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Analysis and Testing of Parsons NGS Solvent Formulation

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EXECUTIVE SUMMARY

Three drums containing solvent used during the Next Generation Solvent Test (NGST) conducted by Parsons in 2014-2015 were received at SRNL. After homogenization, samples from each drum were removed, and a composite sample prepared. This composite was analyzed to determine current SRNL characterization method efficacy, and to determine if the 1,3-dicyclohexyl-2-(isotridecyl) guanidine (DCiTG) suppressor could be selectively removed.

The results of this work indicate that the titration analytical method currently employed at SRNL is effective at quantitating the DCiTG. The nuclear magnetic resonance (NMR) method at SRNL can detect the DCiTG, as well its amine and urea decomposition products. However, further development work will be required to allow the ^{1}H NMR method to quantitate these species.

A series of three washing tests were performed on composite samples of the solvent. The results show that up to 67% of the DCiTG was removed from the solvent by simple washing, at multiple ratios of solvent: aqueous phase. This may indicate that a simple pathway exists to wash out the DCiTG and reclaim the solvent (~150 gallons) for future use at the Salt Waste Processing Facility (SWPF).

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LIST OF ABBREVIATIONS

DCiTG	1,3-dicyclohexyl-2-(isotridecyl) guanidine
Deionized	de-ionized
DOE	Department of Energy
FTIR	Fourier-Transform Infra-Red
GCMS	gas chromatography mass spectrometry
HPLC	High Performance Liquid Chromatography
MCU	Modular Caustic Side Solvent Extraction Unit
NGST	Next Generation Solvent Test
NMR	Nuclear Magnetic Resonance
ORNL	Oak Ridge National Laboratory
RSD	relative standard deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SVOA	Semi-Volatile Organic Analysis
SWPF	Salt Waste Processing Facility
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

In 2014-2015, Parsons performed the Next Generation Solvent Test (NGST). The overall goal of the NGST was to profile solvent recovery, hydraulic and mass transfer performance at varying organic-to-aqueous (O:A) ratios and rotor speeds with the Next Generation Solvent (NGS) flowsheet at increased waste simulant throughput. Unlike the solvent to be used at the start-up of the Salt Waste Processing Facility (SWPF), the NGST solvent was of a different formulation. Once the testing completed, the solvent was stored in three drums.

In 2020, a multidiscipline team utilized SRR-SPT-2011-00095, *Technology Maturation Plan for Next Generation Solvent Implementation in the Modular Caustic-Side Solvent Extraction Unit at Savannah River Site*, as a starting point for identifying technology gaps associated with implementation of NGS in SWPF. As a result of this analysis, several concerns were noted with respect to the solvent formulation used in the NGST.[1]

As part of the effort to examine some of the solvent concerns, the stored solvent ("Parsons-NGS") was sent to SRNL for examination and testing. After mixing and preparing a composite sample from the three drums, SRNL analyzed the solvent by multiple methods, not only to characterize the solvent in the typical manner, but also to look for solvent degradation products. SRNL also simulated washing with several aqueous phases at various volume ratios to provide insight into the removal efficiency of DCiTG.

2.0 Receipt and Initial Observations

The three drums ("Next Generation Solvent 11/22/11 #1", "Next Generation Solvent 11/14/11 #3" and "Next Generation Solvent 11/10/11 #5") of Parsons-NGS solvent was received at SRNL on 16 July 2020. The contents of each drum were thoroughly mixed by a powered agitator for several hours. Drum#1 was estimated to have 30 gallons of material in it, while drums #3 and #5 were estimated to have 50 gallons in each. Drum #3 has a small amount of aqueous material on the bottom of the drum. A ~1L sample of each drum was pulled. Each of the three solutions were clear, with no observable solids. The material from drums #3 and #5 had a pale-yellow tint while the contents of drum #1 were colorless. A volume-adjusted composite sample from the three drums was prepared for further use.

2.1 Initial Analysis

Some of the composite sample was sent for the same suite of analyses performed on the monthly solvent hold tank (SHT) samples from MCU. This suite consists of High-Performance Liquid Chromatography (HPLC), Semi-Volatile Organic Analysis (SVOA), Nuclear Magnetic Resonance (NMR), Fourier-Transform InfraRed spectroscopy (FTIR), viscosity, surface tension, titration, and density. The results are reported in Table 1.

