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Retention: *Permanent*

**Solvent Hold Tank Sample Results for MCU-13-143, MCU-13-144,
MCU-13-145, MCU-13-146, MCU-13-147 and MCU-13-148:
Quarterly Sample from January 2013**

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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-13-143, MCU-13-144, MCU-13-145, MCU-13-146, MCU-13-147 and MCU-13-148 received 29 January 2012 are reported.

The results show that the solvent at MCU does not require an Isopar[®] L addition, but it will require addition of trioctylamine.

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 2012.

LIST OF ABBREVIATIONS

ESS	Extraction, Scrub, and Strip
FTIR	Fourier Transform Infra-red Spectroscopy
HPLC	High Performance Liquid Chromatography
ISDP	Integrated Salt Disposition Project
RSD	Residual Standard Deviation
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
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 On January 29, 2012, Operations personnel delivered six samples from the SHT (MCU-13-143 through MCU-13-148) 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, and Fourier-Transform Infra-Red spectroscopy (FTIR).

Details for the work are contained in a controlled laboratory notebook.²

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 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 0.8412 g/mL (0.43% residual standard deviation - RSD) at 19 °C (or 0.8361 g/mL at 25 °C when corrected for temperature). 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 the addition of Isopar[®]L to this batch.

The analytical data for the composite sample is shown in Table 1. Of all the methods listed, density has the lowest uncertainty. In addition, the results from density measurements are mass balanced. With the exception of the SVOA results for Isopar[®]L and the modifier, the remaining results as a whole are internally consistent between methods. The density result is confirmed by the FTIR result which is a separate method. If we don't include the SVOA results for Isopar[®]L and the modifier, all measurements indicate Isopar[®] L higher than nominal, and Modifier* lower than nominal. The extractant result is within 8% of the nominal value with a lower value expected from Isopar[®] L dilution. This value is within the analytical uncertainty of the reported HPLC value. There are several sources of errors that affect the accuracy of the values reported in Table 1. If dilution (excess Isopar[®] L) was the only effect on composition, then 85% of the nominal composition of the remaining components is expected if we have 4% excess Isopar[®] L. As indicated in Table 1, the Modifier and Isopar[®] L concentrations are consistent within the noise of sample handling and methods uncertainties. The TOA have concentrations much lower than expected. Measurements of a standard CSSX

* 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.

solvent with this sample proved a 117% recovery. The SVOA results (Isopar[®]L and modifier) are not consistent with the other measurements such as density which has a low uncertainty. If the SVOA data is correct, then the sample is diluted with another liquid as all the CSSX components are lowered than their nominal values at the same time. No evidence of a secondary liquid has been detected with this sample. Thus, the SVOA data on the Isopar[®]L and modifier is questionable.

When compared to the MCU density target of 0.845 g/mL, there is no need to add an Isopar[®] L trim.* However, it is advisable to add sufficient trioctylamine (TOA) to return the solvent composition to within specifications as that component has declined to about 44% of the concentration of the expected value (0.12 wt % of the solvent). The TOA measurement was performed twice, so the result is not an analytical aberration. TOA in the quarterly sample of August 2012 was found to be 45.1% of its nominal value at that time. This current sample contains the same concentration of TOA as the sample that was pulled before the addition of 397 grams of TOA to the solvent on November 9, 2012. This loss rate is unexpectedly high.

In addition to the organic analysis, SRNL measured the ¹³⁷Cs activity of the solvent. See Table 2. This measurement is used as an indication of whether or not the solvent is being properly stripped of cesium. The analytical uncertainty 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-13-143/144/145/146/147/148 Composite

Analysis	Method	LIMS #	Result (mg/L) [#]	Nominal Result (mg/L) [*]	% of (Result ÷ Nominal Result)
Isopar [®] L	SVOA	300302979	570.0 E3	589 E3	97%
Isopar [®] L	FTIR	NA	610.3 E3	589 E3	104%
Isopar [®] L	Density [*]	NA	610.6 E3	589 E3	104%
average	all	NA	6.1 E5	5.89 E5	104% [§]
Modifier	SVOA	300302979	190.0 E3	254 E3	82.70%
Modifier	HPLC	300302978	215.0 E3	254 E3	84.65%
Modifier	FTIR	NA	220.3 E3	254 E3	86.73%
Modifier	Density [*]	NA	216.6 E3	254 E3	85.29%
average	all	NA	2.17 E5	2.54 E5	85.43% [§]
trioctylamine	SVOA	300302979	450	1.02 E3	44.12%
Extractant	HPLC	300295714	7.4 E3	8 E3	92.50%
Density (g/mL)	Direct measurement	NA	0.8361	0.852	98.13%

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar[®] L and 10% for Modifier. Density results from the average of replicate volumetric trials typically have a percentage standard deviation of <1% between each value and the average.

^{*} Nominal value is the expected value for freshly prepared solvent with a target density = 0.852 g/mL.³ NA = not applicable

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

is the corresponding uncertainty.

