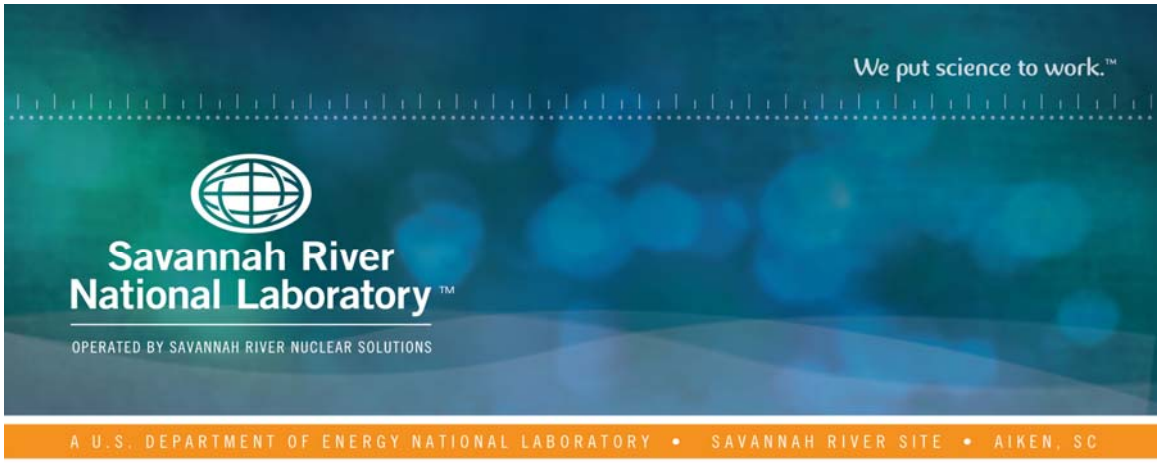

Solvent Hold Tank Sample Results for MCU-13-189, MCU-13-190, and MCU-13-191: Quarterly Sample from September 2013

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October 2013

SRNL-STI-2013-00652, Revision, 0

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Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2013-00652
Revision 0

Keywords: *MCU, ARP, ISDP*

Retention: *Permanent*

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October 2013

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

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed solvent samples from 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-13-189, MCU-13-190, and MCU-13-191 received on September 4, 2013 are reported.

The results show that the solvent (remaining heel in the SHT tank) at MCU contains excess Isopar® L and a deficit concentration of modifier and trioctylamine when compared to the standard MCU solvent. As with the previous solvent sample results, these analyses indicate that the solvent does not require Isopar® L trimming at this time. Since MCU is switching to NGS, there is no need to add TOA nor modifier.

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

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LIST OF ABBREVIATIONS

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
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
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] On September 4, 2013, Operations personnel delivered three samples from the SHT (MCU-13-189, MCU-13-190, and MCU-13-191) for analysis. These samples are intended to verify that the solvent is within the specified composition range. 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), 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.[2]

3.0 Results and Discussion

Each of the three p-nut vials contained a single phase, with no apparent solids contamination or cloudiness. All samples had a pH value of 5. Table 1 contains the results of the analyses for the combined samples.

A triplicate density measurement of the organic phase gave a result of 0.8425 g/mL (0.33% RSD) at 20 °C (or 0.8382 g/mL at 25 °C when corrected for temperature). The calculated density (0.8382 g/mL) is lower than the calculated density obtained from the May 2013 sample.[3] 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 result which is a separate method. With the exception of the SVOA method, all measurements indicate Isopar® L slightly higher than nominal, and Modifier* lower than nominal. This data are similar to the data reported for the May 2013 SHT sample. As indicated in Table 1, the Modifier and Isopar® L concentrations are consistent within the noise of sample handling and method uncertainties. The TOA concentration is much lower than expected. The SVOA method

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

which consists of gas chromatography for separation and a Flame Ionization Detector (FID) for quantifying the eluting component indicates the composite sample contains 35% of the nominal value. The titration method which consists of acidifying the TOA molecules in the solvent (R_3-N to R_3-N^+H Cl^-) with HCl indicates the TOA concentration is 71% of the nominal value. SRNL believe that the titration method is more accurate. In one liter of solvent, the sum of the Isopar® L, modifier, and extractant masses is 841.3 g. A much closer agreement with the density measurement is obtained with the reported titration method (841.3 g + 0.7 g = 842 g in one liter).

Further evidence the TOA level is at 71% nominal is seen upon closer examination of the recent measurements and additions of TOA to MCU. As shown in Table 2, approximately 272 g of TOA was added to MCU in June 2013. This level of addition, to restore the TOA level to the nominal value, was based on the measured TOA level of 45% of nominal done in January 2013. Using this addition, the expected TOA level at MCU, including the 272 g of TOA added in June 2013 is approximately 411 g of TOA. This calculated level is 68% of the nominal value which is very close to the 71% value determined in the titration method.