Table 1. Results of the Parsons-NGS Solvent

Analyte	Method	Value (1-σ uncertainty)
Isopar-L ™	NMR	6.27E+05 mg/L (14%)
Isopar-L ™	density	6.08E+05 mg/L (3.0%)
Isopar-L ™ weighted average		6.09E+05 mg/L
Modifier	HPLC	1.89E+05 mg/L (10%)
Modifier	NMR	1.94E+05 mg/L (10%)
Modifier	density	1.79E+05 mg/L (3.0%)
Modifier weighted average		1.80E+05 mg/L
DCiTG	titration	821 mg/L (10%)
MAXCalix	NMR	4.44E+04 mg/L (13%)
MAXCalix	HPLC	4.10E+04 mg/L (10%)
MAXCalix weighted average		4.21E+04 mg/L
Density	density meter	0.837 g/mL (3.0%)
Surface tension	manual tensiometer	23.6 dynes/cm (11%)
viscosity	viscometer	3.44 cP (3.0%)

The titration analysis did not indicate the presence of other bases, such as the presumed amine decomposition product of DCiTG. The analyzed concentration of DCiTG of 821 mg/L (2.03 mM – a small decline compared to nominal formulation; see Table 2) is rather surprising given how long the solvent has sat in storage (~8 years). This result indicates that while in the quaternized form, these guanidine derivatives display excellent chemical stability.

The current results can be compared to the last two sets of analyses performed on the solvent from 2012, as well as the as-prepared values.[2] See Table 2.

Table 2. Comparison of Current and Most Recent Past Results (mg/L)

	Isopar-L ™	Modifier	MAXCalix	DCiTG
Current Result	6.09E+05	1.80E+05	4.21E+04	8.21E+02
Previous Result 1 [Π]	not analyzed	1.72E+05	4.20E+04	5.87E+02
Previous Result 2 [∇]	6.23E+05	2.09E+05	4.84E+07	7.24E+02
As-prepared	6.13E+05	1.82E+05	5.12E+04	1.25E+03

The most appropriate comparison is between the Previous Result 1 (solvent before being put into storage) and the current result. The Previous Result 2 and As-prepared values reflect the solvent deliberately modified to have different solute concentrations.

Comparing the Current and Previous Results 1, the Modifier and MAXCalix results show excellent agreement. There is no conceivable way the DCITG could increase in concentration over time (it cannot be due to evaporation as the other analytes show no comparable increase), and with the

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[Π] From reference 2, this is from the Next Generation Solvent Test

[∇] From reference 2, this is from the Higher Concentration Waste Demonstration Testing excellent current result agreement with the prepared standards (see below), SRNL believes that the past DCiTG result is biased low.

2.2 Standards Preparation

Of all the components in the Parsons-NGS solvent, the DCiTG is a component that had not been measured before at SRNL. Part of this work was to determine if the standard SRNL analytical methods (^{1}H NMR and titration) were appropriate for this material. To this end, seven standards were gravimetrically prepared (#1 through #7). The composition of each is noted in Table 3. In each case, the diluent is Isopar-L ™.

Table 3. Prepared Composition of the Six Standards.

Standard	DCiTG (mM) [Σ]	Modifier (M) [£]	MAXCalix (mM) [∇]
1	0.559	0.501	50.4
2	1.99	0.500	50.1
3	4.01	0.500	50.2
4	1.05	0.500	50.4
5	3.02	0.500	49.9
6	4.70	0.500	49.8
7	1.04	0.500	50.7

Standards #1, 2, 3, 7 were analyzed for DCiTG content via ^{1}H NMR and titration to corroborate the accuracy of those methods. The results of those analyses are listed in Table 4.

Table 4. NMR and Titration Results for Standards #1, 2, 3 and 7 (mM)

Standard	DCiTG nominal	DCiTG by NMR (% of nominal)	DCiTG by titration (% of nominal)
1	0.559	0.588 (106%)	0.689 (123%)
2	1.99	2.14 (108%)	2.08 (104%)
3	4.01	3.37 (84.0%)	4.08 (102%)
7	1.04	1.35 (130%)	1.04 (100%)

The titration analysis measured a DCiTG concentration closer to the prepared nominal amount than did NMR, with excellent quantitation at ~1mM and higher. The Standard#1 was likely prepared at a level at which the titration method starts to show a bias. The NMR method had more difficulty in matching the DCiTG sample concentrations. The results of this testing indicate that DCiTG is inherently more difficult to analyze via ^{1}H NMR, possibly due to the structural asymmetry of the substituent groups on the nitrogen atoms.

