 0.829 g/mL, there is no need to add an Isopar[®] L trim.* However, addition of TiDG may be prudent. As the Isopar[®] L evaporates the modifier levels will increase to the nominal value.

A further evaluation of the FTIR and FT-HNMR data from this solvent revealed no impurities at the 20 ppm level. The addition of the NGS cocktail has diluted the previously observed impurity containing an aldehyde group in the heel sample.³ No non-solvent organic components were observed by SVOA at 1000 mg/L or higher.

In addition to the organic analysis, SRNL measured the ¹³⁷Cs activity of the solvent. See Table 2 for these results. This measurement is used as an indication of whether or not the solvent is being properly stripped of cesium. In this case, assuming this gamma result is correct the measured gamma is twice the gamma measurement of the previous sample.³ The analytical uncertainty for this measurement is 5%.

* Modifier is (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, also known as Cs-7SB, is added to increase solubility of the extractant.

* Note that while freshly prepared blend solvent has a target density of 0.829 g/mL, the MCU facility targets to maintain the solvent inventory at lower densities to allow longer operating periods before correcting for evaporation.

Table 1. Sample Results for MCU-13-1403, MCU-13-1404, MCU-13-1405, MCU-13-1406, MCU-13-1407, and MCU-13-1408 Composite

Analysis	Method	LIMS #	Result (mg/L) [#]	Nominal Result (mg/L) [*]	% of (Result ÷ Nominal Result)
Isopar [®] L	SVOA	300306802	640 E3	613 E3	104%
Isopar [®] L	FT-HNMR	NA	634 E3	613 E3	103%
Isopar [®] L	FTIR	NA	630 E3	613 E3	103%
Isopar [®] L	Density [*]	NA	620 E3	613 E3	101%
Average	all	NA	6.23 E5	6.13 E5	102%^s
Modifier	HPLC	300306802	154 E3	166 E3	93%
Modifier	FT-HNMR	NA	154 E3	166 E3	93%
Modifier	FTIR	NA	151 E3	166 E3	91%
Modifier	Density [*]	NA	155 E3	166 E3	93%
Average	all	NA	1.53 E5	166 E3	92%^s
TiDG (HCl)	Titration	NA	1.12 E3	1.55 E3	72%
TiDG (HCl)	FT-HNMR	NA	0.81 E3	1.55 E3	52%
Average	All	NA	1.0 E3	1.55 E3	67%^s
trioctylamine	SVOA	300306802	440	0.53 E3	83%
trioctylamine	Titration	NA	562	0.53 E3	106%
Average	All	NA	527	0.53 E3	99%^s
MaxCalix	HPLC	300306802	47.9 E3	44 E3	109%
MaxCalix	FT-HNMR	NA	52.0 E3	44 E3	118%
Average	All	NA	49.4 E3	44 E3	112%^s
BobCalix	HPLC	300306802	3.9 E3	4 E3	98%
Density (g/mL)	Direct measurement	NA	0.824	0.829	99.4%

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar[®] L and 10% for Modifier. Titration method uncertainty is 10%. 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.

* Nominal value is the expected value for freshly prepared blended solvent with a target density of 0.829 g/mL at 25 °C.

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

NA = Not Applicable

Table 2. ^{137}Cs in the CSSX Solvent

Analyte	Result (dpm/mL)
^{137}Cs	4.21E+05

The ^{137}Cs result shown in Table 2 is double the previous measurement despite the solvent being a blend between a cesium-containing heel and a non-radioactive solvent (cocktail).² This data may indicate, if it is correct, that additional cesium loaded onto the blended solvent from within the facility during the mixing process (blending process).

