SRNL-STI-2013-00164
Revision 0

Assessment of the Impact of a New Guanidine Suppressor in NGS on F/H Laboratory Analyses for DWPF and Saltstone MCU Transfers

C. J. Bannochie

April 2013

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *MCU, NGS, DWPF, Saltstone, F/H Laboratories, Isopar L, Suppressor*

Retention: *Permanent*

Assessment of the Impact of a New Guanidine Suppressor in NGS on F/H Laboratory Analyses for DWPF and Saltstone MCU Transfers

C. J. Bannochie

April 2013

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

REVIEWS AND APPROVALS

AUTHOR:

____

C. J. Bannochie, Process Technology Programs Date

TECHNICAL REVIEW:

____

T. B. Peters, Advanced Characterization & Processing Date

APPROVAL:

____

F. M. Pennebaker, Manager Date
Advanced Characterization & Processing

____

S.L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

____

E. A. Brass, Manager Date
Flowsheet Integration & Technology

ACKNOWLEDGEMENTS

The author would like to thank the following individuals for insightful conversation and discussions of the Modular Caustic Side Solvent Extraction Unit (MCU) process and the Next Generation Solvent (NGS) system: M. R. Nelson, D. T. Herman, C. A. Nash, K. M. Taylor-Pashow, and T. B. Peters.

EXECUTIVE SUMMARY

Implementation of the Next Generation Solvent (NGS) in the Modular Caustic-Side Solvent Extraction Unit (MCU) will now proceed with a new suppressor compound, 1,2,3-tris(3,7-dimethyloctyl)guanidine (TiDG), replacing the originally planned suppressor for NGS, 1,3-dicyclohexyl-2-(11-methyldodecyl)guanidine (DCiTG). The Savannah River National Laboratory (SRNL) was tasked with evaluating the potential impact to F/H Laboratory analyses supporting the Defense Waste Processing Facility (DWPF) Waste Acceptance Criteria (WAC) used to qualify transfers of MCU Strip Effluent (SE) into the facility and the Saltstone WAC used to qualify transfers of Tank 50 containing Decontaminated Salt Solution (DSS) from MCU into Saltstone. This assigned scope is covered by a Task Technical and Quality Assurance Plan (TTQAP).

Previous impact evaluations were conducted when the DCiTG suppressor was planned for NGS and concluded that there was no impact to either the determination of MCU SE pH nor the analysis of Isopar® L carryover in the MCU SE and DSS streams. SRNL reported on this series of cross-check studies between the SRNL and F/H Laboratories.

The change in suppressor from DCiTG to TiDG in the NGS should not impact the measurement of Isopar® L or pH in SE or DSS necessary to satisfy DWPF and Saltstone WAC (Tank 50) criteria, respectively. A statistical study of the low bias observed in Isopar® L measurements in both SRNL and F/H Laboratories may be necessary now that the final NGS composition is fixed in order to quantify the low bias so that a proper correction can be applied to measurements critical to the DWPF and Saltstone WACs. Depending upon the final DWPF WAC requirement put in place for SE pH, it could become necessary to implement an alternative ICP-AES measurement of boron. The current blended solvent system testing in SRNL should address any impacts to Isopar® L carryover into either the DSS or the SE.

It is recommended that SRNL monitor the current blended solvent work underway with simulants in SRNL as well as any DWPF CPC testing done with the new SE stream to ascertain whether any need develops that could result in modification of any currently planned F/H Laboratory testing protocols.

