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SOLVENT HOLD TANK SAMPLE RESULTS FOR MCU-13-814, MCU-13-815, MCU-13-816, MCU-13-817, MCU-13-818 AND MCU-13-819: QUARTERLY SAMPLE FROM MAY 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-13-814, MCU-13-815, MCU-13-816, MCU-13-817, MCU-13-818 and MCU-13-819 received May 28, 2013 are reported.

The results show that the solvent at MCU does not require an Isopar® L addition, but it will require addition of trioctylamine despite of the 272 g of TOA that was added to the solvent on June 5, 2013 based on the solvent containing a TOA level of 45% of nominal. A new TOA analysis method (HCl titration) has been used and its output was statistically similar to the results from the SVOA-TOA method. This method provides an independent method for measuring TOA and TiDG in MCU-NG solvent. An impurity containing a tert-butyl group was detected in the solvent and further analytical analysis is needed to identify it. SRNL recommends determining the impact of this impurity on the mass transfer ability of the solvent.

SRNL also analyzed the SHT sample for ^{137}Cs content and determined the measured value is above the results observed from the January 2013.

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LIST OF ABBREVIATIONS

ESS	Extraction, Scrub, and Strip
FTIR	Fourier-Transformed Infrared Spectroscopy
HPLC	High Performance Liquid Chromatography
RSD	Residual standard deviation
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 May 28, 2013, Operations personnel delivered six samples from the SHT (MCU-13-814 through MCU-13-819) 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 non-aqueous acid titration. Fourier-Transform Infra-Red spectroscopy (FTIR) analysis was not possible at this time.

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

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.

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 an apparent pH value of 5 (pH paper is being used to detect gross amount of aqueous solution in these vials). The pH paper is unchanged in organic media and the reflection of light from a sodium lamp gives the reflecting object a yellowish tint. In the case of a pH paper illuminated with a sodium lamp, the pH paper appears to have 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 0.8413 g/mL (0.48% residual standard deviation - RSD) at 25.1 °C. 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. The average values shown in Table 1 are the weighted average values obtained from different methods. Of all the methods listed, density has the lowest uncertainty. The density result is confirmed by the HPLC result which is a separate method. All measurements indicate Isopar® L is higher than nominal, and Modifier[*] lower than nominal. The FTIR results indicate the results are closer to nominal values. The FTIR results may have been affected by the sample storage condition where approximately one mL of SHT 814 to 819 was contained in a three mL vial where some of the Isopar®L may have evaporated into the headspace. The FTIR analysis also revealed the presence of an impurity in the SHT sample. Based on the FTIR spectrum of the impurity (Fig. 1), the impurity may have a tert-butyl group. The impurity may have transferred from the waste or other aqueous streams (caustic, scrubbing or stripping solutions) or originated from the decomposition of the MCU solvent components. At a first glance the FTIR spectrum of the impurity observed shown in Fig. 1 can't be explained with the spectrum of sec-butyl phenol (a degradation product of the Cs-7SB typically found in the past). In addition, a significant amount of energy is required (along with additional chemical reactions) to convert the sec-butyl group (or the alcohol group) in Cs-7SB to a tert-butyl group. A similar reason excludes decomposition of Isopar®L as a source of this impurity. Of the MCU components, only the extractant contains a tert-butyl group and yet the extractant result is within 5% 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 concentration. Additional analytical analysis is needed to completely identify the impurity. The impurity effect on the solvent performance (extract, scrub, strip, and wash) is not understood at this point.

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 90% of the nominal composition of the remaining components is expected if we have 2.4% 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 measurements have concentrations much lower than expected as measured by SVOA-TOA and titration with HCl.[3] The total mass per unit volume (mg/L) calculated from the SVOA method is 820 E3 ± 164 E3mg/L (Isopar®L + modifier + TOA). As shown in Table 1, the measured density is 841 ± 84 E3 mg/L. A mass difference of 21 E3 mg/L between the calculated mass from the SVOA method and the measured density is more than double the expected nominal extractant concentration of 8 E3 mg/L. The mass deficit observed in the SVOA measurements is probably due to a combination of large uncertainties and biases in the method. Since density is a gravimetric measurement, the concentration of the major MCU solvent components (modifier and Isopar®L) derived from the density measurement are more precise and with less bias. The apparent partial molar density of both the modifier and Isopar®L is nearly equal the inverse of their densities.

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[*] 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.