[Σ] DCiTG is the short-hand name for N, N' dicyclohexyl, N"isotridecylguanidine and is added as the HCl salt.

[£] Modifier is 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol.

[∇] MAXCalix is 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6

For standards #4-#6, attempts were made to institute decomposition of the DCiTG, with the goal of generating detectable amounts of the degradation products. Each of these three standards were contacted with 1 M NaOH for two different periods of time. In the first case, the contact time was 1 hour, at 40 ˚C. These sample were then analyzed for DCiTG content via NMR and titration, as well as for potential decomposition products by NMR. The results of these analyses are listed in Table 5.

Table 5. Effects of 40 ˚C Temperature Contact with 1M NaOH, 1 Hour (mM)

Standard	DCiTG titration (% of nominal)	DCiTG NMR (% of nominal)	Amine NMR	Urea NMR
4	1.08 (103%)	1.29 (123%)	detected, but unable to quantify	
5	3.00 (99.3%)	2.91 (96.4%)		
6	4.67 (99.4%)	3.99 (84.9%)		

The titration analysis did not indicate any decomposition, nor the presence of other bases, such as the presumed amine decomposition products of DCiTG. Again, the NMR method had more difficulty in matching the DCiTG sample concentrations than the titration method.

In the second case, the contact time was 50 hours at 40 ˚C, following the same process as for the one-hour samples (Table 6).

Table 6. Effects of 40 ˚C Temperature Contact with 1M NaOH, 50 Hours (mM)

Standard	DCiTG titration (% of nominal)	DCiTG NMR (% of nominal)	Amine NMR	Urea NMR
4	1.158 (110%)	1.41 (134%)	detected, unable to quantify	
5	3.072 (102%)	2.62 (86.8%)		
6	4.74 (101%)	3.50 (74.5%)		

The titration analysis did not indicate any DCiTG decomposition, nor the presence of other bases, such as the presumed amine decomposition products of DCiTG. Again, the NMR method had more difficulty in matching the DCiTG sample concentrations than the titration method.

Relatively short contact times, even at elevated temperature are not effective in rapidly degrading the DCiTG.

Lastly, the 1M NaOH aqueous phases used to contact Standards 1, 2, and 3 were analyzed and while the species could not be quantified due to very low concentrations, several species were positively identified. See Figure 1. These organic species appeared to be modified Modifier and modified suppressor (from the NaOH contact), confirming that there is some slight solubility of these species in caustic aqueous phases. A more definite identification of the organics that transferred to the aqueous solution was observed when the Parsons solvent was contacted with nitric acid, sulfuric acid, and water at different organic to aqueous ratios. See Figure 2 (water results are not shown but were similar). In Figure 2, urea, an expected by-product of the suppressor, and Isopar-L™ were clearly seen. Evidence for aliphatic amines was not detected (possibly below the detection limit of this method).