TABLE OF CONTENTS

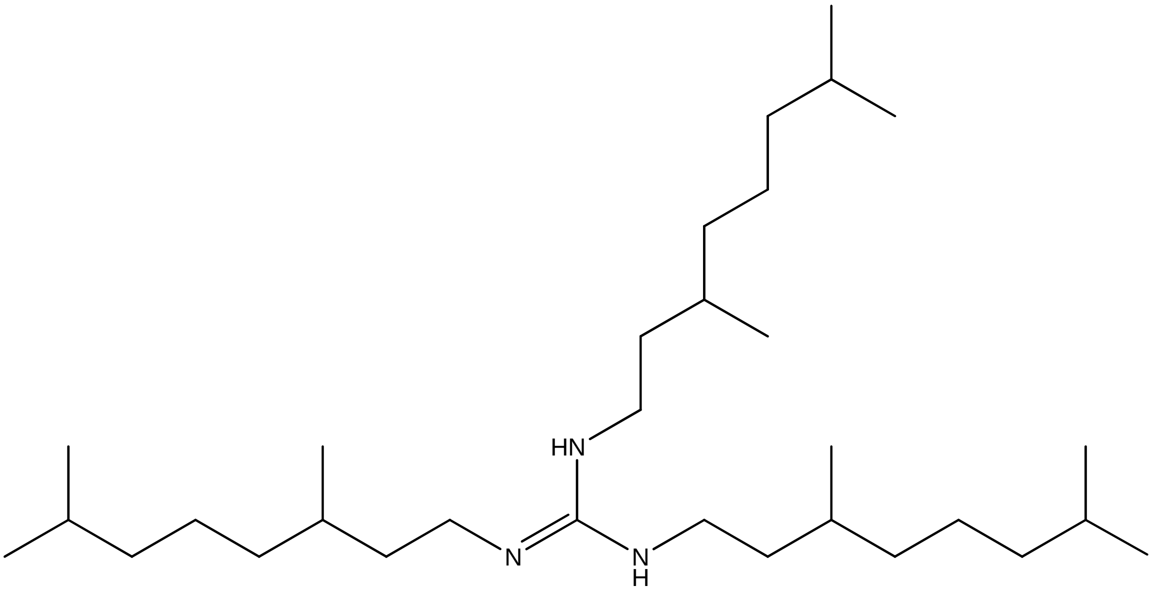
LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

CPC	Chemical Process Cell (DWPF)
CSSE	Caustic Side Solvent Extraction
DCiTG	1,3-dicyclohexyl-2-(11-methyldodecyl)guanidine
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
GC	Gas Chromatograph
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
LOD	Limit of Detection
LOQ	Limit of Quantification
MCU	Modular Caustic Side Solvent Extraction Unit
MRL	Method Reporting Limit
NGS	Next Generation Solvent
P_{Gua}	Guanidine Partition Ratio
SAC	Specific Administrative Controls
SDU	Saltstone Disposal Units
SE	Strip Effluent
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SVOA	Semivolatile Organic Analysis
TiDG	1,2,3-tris(3,7-dimethyloctyl)guanidine
TPB	Tetraphenylborate
TSR	Technical Safety Requirements
TTR	Technical Task Request
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

1.0 Introduction

Implementation of the Next Generation Solvent (NGS) in the Modular Caustic-Side Solvent Extraction Unit (MCU) will now proceed with a new suppressor compound, 1,2,3-tris(3,7-dimethyloctyl)guanidine (TiDG), Figure 1-1, replacing the originally planned suppressor for NGS, 1,3-dicyclohexyl-2-(11-methyldodecyl)guanidine (DCiTG), Figure 1-2. The Savannah River National Laboratory (SRNL) was tasked[1] with evaluating the potential impact to F/H Laboratory analyses supporting the Defense Waste Processing Facility (DWPF) Waste Acceptance Criteria (WAC)[2] used to qualify transfers of MCU strip effluent (SE) into the facility and the Saltstone WAC[3] used to qualify transfers of Tank 50 containing Decontaminated Salt Solution (DSS) from MCU into Saltstone. This assigned scope is covered by a Task Technical and Quality Assurance Plan (TTQAP).[4]



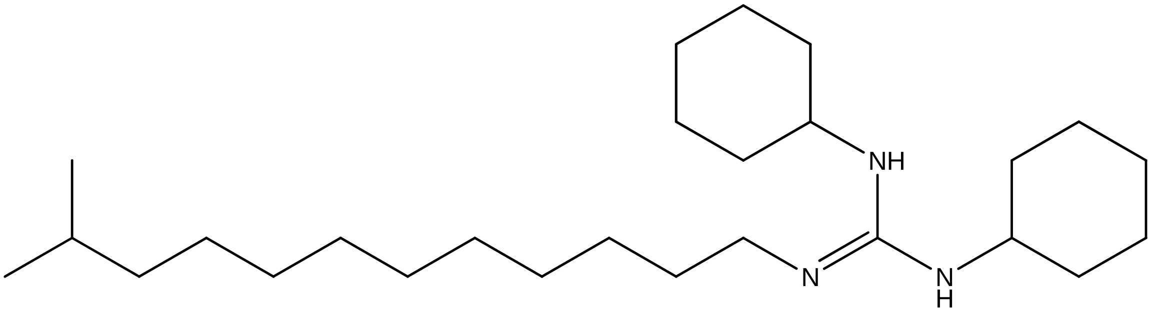
1,2,3-tris(3,7-dimethyloctyl)guanidine
Molecular Weight: 479.87
TiDG