Table 2. ¹³⁷Cs in the CSSX Solvent

Analyte	Result (dpm/mL)
¹³⁷ Cs	2.74E+05

This result is much lower than previous measurements.^{4,5} However, as can be seen in Fig. 2, the current data is within historical value and it may indicate cesium concentration return to steady state value.

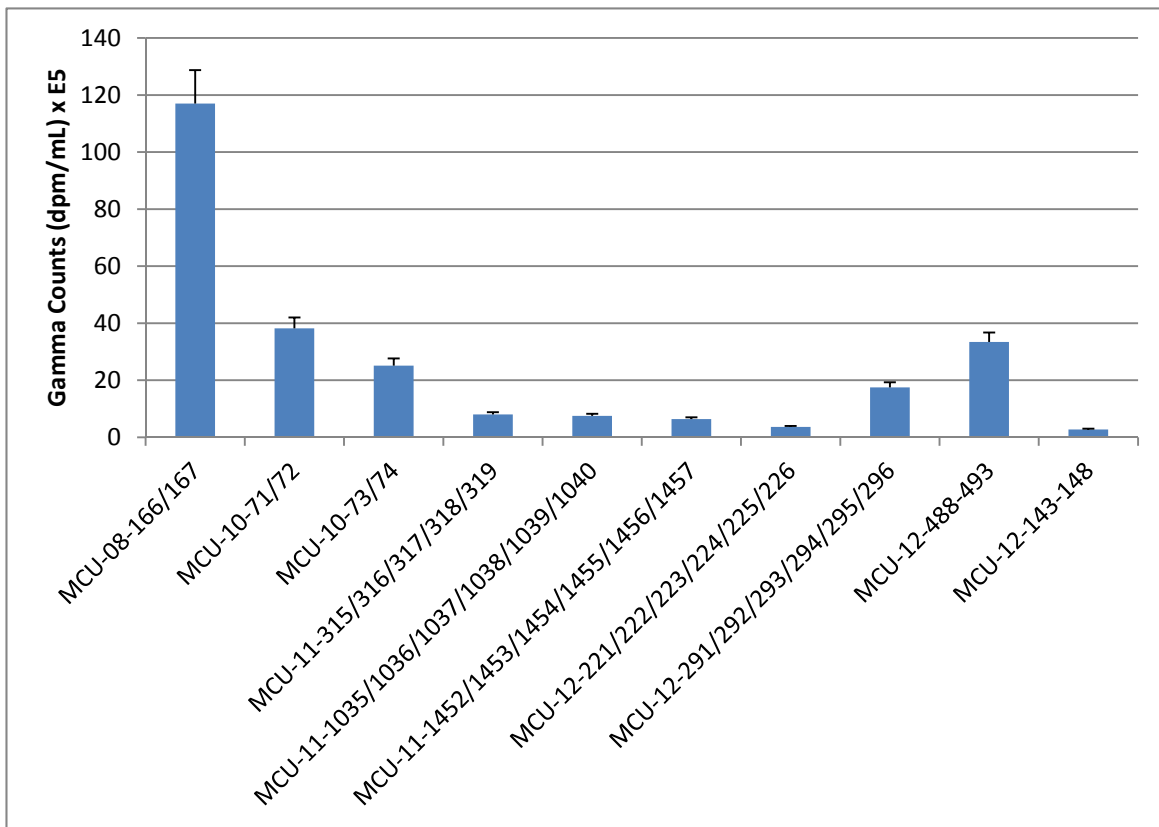


Figure 1. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

As with the previous solvent sample results,⁵ these analyses indicate that the solvent does not require Isopar[®] L trimming at this time. However, addition of TOA is warranted. These findings indicate that the protocols for solvent monitoring and control are yielding useful information. The deviation in the TOA concentration since the last analysis indicates continued periodic (i.e., quarterly) monitoring is recommended.

5.0 References

- ¹ W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.
- ² T. B. Peters, “ISDP4”, SRNL-NB-2011-00027, February 18, 2011.
- ³ L.H. Delmau, J. F. Birdwell Jr., P. V. Bonnesen, L. J. Foote, T. J. Haverlock, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloop Jr., B. A. Tomkins, “Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent”, October 2002, ORNL/TM-2002/190.
- ⁴ F. F. Fondeur, T. B. Peters, and S. D. Fink, “Quarterly Solvent Hold Tank Sample Results For August 2012: Samples MCU-12-291, MCU-12-292, MCU-12-293, MCU-12-294, MCU-12-295, and MCU-12-296”, SRNL-STI-2012-00637, October 2012.
- ⁵ T. B. Peters, F. F. Fondeur, S. D. Fink, “Solvent Hold Tank Sample Results for MCU-11-1035, MCU-11-1036, MCU-11-1037, MCU-11-1038, MCU-11-1039 and MCU-11-1040”, SRNL-STI-2011-00593, October 2011.