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 by 77% of the concentration of the expected value (0.12 wt % of the solvent). The TOA measurement was performed by two independent methods (SVOA and HCl titration[3]), so the result is not an analytical aberration. TOA in the quarterly sample of January 2013 was found to be 45.1% of its nominal value at that time. This sample, pulled on May 2013, contains a very low concentration of TOA despite the addition of 397 grams of TOA to the solvent on November 9, 2012. Using the current TOA measurement and that of January 2013, the loss rate is approximately 2 mg/L*day (assuming continuous operation). At this level of TOA, the solvent is susceptible to impurities and cesium-pair associations with organic complexants that may affect stripping. This sample was pulled before 272 g of TOA was added to the solvent on June 5, 2013 which presumably restored the TOA concentration closer to the nominal level.

In addition to the organic analysis, SRNL measured the ^{137}Cs 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%.

The current result is statistically higher (with a greater than 95% confidence) than the previous results obtained with the sample pulled in January 2013 (MCU-12-143 to 148)[4] but significantly lower than the measurements done on samples previously pulled before December 2012.[5,6] However, as can be seen in Fig. 2, the current data is within historical values and it may indicate that the cesium concentration is returning to steady state value. Examination of the last two reports shows that there is no clear correlation between cesium and TOA concentrations in the solvent. There may be, however, an increase in the solvent cesium concentration at very low TOA levels if there are organic complexants in the solvent. The lack of correlation could be evidence that the impurity levels in the solvent are not sufficient to affect the cesium concentration at these TOA levels.

♣ 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-13-814/815/816/817/818/819 Composite

Analysis	Method	LIMS #	Result (mg/L)[#]	Nominal[*] Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar® L	SVOA	300304946	6.10 E5	5.89 E5	104%
Isopar® L	Density[*]	NA	6.04 E5	5.89 E5	102%
Isopar® L	FTIR	NA	5.95 E5	5.89 E5	101%
average	All	NA	6.02 E5	5.89 E5	102%[$]
Modifier	SVOA	300304946	2.10 E5	2.54 E5	82.70%
Modifier	HPLC	300304946	2.30 E5	2.54 E5	90.55%
Modifier	Density[*]	NA	2.29 E5	2.54 E5	90.12%
Modifier	FTIR	NA	2.45 E5	2.54 E5	96.5%
average	all	NA	2.29 E5	2.54 E5	90.2%[$]
trioctylamine	SVOA	300304946	230	1.02 E3	22.55%
trioctylamine	HCl Titration[ɣ]	NA	239	1.02 E3	23.43%
average	all	NA	239	1.02 E3	23%
Extractant	HPLC	300304946	7.6 E3	8 E3	95%
Density (g/mL)	Direct measurement	NA	0.8413	0.852	98.76%

[#] Analytical uncertainty is 20% for SVOA, 10% for HPLC, and 10 % for FTIR. 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.[7] NA = not applicable

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

[ɣ] HCl-titration uncertainty is 3%.