Figure 1-1. MCU NGS Suppressor 1,2,3-tris(3,7-dimethyloctyl)guanidine, alternatively referred to as N,N',N"-tris(isodecyl)guanidine (TiDG)[a]

The present MCU solvent system is comprised of four components: the extractant, 0.007M calix[4]arene-bis(*tert*-oxtylbenzo-18-crown-6) (BOBCalixC6); the modifier, 0.75M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB); the suppressor, 0.003M tri-*n*-octylamine (TOA); and the solvent, Isopar® L, an alkane diluent. The NGS system is also comprised of four components: the extractant, 0.050M 1,3-alt-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzo-18-crown-6 (MaxCalix); the modifier, 0.50M Cs-7SB; the suppressor, 0.003M TiDG; and the solvent, Isopar® L, an alkane diluent. During implementation of the NGS system, there will be a period of a blended solvent system as the process transitions from BOBCalixC6 to MaxCalix, and this transition is the subject of planned testing in SRNL.[5]

---

[a] The non-IUPAC name uses the isodecyl group incorrectly to refer to a dimethyl substituted eight carbon alkyl chain. The isodecyl group would refer to a single methyl substituted nine carbon alkyl chain or an 8-methylnonyl group.



1,3-dicyclohexyl-2-(11-methyldodecyl)guanidine
Molecular Weight: 405.70

DCiTG

Figure 1-2. MCU NGS Suppressor 1,3-dicyclohexyl-2-(11-methyldodecyl)guanidine, alternatively referred to as N, N'-dicyclohexyl-N"-isotridecylguanidine (DCiTG)

While the NGS transition will be gradual, the transition in the scrub and SE streams will be immediate. The BOBCalixC6 scrub solution comprised of 0.050M HNO_3 and the strip solution comprised of 0.001M HNO_3 will change to a scrub solution comprised of 0.025M NaOH and a strip solution comprised of 0.010 H_3BO_3 for use with the NGS system. The scrub effluent folds back into the DSS stream bound for Tank 50 and Saltstone. The SE and the DSS will be analyzed by F/H Laboratories for Isopar® L entrainment and pH.

Previous impact evaluations were conducted when the DCiTG suppressor was planned for NGS. This work concluded that there was no impact to either the determination of MCU SE pH [6] nor the analysis of Isopar® L carryover in the MCU SE and DSS streams.[7] SRNL reported on this series of cross-check studies between the SRNL and F/H Laboratories and the findings will be discussed in the next section.[8]

The TTR specifies that the impact to F/H Laboratories of concern for MCU is the period of blended solvent as the MCU transitions from the current BOBCalixC6 solvent to the NGS with TiDG as the suppressor.[1] The TTQAP emphasizes identifying any testing necessary to support implementation of the NGS system.[4] Hence this report will look at the all previous work done to assess the NGS when DCiTG was the suppressor, as well as the analytical requirements placed on F/H Laboratories by their Saltstone and DWPF customers to evaluate whether the change to TiDG as the suppressor will result in any upset to F/H Laboratory measurements.

2.0 Results and Discussion

2.1 Isopar® L Measurement

F/H Laboratories are tasked with qualifying MCU SE stream for eventual transfer to the Chemical Processing Cell (CPC) in DWPF. Specifically the DWPF WAC[2] specifies the following key qualifications:

> 5.4.13.1 Criteria: Organic material present in sludge feed transferred to DWPF shall contribute less than 0.1% to the hydrogen LFL except for transfers from MCU.
>
> Transfers of strip effluent from MCU shall be tracked and characterized by the sending facility prior to entering the DWPF Chemical Process Cell (CPC):

a) Transfers of strip effluent from MCU shall not exceed 87 ppm Isopar L accounting for analytical uncertainty.
b) In the event of a process upset, transfers of strip effluent from MCU may be greater than 87 ppm Isopar L but shall not exceed 600 ppm Isopar L accounting for analytical uncertainty.

