



Results of Analysis of NGS Concentrate Drum Samples

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) prepared two drums (50 gallons each in “Drum#2” and “Drum#4”) of NGS-MCU (Next Generation Solvent-Modular CSSX Unit) concentrate for future use at MCU in downblending the BOBCalixC6 based solvent to produce NGS-MCU solvent. Samples of each drum were sent for analysis. The results of all the analyses indicate that the blend concentrate is of the correct composition and should produce a blended solvent at MCU of the desired formulation.

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LIST OF ABBREVIATIONS

CSSX	Caustic-Side Solvent Extraction
FTIR	Fourier Transform InfraRed spectroscopy
HPLC	High Performance Liquid Chromatography
NGS-MCU	Next Generation Solvent-Modular CSSX Unit
NMR	Nuclear Magnetic Resonance
RSD	Relative Standard Deviation
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TiDG	<i>N,N',N''</i> –tris(3,7-dimethyloctyl)guanidine
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
UET	Use Every Time

1.0 Introduction

The Modular Caustic-Side Solvent Extraction (MCU) process currently operates with a four component organic solvent which removes cesium from clarified salt solution. The current solvent, designated BOBCalixC6 based solvent, is comprised of BOBCalixC6 (extractant), TOA (suppressor), Cs-7SB (modifier), and Isopar-L (diluent). In the near future, MCU will shift from using a BOBCalixC6 based organic solvent for cesium removal to use of Next Generation Solvent (NGS). NGS introduces a new extractant and suppressor to MCU; it is a four component mixture comprised of MaxCalix (extractant), TiDG (suppressor), Cs-7SB (modifier), and Isopar-L (diluent). The shift will involve addition of a blend concentrate to the current solvent inventory to generate a blended solvent that will then be used for cesium removal. SRNL was tasked with preparation of the blend concentrate. After preparation, SRNL extensively analyzed samples from each drum. This document reports the complete set of results for the downblending effort, with a partial analytical battery already reported in a previous document.ⁱ

This work is being performed per a customer TTRⁱⁱ and SRNL TTQAP.ⁱⁱⁱ

2.0 Experimental Procedure

On July 30-31, 2013, Savannah River National Laboratory (SRNL) prepared two drums (50 gallons each in “Drum#2” and “Drum#4”) of NGS-MCU (Next Generation Solvent-Modular CSSX Unit) concentrate for future use at MCU in downblending the BOBCalixC6 based solvent to produce NGS-MCU solvent. The contents of each drum were prepared by a Use Every Time (UET) procedure that carefully tracked the masses of each component.^{iv} After the contents of each drum were added and thoroughly mixed, a ~100 mL sample from each drum was removed and stored separately.

Samples from each drum were removed using a Coliwas sampler and stored in glass jars with Teflon caps. Samples from each jar were analyzed without dilution or other modifications. Samples were sent forward for *N,N',N''*-tris(3,7-dimethyloctyl)guanidine (TiDG) analysis^{vi}, Semi-Volatile Organic Analysis (SVOA), High Performance Liquid Chromatography (HPLC), density measurement^Σ, as well as analysis by Nuclear Magnetic Resonance (NMR)^v and Fourier Transform InfraRed spectroscopy (FTIR)^Π for determination of NGS solvent components. As multiple different analytical methods were used, these samples were analyzed once except for the TiDG analysis^{vi} which was performed in triplicate.

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.

^Σ The density was measured using a 2 mL volumetric flask.

^Π The FTIR work was done on a Nexus 670 using a TGiS detector. at a speed of 0.658 cm/sec, resolution 4 cm⁻¹, 128 scans, and in transmission mode. The peak area at 1377-1365 cm⁻¹ is for IsoparL and 831 cm⁻¹ for Cs-7SB.

3.0 Results and Discussion

A visual analysis of the samples showed no undissolved solids or unexpected colors.

Table 1 contains the results from the analyses of each sample, as well as averages where appropriate and the targets. Values in parentheses for the TiDG titration average results are the relative standard deviation (RSD).

