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

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

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K. M. L. Taylor-Pashow

November 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 $^{137}$Cs 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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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOBCalixC6</td>
<td>Calix[4]arene-bis(tert-octylbenzo-crown-6)</td>
</tr>
<tr>
<td>CSSX</td>
<td>Caustic Side Solvent Extraction</td>
</tr>
<tr>
<td>ESS</td>
<td>Extraction, Scrub, and Strip</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FT-HNMR</td>
<td>Fourier Transform Hydrogen Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra-red spectroscopy</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>ISDP</td>
<td>Integrated Salt Disposition Project</td>
</tr>
<tr>
<td>MCU</td>
<td>Modular Caustic-Side Solvent Extraction Unit</td>
</tr>
<tr>
<td>MaxCalix</td>
<td>1,3-alt-25,27-Bix(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6</td>
</tr>
<tr>
<td>NGS</td>
<td>Next Generation Solvent</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation or the absolute value of the Coefficient of Variation</td>
</tr>
<tr>
<td>SHT</td>
<td>Solvent Hold Tank</td>
</tr>
<tr>
<td>SRNL</td>
<td>Savannah River National Laboratory</td>
</tr>
<tr>
<td>SVOA</td>
<td>Semi-Volatile Organic Analysis</td>
</tr>
<tr>
<td>TiDG</td>
<td>$N,N',N''$–tris(3,7-dimethyloctyl)guanidine</td>
</tr>
<tr>
<td>TOA</td>
<td>Trioctylamine</td>
</tr>
</tbody>
</table>
1.0 Introduction

Solvent Hold Tank (SHT) samples are sent to Savannah River National Laboratory (SRNL) to examine solvent composition changes over time. 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” and CSSX heel solvent) 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.

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\textsuperscript{*}. 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.\textsuperscript{*} 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.\textsuperscript{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 $^{137}$Cs 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.\textsuperscript{3} The analytical uncertainty for this measurement is 5%.

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

\textsuperscript{3} 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

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

# Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar<sup>®</sup> 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<sup>®</sup> L, and 20% for TiDG.
xi stands for the concentration obtained at a given method and \( \delta_i \) is the corresponding uncertainty.

\[
\chi = \frac{\sum_i \left( \frac{x_i}{\delta_i^2} \right)}{\sum_i \left( \frac{1}{\delta_i^2} \right)},
\]

\( \chi \) stands for the concentration obtained at a given method and \( \delta_i \) is the corresponding uncertainty.

\[
x = \frac{\sum_i (x_i / \delta_i^2)}{\sum_i (1 / \delta_i^2)};
\]

\( \chi \) stands for the concentration obtained at a given method and \( \delta_i \) is the corresponding uncertainty.

NA = Not Applicable

### Table 2. \(^{137}\text{Cs} \) in the CSSX Solvent

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result (dpm/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{137}\text{Cs} )</td>
<td>4.21E+05</td>
</tr>
</tbody>
</table>

The \(^{137}\text{Cs} \) 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.


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.  b. bernard.brown@ferto.doe.gov
To: yuehan.marsh@ferto.doe.gov; twilke.pernobalt@ferto.doe.gov

11/22/2013 10:30 AM

Hi Fernando,

You are never intruding! So, there is no danger of third-phase formation due to the presence or absence of TiA. The only cause of third-phase formation we have identified is due to the combined effects of low temperature and high potassium levels. We suspect that has not been implicated in the observation of a third phase, regardless of whether in has been TiA or one of the quaternaries.

Best regards,

Bruce
Distribution:

T. B. Brown, 773-A
S. D. Fink, 773-A
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E. N. Hoffman, 999-W
S. L. Marra, 773-A
D. H. McGuire, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A

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B. A. Gifford, 704-56H
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E. A. Brass, 241-121H

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