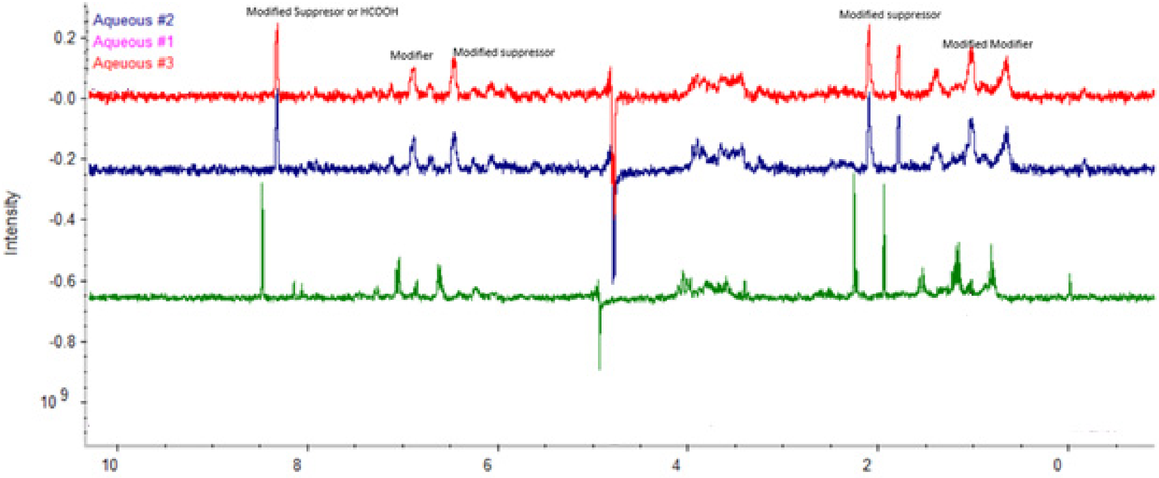

Figure 1. NMR Spectrum of the 1M NaOH Aqueous Phases after Contact with Standards 1, 2, and 3

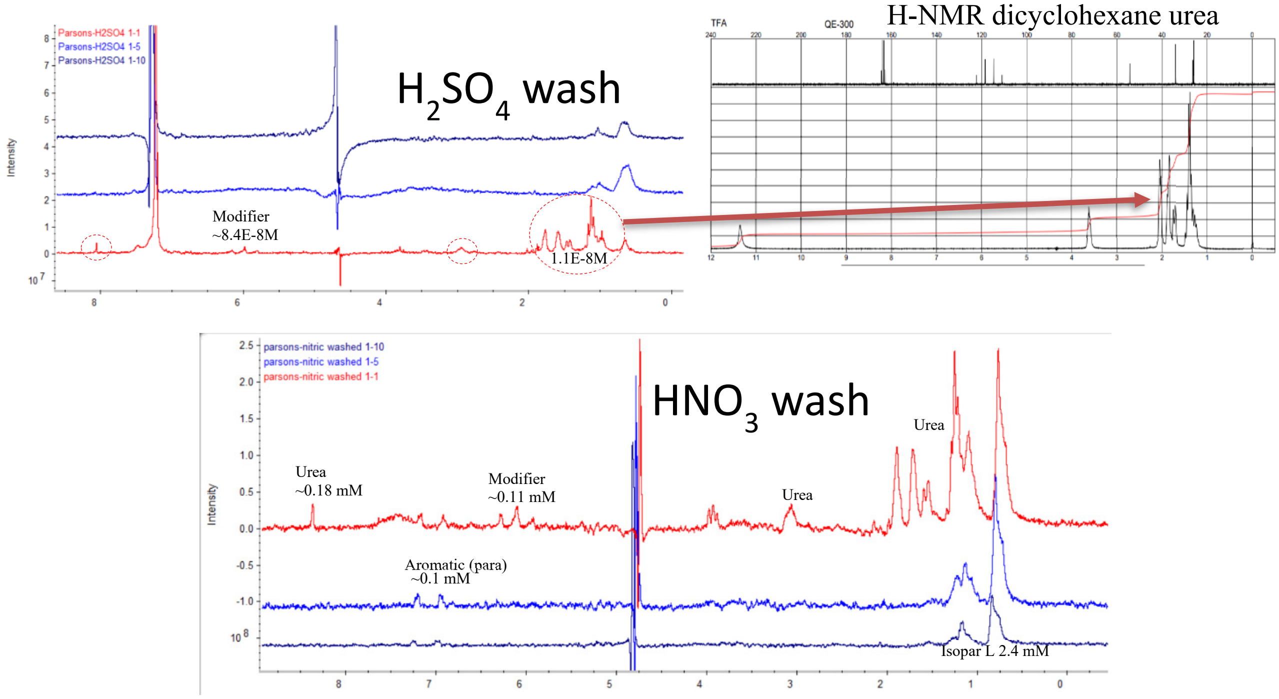

Figure 2. HNMR Spectra of the nitric acid and sulfuric that contacted Parsons solvent showing Urea and Isopar-L™ (concentrations are listed in the figures)

2.3 DCiTG Partitioning

During the Gap Analysis, a concern was voiced in regards to the use of DCiTG, which has been experimentally shown to have a higher partitioning into water, compared to the suppressor used at the Modular Caustic Side Solvent Extraction Unit (MCU).[3] The relatively high partitioning value offers a potential avenue to reclaim the solvent from the Parsons-NGST drums for use at SWPF at a later date, if the DCiTG can be removed by washing it out into an aqueous phase.