At this TOA level, the solvent is susceptible to third phase formation that may increase the phase carry over to the stripping solution. In addition, anionic impurities may ionic pair with cesium increasing the activity level in the solvent. Since MCU is to switch to the Next Generation Solvent (NGS), these issues will have lesser impact.

When compared to the MCU density target of 0.852 g/mL, there is no need to add an Isopar® L trim.[♣] Since MCU is switching to the NGS, there is no need to add TOA or Isopar® L. Only minor addition of modifier would normally be recommended, but it can be accommodated in the switch to the NGS.

A further evaluation of the FTIR data from this solvent revealed the presence of an impurity as shown in Figure 1. A closer look at Fig. 1 (the insert also shows the H-NMR of this impurity) shows that the impurity has vibrational peaks similar to Isopar® L. The impurity could be identified as oxidized aliphatic oil (aldehyde) of the type typically seen in burned oil. However, 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 3 for these results. This measurement is used as an indication of whether or not the solvent is being properly stripped of cesium. The analytical uncertainty for this measurement is 5%.

[♣] Note that while freshly prepared MCU solvent has a target density of 0.852 g/mL, the MCU facility targets tries to maintain the solvent inventory at 0.845 g/mL to allow longer operating periods before correcting for evaporation.

Table 1. Sample Results for MCU-13-189/190/191 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300306585	530 E3	589 E3	90%
Isopar® L	FT-HNMR	NA	603.8 E3	589 E3	103%
Isopar® L	FTIR	NA	595.8 E3	589 E3	101%
Isopar® L	Density[*]	NA	594.9 E3	589 E3	101%
average	all	NA	5.95 E5	5.89 E5	101%[$]
Modifier	HPLC	300306585	241 E3	254 E3	95%
Modifier	FT-HNMR	NA	240 E3	254 E3	94.4 %
Modifier	FTIR	NA	244.4 E3	254 E3	96.2%
Modifier	Density[*]	NA	238 E3	254 E3	93.7%
average	all	NA	2.38 E5	2.54 E5	93.7%[$]
trioctylamine	SVOA	300306585	360	1.02 E3	35.3%
trioctylamine	Titration	NA	726	1.02 E3	71.2%
average	all	NA	541	1.02 E3	53%[$]
Extractant	HPLC	300306585	8.3 E3	8 E3	104%
Density (g/mL)	Direct measurement	NA	0.838	0.852	98.4%

[#] 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 <1% between each value and the average. NMR analytical uncertainty is 10% for the modifier and 14% for Isopar® L.

[*] Nominal value is the expected value for freshly prepared solvent with a target density = 0.852 g/mL.[4]

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

NA = Not Applicable

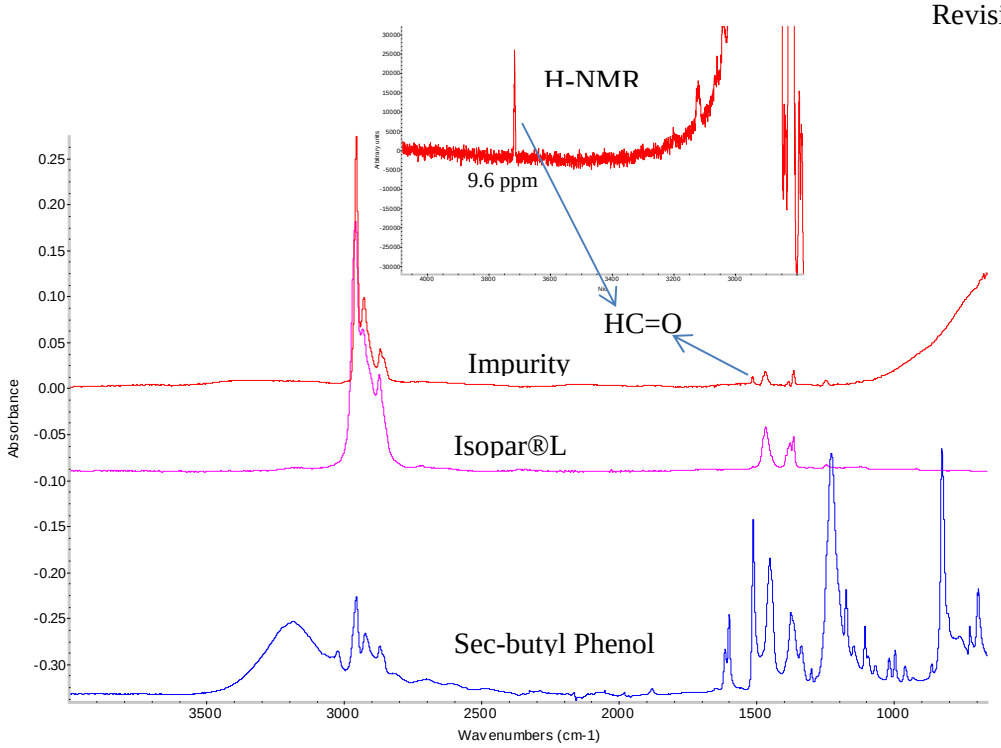

Figure 1. The FTIR spectrum of an unknown substance present in this sample (inset shows a portion of the HNMR spectrum of this sample).

