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Results from the Analyses of the SRNL Solvent Components

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EXECUTIVE SUMMARY

At the request of the Savannah River Mission Completion (SRMC), personnel at Savannah River Site (SRS) performed analyses on the remaining solvent components that are being stored at the Savannah River National Laboratory (SRNL). This was done to determine if the remaining stock of materials were still suitable for use for the Salt Waste processing Facility (SWPF). Two drums of Modifier, two drums BOBCalix, four drums of MAXCalix, and four jars of TiDG*HCl were analyzed. All were found to be of acceptable purity for use.

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LIST OF ABBREVIATIONS

DOE	Department of Energy
HPLC	High Performance Liquid Chromatography
MCU	Modular Caustic-Side Solvent Extraction Unit
NMR	Nuclear Magnetic Resonance
PS	Production Support
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility

1.0 Introduction

The Modular Caustic-Side Solvent Extraction Unit (MCU) stopped operations on May 22, 2019. As part of MCU operations, SRNL maintained stocks of components used for both the original BOBCalix formulation♦ and MAXCalix formulation,♥ and will likely be used for a future solvent blend for use at theSalt Waste Processing Facility (SWPF). Since SWPF began operations, the Savannah River National Laboratory (SRNL) has prepared solvent batches for that facility and still maintains some stock of materials.

Recently, the Savannah River Mission Completion (SRMC) requested that SRNL analyze the remaining stock to determine if they were still effectively pure materials available for future use. While it was not expected that these components had degraded, enough time has passed since the purchase of some of these (10+ years) to warrant an examination. Identification of possible impurities did not fall within the scope of the document.

2.0 Background

At the time of the request, SRNL still retained two drums of Cs-7SB modifier, four jars of TiDG*HCl, four containers of MAXCalix, one drum of BOBCalix, and one drum of calixarene of unknown species (due to aged labeling). This gave a total of 12 samples.

Samples of Modifier, BOBCalix and MAXCalix were analyzed by Nuclear Magnetic Resonance (NMR) and High Performance Liquid Chromatography (HPLC). Samples of TiDG*HCl$^{\Sigma}$ were analyzed by titration.

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. This work is considered Production Support (PS). Per E7, 3.60, a technical report associated with a functional classification of PS is required to undergo, at a minimum, a Design Check. Therefore, the contents of this report have been subjected to a Design Check in accordance with E7, 2.60.

3.0 Experimental Procedure

All of the materials had been stored indoors under class B (semi-climate controlled) conditions for several years. Calixarene and modifier samples were removed from the source containers and

♦ "BOBCalix solvent" is a shorthand notation for an organic liquid composed of 0.007 M Calix(4)arene-bis(t-octylbenzo-crown-6), 0.75M 1-(2,2,3,3-tetrafluoro-propoxy)-3-(4-sec-butylphenoxy)-2-propanol, 0.003M trioctylamine, and the balance Isopar-L ™. Bulk solvent preparation is typically done at SRNL

♥"MAXCalix solvent" stands for Next Generation Solvent and is a liquid composed of 0.05M 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6, 0.5M 1-(2,2,3,3-tetrafluoro-propoxy)-3-(4-sec-butylphenoxy)-2-propanol, 0.003M N,N',N''-Tris(3,7-dimethyloctyl)guanidine, and the balance Isopar-L ™. Bulk solvent preparation is typically done at SRNL.

$^{\Sigma}$ TiDG*HCl is shorthand for N, N', N'' tris-isodecyl urea hydrochloride salt.

submitted without alteration. TiDG*HCl samples were dissolved in a stock solution of Isopar-L™ and Modifier. In this case, a weighed amount of TiDG*HCl was dissolved into a measured volume of stock solution to generate a nominal concentration of 20 mM. These dissolutions were then submitted for TiDG measurement via titration.

3.1 NMR Analysis

^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) was used to analyze samples of the Modifier, MAXCalix and BOBCalix. ^{1}H and ^{13}C can be used for all the samples, but ^{19}F is specific to the Modifier. An example of a NMR spectrum is presented as Figure 1.