To test this approach, researchers performed three multi-tier tests. A 100 mL portion of the composite sample was contacted with 100 mL of an aqueous phase in a glass separatory funnel (1O:1A volume ratio). After vigorous hand-mixing for 4 minutes, the mixture was then allowed to settle until the phases clearly separated. The phases were separated, and a 33 mL sample of the organic phase was analyzed for DCiTG content. The remainder of the organic phase (~66 mL) was placed back into the funnel with 335 mL of a fresh aqueous phase (1O:5A). After vigorous hand-mixing for 4 minutes, the mixture was then allowed to settle until the phases clearly separated. The phases were separated, and a 33 mL sample of the organic phase was analyzed for DCiTG content. The remainder of the organic phase (~33 mL) was placed back into the funnel with 330 mL of a fresh aqueous phase (1O:10A). Using vigorous hand-mixing for 4 minutes, the mixture was then allowed to settle until the phases clearly separated. The phases were separated, and a 33 mL sample of the organic phase was analyzed for DCiTG content.

In each test, the same organic phase was used between the three O:A ratios under the assumption that the DCiTG loss was small compared to the starting concentration.

Three tests were performed using the methodology described above. The three aqueous phases used were deionized (DI) water, 0.005M nitric acid, and 0.005 M sulfuric acid. The choice of dilute acids was derived from a consultation with researchers at Oak Ridge National Laboratory (ORNL).

Each of the three organic post-contact phases in each test were analyzed via titration for DCiTG content, and the results reported in Table 7. The "Before Contact" result was a separate analysis of the composite performed with the other titrations and while this result differs from the original result of 2.03 mM (Table 1), the difference is less than the sum of the analytical uncertainties of the two measurements (10% each), and are therefore not statistically different.

Table 7. DCiTG Concentrations in the Post-Contact Organic Phases

	Titration Results, mM		
Sample	DI water	0.005M nitric acid	0.005M sulfuric acid
Before Contact	2.36	2.36	2.36
1O: 1A	2.06	1.56	1.39
1O: 5A	1.67	1.08	0.974
1O: 10A	1.31	0.854	0.775

The 1-s analytical uncertainty for the titration measurements is 10%.

The results indicate that increasing amounts (13 – 67%) of DCiTG are lost to the aqueous phase as the A:O phase ratio increases. While the loss to DI water in a 1:1 contact may not be statistically significant for the water contact, in all other cases, the loss is statistically significant. We also note that the dilute acid washes also remove more DCiTG than the DI water, although we cannot declare which acid is superior to the other acid.

These results suggest that multiple cycles of a dilute acid short-contact wash will deplete the DCiTG from the organic phase. As it is desirable to minimize the generation of an aqueous waste stream, it may be possible to reuse a dilute acid by cycling this used stream through a simple cartridge filter containing an organic-sequestering agent, such as decolorizing carbon.

Once the DCiTG is removed, the remaining solvent must be trimmed with the appropriate components to achieve the correct composition for future use at SWPF.

3.0 Conclusions

The titration method used at SRNL for the analysis of solvent samples from MCU can also quantitate the DCiTG guanidine used in the Parsons NGS solvent. It is quite likely that all guanidine derivatives will be amenable to the titration method.

The results of this work indicate that the titration analytical method currently employed at SRNL is effective at quantitating the DCiTG. The ^{1}H nuclear magnetic resonance (NMR) method at

SRNL can detect the DCiTG, as well its amine and urea decomposition products. However, further development work will be required to allow the ^{1}H NMR method to quantitate these species. Future work should also investigate the use of ^{14}N NMR as a detection method.

A series of three washing tests were performed on composite samples of the solvent. The results show that up to 67% of the DCiTG was removed from the solvent by simple washing, at multiple ratios of solvent: aqueous phase. This may indicate that a simple pathway exists to wash out the DCiTG and reclaim the solvent (~150 gallons) for future use at the Salt Waste Processing Facility (SWPF.

Future work should consider the possibility that increased removal may occur if the DCiTG is converted to the less stable freebase form. This can be accomplished through a brief contact with dilute NaOH. Once in the freebase form, the solvent can be contacted with the dilute acid washes in the same manner as the work described in this document.

4.0 Reference

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