Table 2. Log of recent measurements of the SHT content and TOA additions to MCU

Date	Event	Calculated TOA Level in MCU (g)
November 9, 2012	397 g added to SHT	604.4*
January 2013	TOA level at 45% nominal (measured)	272
May 2013	TOA level at 23% nominal (measured)	139
June 2013	272 g added to SHT	411

*Nominal TOA level in MCU is approximately 604.4 g

Table 3. ^{137}Cs in the CSSX Solvent

Analyte	Result (dpm/mL)
^{137}Cs	2.02E+05

The ^{137}Cs result shown in Table 3 is much lower than previous measurements.[5,6] However, as can be seen in Fig. 2, the current data is at the low end of the historical range. It may indicate a returning of the cesium concentration to a steady state value.

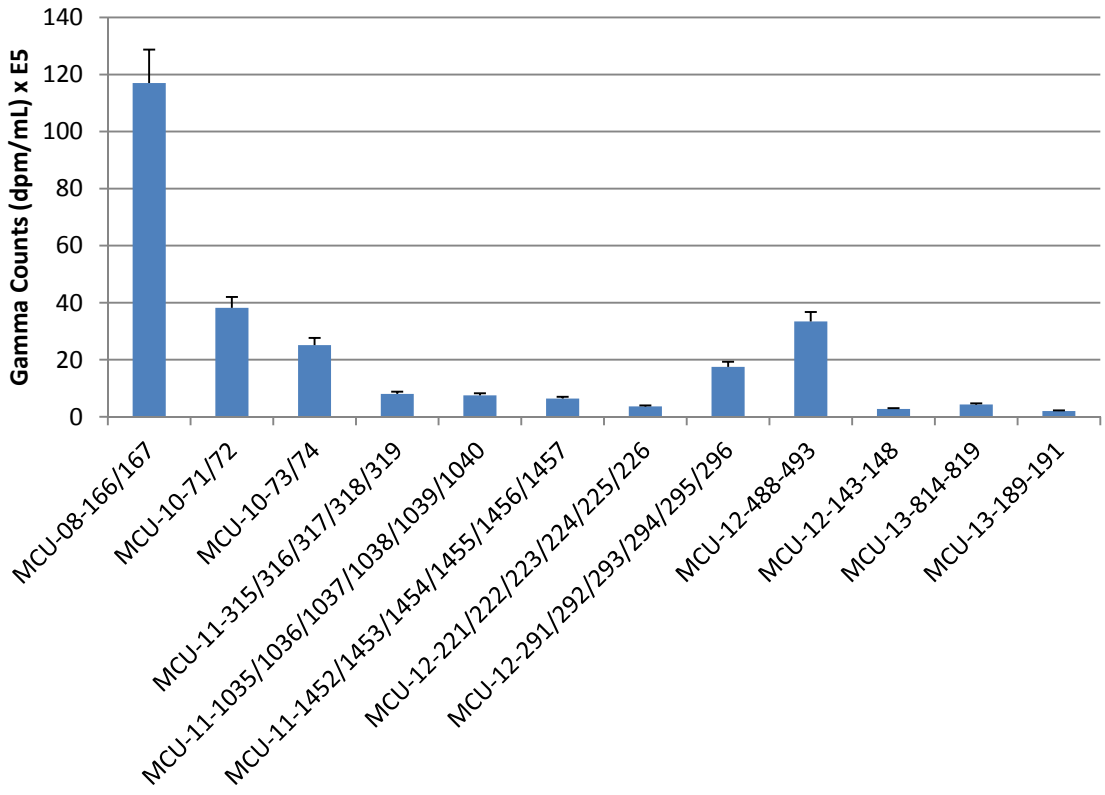

Figure 2. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

As with the previous solvent sample results,[5,6] these analyses indicate that the solvent does not require Isopar® L trimming at this time. Since MCU is switching to NGS, there is no need to add TOA nor modifier. This report showed that a different TOA value was obtained by titrating the solvent with HCl versus the SVOA method. An impurity that resembles "burned" kerosene was found in the FTIR data believe to originate from spent Isopar® L.

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