F/H Laboratories are also tasked with qualifying decontaminated salt solution for release to Tank 50 in preparation for receipt by the Saltstone Facility. Specifically, the Saltstone WAC[3] for specifies:

> 5.4.3.3 Background: In order to protect assumptions associated with flammability in [Saltstone Disposal Units] SDUs, the facility has set maximum WAC LIMITS on the following chemicals: Isopar® L, TPB and ammonia (analyte measured is ammonium).
>
> Salt solution from the MCU waste stream will contain Isopar® L, which can be released under certain conditions to produce flammable vapors. The Isopar® L concentration in salt solution shall be limited by the WAC to be less than or equal to 11 ppm.

The Saltstone WAC does not specify limits for other potential organic streams such as the extractant or the suppressor since they are not considered flammable. The strict limit is placed only on Isopar® L.[3]

It should be noted that the current Saltstone WAC flammability limit on Isopar® L of 11 ppm or 13 mg/L assuming a slurry density of 1.22. F/H Labs reports a detection limit (LOD) of 11 mg/L and a quantification limit (LOQ) of 16 mg/L (13 ppm with a slurry density of 1.22) at the instrument.[9] The LOQ of 16 mg/L corresponds to 4 ± 1 mg/L at the sample level (method) at the 95% confidence level.[9] SRNL reports a method reporting limit (MRL) of 7.0 ± 1.4 mg/L at the 95% confidence level for "samples received in p-nut vials or similar small containers from MCU".[10, 11] For non-MCU customers and other sample types SRNL reports a MRL of 33 ± 10 mg/L.

In light of the Saltstone WAC assumption regarding organics, the change in suppressor from DCiTG to TiDG should not be a concern with respect to the amount entrained with the Isopar® L in the SE. Additionally, the partition coefficient of the new suppressor, TiDG, is vastly superior to the behavior of DCiTG, for NGS in contact with 0.010M H_3BO_3.[12] Moyer et al. reported a Guanidine Partition Ratio (P_{Gua}) of >1000 as compared to a P_{Gua} of 30.2 for DCiTG.[12] Therefore, the amount of TiDG dissolved into, as opposed to entrained with Isopar® L, should be significantly smaller. The current assessment of the impact to the DWPF melter off-gas flammability assumes that 6 ppm of TiDG partitions to the SE.[13]

In the gas chromatography (GC) spectra of hexane[b] extractions of SE and DSS conducted by F/H Laboratories, no DCiTG suppressor was observed.[14] See Figure 2-1 and Figure 2-2. The Isopar® L peaks are seen in the center of the chromatogram as a series of small peaks. The large peak at the beginning of each chromatogram (far left) is the hexane extractant and the peak labeled phenyloctane is the internal standard. If modifier is seen, its peak lies to the right of the internal standard, phenyloctane. The relative solubility's of the two suppressors in hexane is unclear, but it seems unlikely that the solvent containing the dissolved extractant, modifier, and suppressor species would be extracted while leaving behind one of the three dissolved species, be that the DCiTG or the TiDG. It is possible that the concentrations are just too low for quantification. An issue observed with the quantification of DCiTG via semi-volatile organic analysis (SVOA) was

---

[b] While the solubility of TiDG in hexane has not been explicitly measured, it is believed to be high enough to not present an issue.

two fold: the material was observed to decompose on the GC column and the variability in the methyl substitution of the dodecyl group appendage lead to a broad poorly defined peak. A factor which may impact the extractability of TiDG is that NGS is prepared from the HCl salt of the guanidine rather than from the free-base.