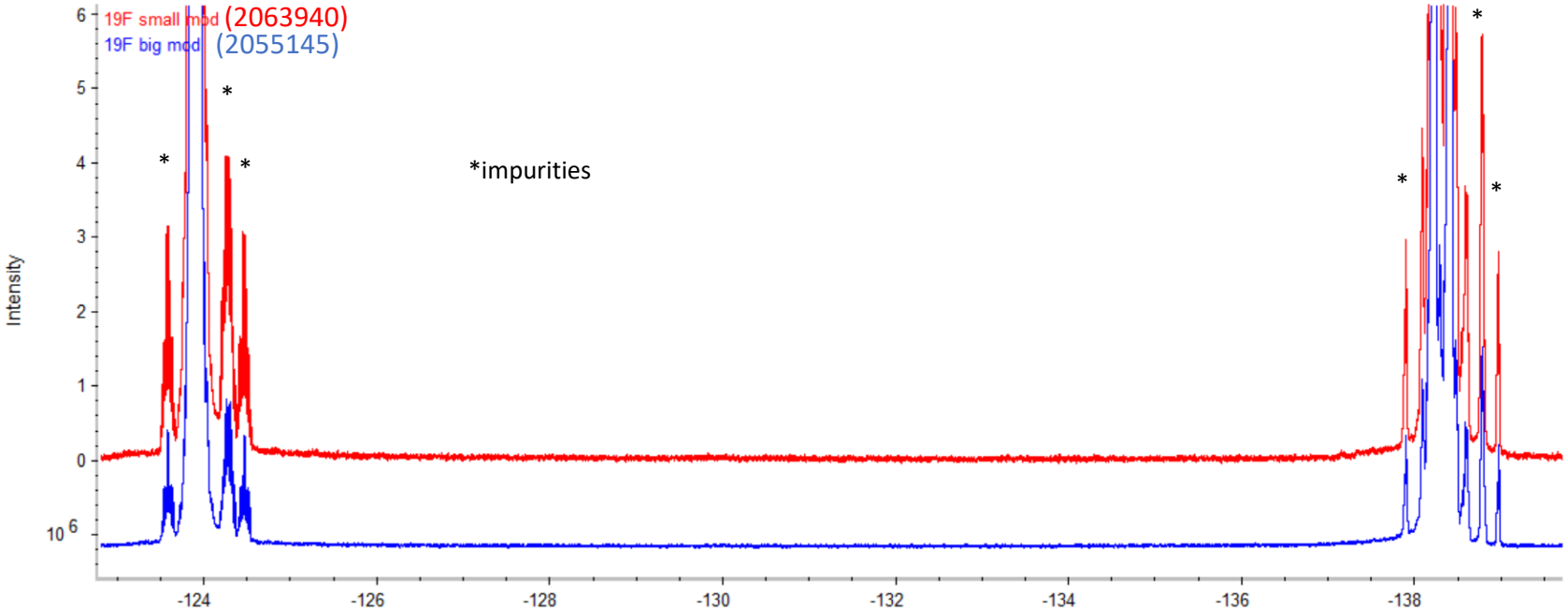
In Figure 1, the peaks marked with an asterisk represent a small amount of F-containing species, likely the F-containing precursor compound in the synthesis of the Modifier, which are present in both Modifier samples. From the area integration of the various peaks in the ^{19}F-NMR spectra, the % purity of the compound can be ascertained by assuming 1) degradation products contain comparable numbers of fluorine atoms, and 2) degradation products exhibit lower molecular weights than the pure modifier molecule. There was no evidence of 4-*sec*-butyl phenol by ^{1}H or ^{13}C. See Table 1 for the results (note that the analytical uncertainty for each identified sample is 15%).