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

Analyte	Result (dpm/mL)
^{137}Cs	4.28E+05

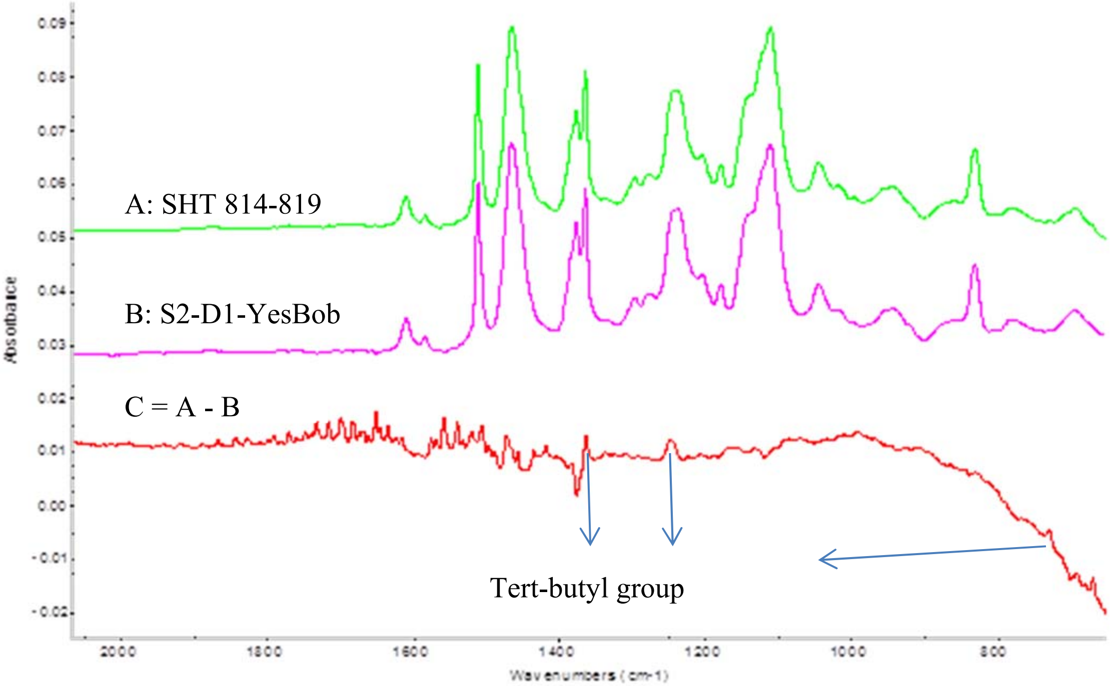

Figure 1. The FTIR spectrum of MCU-SHT-814-819 sample. The difference spectrum shows the presence of an impurity that contains a tert-butyl group.

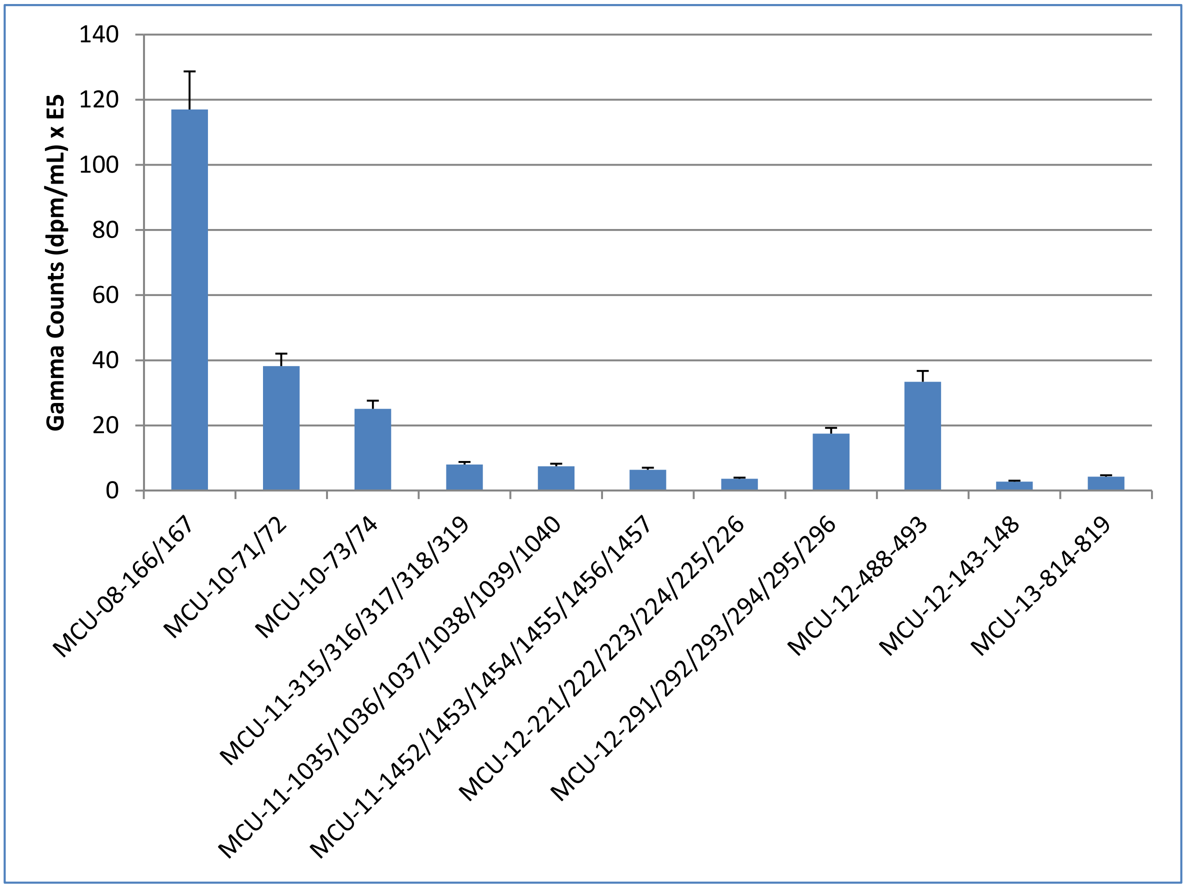

Figure 2. The gamma count of selected SHT samples. One standard deviation is 5%.

4.0 Conclusions

As with the previous solvent sample results,[4] 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. A new TOA analysis method (HCl titration) has been used and its output was statistically similar to the results from the SVOA-TOA method. This method provides an independent method for measuring TOA, TiDG, and can provide a guesstimate concentration of basic substance in the solvent (for example degradation products from the suppressor).

5.0 References

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