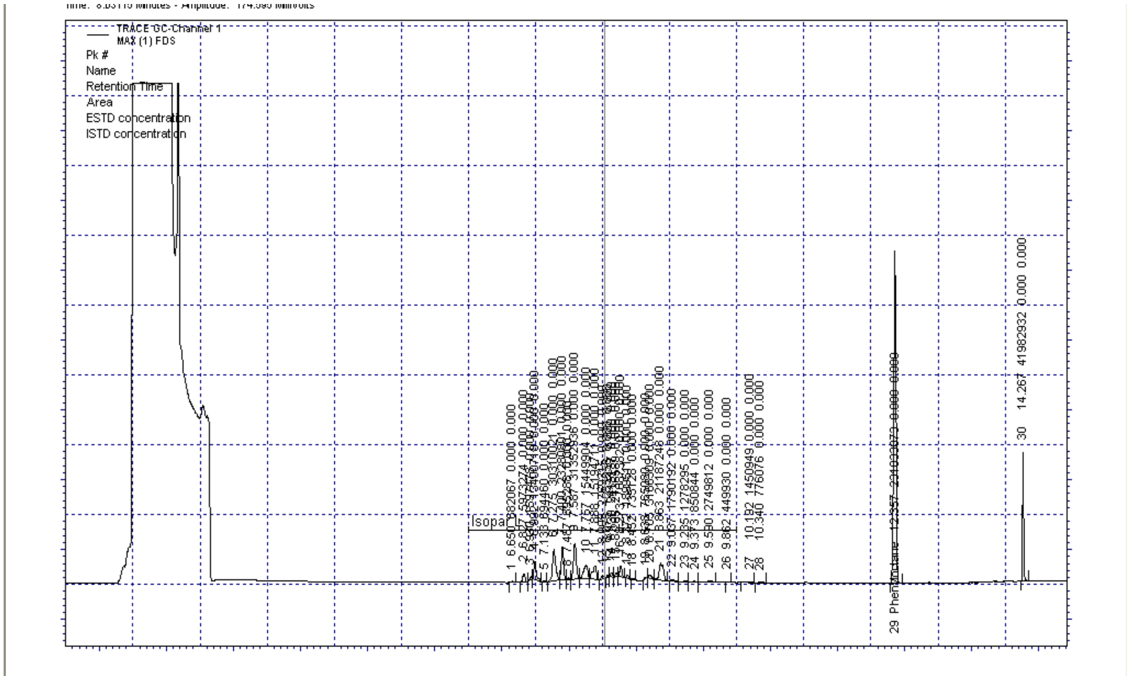


Figure 2-1. GC Spectra of NGS Strip Effluent

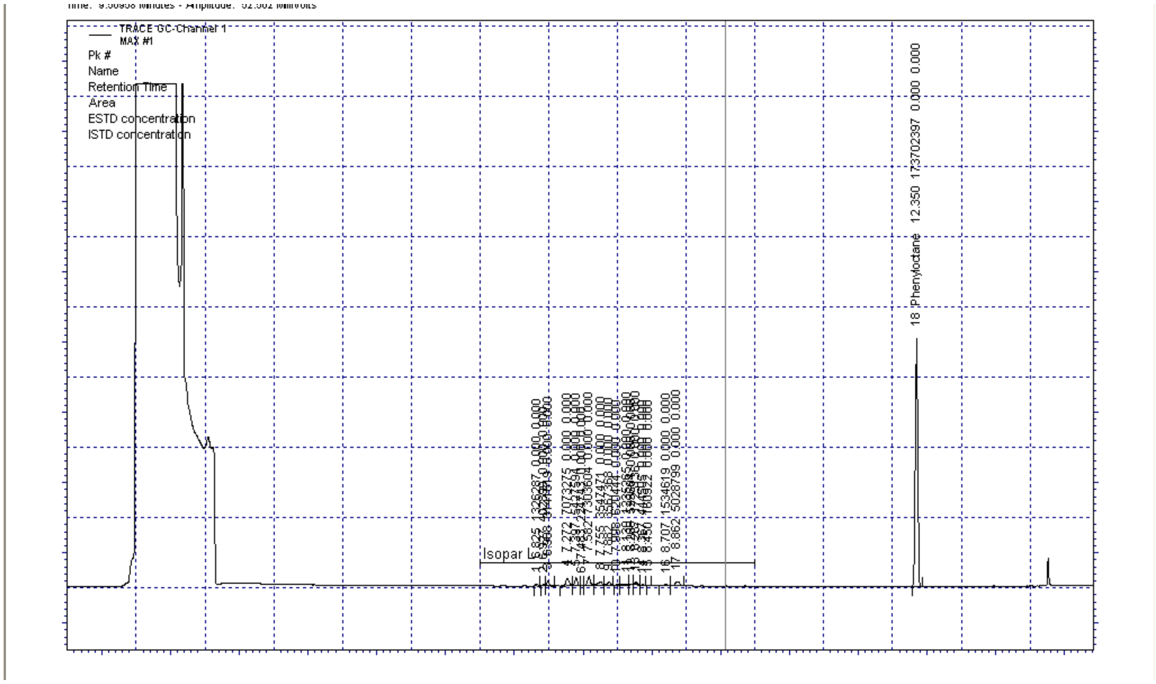


Figure 2-2. GC Spectra of NGS Decontaminated Salt Solution (DSS)

The new scrub effluent, 0.025M NaOH, being a base would not be expected to dissolve significant guanidine suppressor since it would be deprotonated in caustic solution. Hence the only suppressor carryover into the scrub effluent would be that entrained with Isopar® L. Again, since the scrub effluent is not analyzed apart from the DSS, the DSS analysis should capture any entrained Isopar® L.