Table 1. Results of the Drum Samples Analyses

Analyte	Drum #2	Drum #4
density (g/mL)	0.8114	0.8104
Isopar L (wt%) FTIR	73.5	75.6
Isopar L (wt%) NMR	76.8	76.5
Isopar L (wt%) SVOA	83.8	87.6
Isopar L (wt%) average	78.0	79.9
Isopar L (wt%) gravimetric	78.9	78.9
Isopar L (wt%) target	78.9	78.9
Cs-7SB Modifier (M) FTIR	0.251	0.263
Cs-7SB Modifier (M) NMR	0.245	0.237
Cs-7SB Modifier (M) SVOA	0.269	0.284
Cs-7SB Modifier (M) HPLC	0.248	0.266
Cs-7SB Modifier (M) average	0.253	0.263
Cs-7SB Modifier (M) gravimetric	0.250	0.250
Cs-7SB Modifier (M) target	0.250	0.250
MaxCalix (M) NMR *	0.111	0.101
MaxCalix (M) HPLC	0.0858	0.0879
MaxCalix (M) gravimetric	0.093	0.093
MaxCalix (M) target	0.093	0.093
TiDG (M) Titration	0.00583 (0.76%)	0.00583 (0.37%)
TiDG (M) NMR	0.0063	0.0066
TiDG (M) average	0.00607	0.00622
TiDG (M) gravimetric	0.0605	0.0605
TiDG (M) target	0.006	0.006

* MaxCalix average result not reported based on NMR results being slightly high

The analytical uncertainty is typically <1% for density measurements. FTIR analytical uncertainty is 15% for Isopar[®] L and 10% for Cs-7SB Modifier. The uncertainty for HPLC is 10%. The uncertainty for the SVOA is 20%. The uncertainty for the NMR method is 10%. The TiDG titration method has an analytical uncertainty of 10%.

A previous unreported density measurement on a laboratory sample of the NGS-MCU concentrate material gave a result of 0.817 g/mL. This is corroboration that the density result is expected.

The TiDG titration and NMR method each give results consistent with the measured weights of components considering the uncertainties of each method, with the exception of the MaxCalix for the NMR. The NMR method gives results that are slightly high for the MaxCalix compared to the measured gravimetric preparation even given the analytical uncertainty. This is the first attempt to use the NMR to measure solvent components so while the method is valid some refinement is necessary. The High Performance Liquid Chromatography (HPLC) method gave appropriate results for all analytes, as did the Semi-Volatile Organic Analysis (SVOA) method, considering the uncertainties of each method.

Table 1 also provides the averages of the various measurements for the Isopar L, Modifier and TiDG. The average results show a $\leq 1.3\%$ variance from target values for Isopar L, $\leq 5.2\%$ for Modifier, and a $\leq 3.7\%$ variance for TiDG.

4.0 Conclusions

The drum samples were visually free of solids or unusual observations. The density measurements are consistent with previous density measurements of similar material. In general, the analytical measurements corroborate the gravimetrically measured constituents in each of the solvent drums. The NMR method gave a MaxCalix value that was higher than anticipated, and is being examined whether or not the NMR method requires further refinement. The HPLC method gave consistent results for the MaxCalix.

SRNL concludes that the preparation of the blend concentrate was successful.

5.0 Recommendations

SRNL recommends that further refinement of the NMR method be performed. As NMR data will already be collected to measure the TiDG, data should also be collected for MaxCalix for those samples.

6.0 Referen

ⁱ T. B. Peters, "Initial Analysis of NGS-MCU Cocktail Drum Samples", SRNL-L3100-2013-00145, August 19, 2013

ⁱⁱ E. T. Ketusky, "FY2013 SRNL Testing & Support for TF Aspects of NGS", HLE-TTR-2012-010, February 12, 2013.

ⁱⁱⁱ D. T. Herman and M. R. Williams, "Task Technical and Quality Assurance Plan for MCU NGS Implementation Coalescer and Contactor Testing", SRNL-RP-2013-00006, Rev. 1, May 2013.

^{iv} L29, ITS-0173, "Next Generation Solvent Preparation", July 11, 2013.

^v L29, ITS-0202, "Measurement of *N*, *N'*, *N''* -tris(3,7-dimethyloctyl)guanidine by Hydrogen Nuclear Magnetic Resonance", August 16, 2013.

^{vi} L29, ITS-0199, "Non-Aqueous Titrations using Mettler-Toledo T50 Auto-Titrator", July 11, 2013

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