Table 1. Results of NMR Analyses of Modifier, MAXCalix and BOBCalix

Sample ID (inventory #)	% Purity
Modifier (2063940)	97.5%
Modifier (2055145)	98%
MAXCalix (2055151)	99%+†
MAXCalix (20551540	99%+†
MAXCalix (2055152)	99%+†
MAXCalix (2044233)	99%+†
BOBCalix (misc drum)	99%+†
BOB/MAX? (2055153)	99%+†

†Calixarene samples were determined to be pure by the absence of peaks due to impurities in ^{19}F-, ^{13}C-, or ^{1}H-NMR spectra.

Figure 1. ^{19}F NMR of the Two Modifier Samples



The unidentifiable "BOB/MAX?" sample was a drum of calixarene that was missing some labeling and therefore was not initially precisely identified. NMR identifies this as BOBCalix.

From the Modifier and calixarene samples, none showed measurable amounts of impurities, with the exception that the Modifier samples showed slight impurities from F-containing species (likely precursors in the Modifier synthesis) as well as traces (could not quantify) of non-silicon based lubricants in the 2063940 drum sample.

Previous work in 2014 [1] that examined the purity of Modifier samples by ^{1}H and ^{13}C NMR showed spectrum identical to the certificates of analysis from the vendor (*i.e.*, indicating a pure material), including a small amount cyclohexane (~30 ppm) in drum 2055145. A careful examination of the ^{1}H NMR spectrum of this same drum also found a small amount (~0.2 ppm) of cyclohexane. It is possible that the cyclohexane (boiling point = 81 °C) has volatilized in the 8 years since the last measurement. The small remaining amount should not be considered a risk.

3.2 HPLC Analysis

HPLC analysis was performed on the Modifier and calixarene samples. The results are reported in Table 2. Note that the analytical uncertainty for species quantified by HPLC is 10%. The HPLC detection limit for 4-*sec*-butyphenol and other impurities is 100 mg/L (none detected).

Table 2. Results of HPLC Analyses of Modifier, MAXCalix and BOBCalix

Sample ID (inventory #)	% Purity
Modifier (2063940)	98.6%
Modifier (2055145)	106%
MAXCalix (2055151)	100%
MAXCalix (2055154)	103%
MAXCalix (2055152)	108%
MAXCalix (2044233)	108%
BOBCalix (misc drum)	98.8%
BOB/MAX? (2055153)	98%

The BOB/MAX? sample was shown to be BOBCalix by both NMR and HPLC. The results of the HPLC corroborate the NMR results that indicate the samples are high purity.

Previous work in 2014 [1] that examined the purity of Modifier samples by HPLC gave purity ranges from 96.9 to 100% with the HPLC detection limit for 4-*sec*-butyphenol and other impurities being 100 mg/L (none detected).

3.3 TiDG*HCl Titration Analysis

Samples of the TiDG*HCl were analyzed via titration. This is the accepted method for analysis, as opposed to NMR and HPLC. The analytical uncertainty on measurements made by titration are 10%.

Table 3. Results of Titration Analysis for the TiDG*HCl Samples

Sample ID (inventory #)	% Purity
TiDG*HCl (2055147)	104%
TiDG*HCl (2055148)	111%
TiDG*HCl (2055149)	108%
TiDG*HCl (2055150)	110%

The titration results in Table 3 indicate that the samples are pure, with the higher than nominal 100% possibly indicating a slight evaporation of Isopar-L ™ during the preparation and handling of the materials.

4.0 Results and Discussion

All of the compounds are analyzed as essentially pure compounds, with each measurement being within its analytical uncertainty of 100% (pure). While one of the four titration analyses on the TiDG*HCl samples registered very slightly over the 10% uncertainty, this is acceptable as this result was conservative.

5.0 Conclusions

All of the analyzed materials were shown to be ~pure within the limits of the specified methods. The unknown calixarene material was identified as BOBCalix. SRNL recommends using these materials for future solvent use.

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[1] C. L. Crawford, "Analysis of Out of Date MCU Modifier Located in SRNL", SRNL-STI-2014-00420, October 2014.