F/H Laboratories and SRNL reported observing a low bias in the measurement of Isopar® L for NGS, but this had also been the case for the current solvent system.[8] At the time of the study, F/H Laboratories did not feel a need to adjust the bias of the method, and in light of the suppressor change, this was a good decision. However, a statistical study of this bias may be necessary now to quantify the bias so that a proper correction can be applied to measurements critical to the DWPF and Saltstone WACs.

2.2 pH Measurements

The measurement of pH is required for DWPF receipt of SE.[2]

> 5.4.14.1 Criteria: Transfers from MCU must meet the following pH constraints:
> a) Strip effluent shall have a pH ≥ 2 and ≤ 4
>
> 5.4.14.4 Background: … NOTE: The upper pH limit (pH $\leq$ 4) is not part of [Technical Safety Requirements] TSR [Specific Administrative Controls] SAC 5.8.2.11; however, this limit is required for [Sludge Receipt and Adjustment Tank] SRAT processing purposes.

The calculated pH of a 0.01M H_3BO_3 solution is 5.6.[6] The current DWPF WAC will need to be revised to accommodate a SE with a pH >4, the currently specified limit. Based on communication with DWPF there is a plan to modify their WAC to accommodate the higher pH of the H_3BO_3 SE.[15]

A proposal by SRNL for F/H Laboratories to consider replacing the pH measurement of SE with a boron measurement via inductively coupled plasma – atomic emission spectroscopy (ICP-AES) was previously made.[8] Depending upon the new DWPF WAC limitation on pH, this recommendation may or may not be considered further. If, as F/H Laboratories assumes, the requirement is simply to ensure the pH is above 2, there is no need for precision since the pH measurements on dilute H_3BO_3 that were made are in the range of 6.6 – 7.7 in their study.[8] The authors suggested that atmospheric CO_2 was altering the measurement of dilute H_3BO_3 solutions. It could be postulated that dissolved CO_2 already present in the dilution water may have played a role, but it will also play a role in the actual SE to be measured, raising the pH over that of a pure H_3BO_3 solution. If a strict upper limit is imposed by DWPF for processing reasons, the alternative measurement method may warrant further consideration.

2.3 Blended Solvent Impacts

The one area not previously tested is the impact on SE and DSS streams from a blended solvent system during transition from the current BobCalixC6 solvent system to the NGS system. While this may impact the carryover of Isopar® L, current testing underway should provide insight on this question.[5] It is unlikely that the minor components of the solvent, either the modifier or the suppressor, will even be measurable unless the Isopar® L carryover changes dramatically.

3.0 Conclusions

The change in suppressor from DCiTG to TiDG in the NGS should not impact the measurement of Isopar® L or pH in SE or DSS necessary to satisfy DWPF and Saltstone WAC (Tank 50) criteria, respectively. A statistical study of the low bias observed in Isopar® L measurements in both SRNL and F/H Laboratories may be necessary now that the final NGS composition is fixed in order to quantify it so that a proper correction can be applied to measurements critical to the DWPF and Saltstone WACs. Depending upon the final DWPF WAC requirement put in place for SE pH, it could become necessary to implement an alternative ICP-AES measurement of boron. The current blended solvent system testing in SRNL should address any impacts to Isopar® L carryover into either the DSS or the SE.

4.0 Recommendations

It is recommended that SRNL monitor the current blended solvent work underway with simulants in SRNL as well as any DWPF CPC testing done with the new SE stream to ascertain whether any need develops that could result in modification of any currently planned F/H Laboratory testing protocols. SRNL and F/H Labs should consider a statistical study to address any potential low bias in the measurement of Isopar® L.

5.0 References

1. Ketusky, E. T. *FY2013 SRNL Testing & Support for TF Aspects of NGS*, HLE-TTR-2012-010, Rev. 2, Savannah River Site, Aiken, SC 29808, 2013.