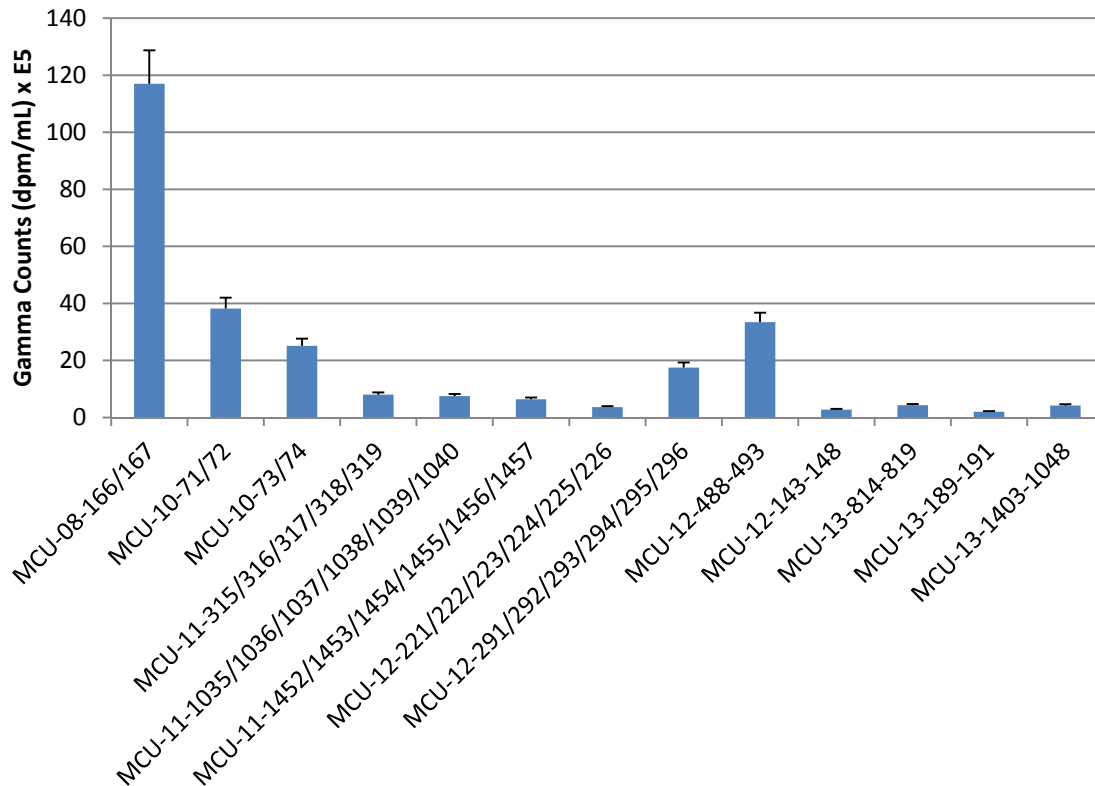


Figure 1. The gamma count of selected SHT samples. One standard deviation is 5%.

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. However, the addition of TiDG (suppressor) to the blended solvent is recommended. No organic impurities were detected in this solvent.

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 F. F. Fondeur and K. M. Taylor-Pashow, “Solvent Hold Tank Sample Results for MCU-13-189/190/191: Quarterly Sample from September 2013, SRNL-STI-2013-00652, October 2013.

⁴ T. B. Peters, “ISDP4”, SRNL-NB-2011-00027, February 18, 2011.

Appendix A: Correspondence on the effect of TOA/TiDG on third phase formation



Re: Dr. Moyer, please pardon my intrusion but we have a question that hopefully you can help us with.

Moyer, Bruce A. to: fernando.fondeur@srl.doe.gov

Cc: "charles.nash@srl.doe.gov", "frank.pennebaker@srl.doe.gov"

11/12/2013 10:15 AM

[Show Details](#)

Hi Fernando,

You are never intruding! No, there is no danger of third-phase formation due to the presence or absence of TOA. The only cause of third-phase formation we have identified is due to the combined effects of low temperature and high potassium loading. The suppressor has not been implicated in the observation of a third phase, regardless of whether it has been TOA or one of the guanidines.

Best regards,

Bruce

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