2. Ray, J. W. *Waste Acceptance Criteria for Sludge, ARP, and MCU Process Transfers to 512-S and DWPF*, X-SD-G-00008, Rev. 10, Savannah River Site, Aiken, SC 29808, 2012.

3. Chiu, C. K. *Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility*, X-SD-Z-00001, Rev. 11, Savannah River Site, Aiken, SC 29808, 2012.

4. Peters, T. B., Nash, C. A. *Task Technical and Quality Assurance Plan for Cesium Mass Transfer Test with Next Generation Solvent (NGS) and Miscellaneous White Papers*, SRNL-RP-2012-00842, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808, 2013.

5. Herman, D. T., Williams, M. R. *Task Technical and Quality Assurance Plan for MCU NGS Implementation Coalescer and Contactor Testing*, SRNL-RP-2013-00006, Savannah River National Laboratory, Aiken, SC 29808, 2013.

6. Nelson, M. R. *Next Generation MCU Solvent Testing of pH Analysis in FHL*, SRNS-N3100-2011-00056, Savannah River Site, Aiken, SC 29808, 2011.

7. Phillips, M. J., Nelson, M. R. *Next Generation MCU Solvent Testing of Isopar® L Analysis in FHL*, SRNS-N3100-2011-00057, Savannah River Site, Aiken, SC 29808, 2011.

8. Peters, T. B., Fink, S. D. Results of Analytical Sample Crosschecks for Next Generation Solvent Extraction Samples: Isopar® L Concentration and pH, SRNL-STI-2011-00586, Savannah River National Laboratory, Aiken, SC 29808, 2011.

9. Wills, G. P., Johns, N. A., Nelson, M. R. *Evaluation of Lowering the GC Isopar Calibration Curve and Determination of the Limit of Quantification*, SRNS-N3100-2008-00042, Savannah River Site, Aiken, SC 29808, 2009.

10. Crump, S. L. *Determination of Method Reporting Limits for Select Analytes by GC/MS*, SRNL-TR-2010-00206, Savannah River National Laboratory, Aiken, SC 29808, 2010.

11. Crump, S. L., Harris, S. P. *Revised Evaluation of Method Reporting Parameters for Measurement of Isopar in Aqueous Samples Using Gas Chromatography With Flame Ionization Detection*, SRNL-TR-2009-00405, Savannah River National Laboratory, Aiken, SC 29808, 2009.

12. Moyer, B. A., Delmau, L. H., Duncan, N. C., Ensor, D. D., Hill, T. G., Lee, D. L., Roach, B. D., Sloop, Jr., F. V., Williams, N. J. *Recommended Guanidine Suppressor for the Next-Generation Caustic-Side Solvent Extraction Process*, ORNL/TM-2012/625, Oak Ridge National Laboratory, Oak Ridge, TN 37831, 2013.

13. Daniel, W. E., *Assessment of the Impact of Next Generation Solvent on DWPF Melter Off-Gas Flammability*, SRNL-STI-2013-00035, Savannah River National Laboratory, Aiken, SC 29808, 2013.

14. Bannochie, C. J. SRNL Electronic Laboratory Notebook, L2320-00016-08, Savannah River National Laboratory, Aiken, SC 29808, 2013.

15. Samadi-Dezfouli, A. DWPF WAC Email, SRNL Electronic Laboratory Notebook, L2320-00016-08, Savannah River National Laboratory, Aiken, SC 29808, 2013.

Distribution:

T. B. Brown, 773-A
D. R. Click, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A

C. J. Bannochie, 773-42A
T. B. Peters, 773-42A
D. T. Herman, 735-11A
M. R. Williams, 786-5A
C. A. Nash, 773-42A
K. M. Taylor-Pashow, 773-A
S. L. Crump, 773-A
T. L. White, 773-A

M. J. Phillips, 772-F
M. R. Nelson, 772-F

E. J. Freed, 704-S
A. Samadi-Dezfouli, 704-27S
D. J. Martin, 241-152H
T. A. Le, 766-H
B. A. Gifford, 704-56H
R. M. Wolfenden, 704-56H
E. A. Brass, 249-8H
A. G. Garrison, 249-8H
E. T. Ketusky, 249-8H
R. H. Spires, 241-156H
C. I. Aponte, 249-8H
S. M. Spell, 704-56H

P. R. Jackson, DOE-SR, 703-46A
K. H. Subramanian, 766-H

Records Administration (EDWS)