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Non-Aqueous Titration Method for Determining Suppressor Concentration in the MCU Next Generation Solvent (NGS)

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Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

A non-aqueous titration method has been used for quantifying the suppressor concentration in the MCU solvent hold tank (SHT) monthly samples since the Next Generation Solvent (NGS) was implemented in 2013. The titration method measures the concentration of the NGS suppressor (TiDG) as well as the residual tri-*n*-octylamine (TOA) that is a carryover from the previous solvent. As the TOA concentration has decreased over time, it has become difficult to resolve the TiDG equivalence point as the TOA equivalence point has moved closer. In recent samples, the TiDG equivalence point could not be resolved, and therefore, the TiDG concentration was determined by subtracting the TOA concentration as measured by semi-volatile organic analysis (SVOA) from the total base concentration as measured by titration.

In order to improve the titration method so that the TiDG concentration can be measured directly, without the need for the SVOA data, a new method has been developed that involves spiking of the sample with additional TOA to further separate the two equivalence points in the titration. This method has been demonstrated on four recent SHT samples and comparison to results obtained using the SVOA TOA subtraction method shows good agreement. Therefore, it is recommended that the titration procedure be revised to include the TOA spike addition, and this to become the primary method for quantifying the TiDG.

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LIST OF ABBREVIATIONS

MCU	Modular Caustic-Side Solvent Extraction Unit
NGS	Next Generation Solvent
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-volatile organic analysis
TiDG	N,N',N"-tris(3,7-dimethyloctyl)guanidine
TOA	Tri-*n*-octylamine

1.0 Introduction

In late FY13, Savannah River Remediation (SRR) implemented the NGS flow sheet in the Modular Caustic-Side Solvent Extraction Unit (MCU). Facility personnel implemented the switch by adding a non-radioactive, NGS "cocktail" containing the new extractant (MaxCalix) and a new suppressor (N,N',N"-tris(3,7-dimethyloctyl)guanidine or TiDG) to the SHT heel. The resulting "blend" solvent ("NGS Blend solvent") is essentially NGS with residual amounts of BOBCalixC6 and TOA. Because the NGS contained a new suppressor (TiDG), Savannah River National Laboratory (SRNL) was tasked with developing an analytical method for measuring the suppressor concentration in routine SHT samples. SRNL developed a non-aqueous titration method as the primary method for determining TiDG concentrations in the SHT samples. The method screening and development work was documented in SRNL-STI-2013-00435.[1] Since implementation of NGS, SRNL has analyzed the monthly SHT samples using the non-aqueous titration method.[2] Because the NGS Blend solvent contains residual TOA from the solvent heel present when NGS was implemented, the titration method measures both bases (TiDG and TOA) by the detection of two equivalence points. Since the TOA component of the solvent is no longer replenished, it has been slowly decreasing in concentration. As the TOA concentration decreases, the two equivalence points identified in the titration have been coming closer together, making the differentiation of the two equivalence points more difficult. The May 2016 SHT sample (MCU-16-701, 702, 703) was the first sample where a TiDG equivalence point could not be resolved.[3] In order to determine the TiDG concentration in that sample the total base concentration was calculated using the second and final equivalence point (TOA) in the titration. The TOA concentration as determined by SVOA was then subtracted from the total base to give the TiDG concentration. This method has been used for all samples since MCU-16-701, 702, 703; however, it introduces additional uncertainty in the measurement especially due to the large method uncertainty (20%) reported for the SVOA. In samples where the TiDG equivalence point could be determined, results from both methods were reported. In order to improve the non-aqueous titration method so that it does not have to rely on the SVOA results, it was hypothesized that adding an additional spike of TOA to the sample prior to titration could separate the two equivalence points enough that the TiDG equivalence point could be resolved. This new method was implemented alongside the standard method starting with the February 2017 monthly sample, MCU-17-119, 120, 121. Details of the method and comparison of the results are discussed below.

2.0 Experimental Procedure

2.1 Non-Aqueous Titration SVOA Subtraction Method

The development of the non-aqueous titration method for measurement of TiDG concentrations in the SHT samples has been previously documented[1] and is implemented in SRNL procedure ITS-0199[4]. The TOA subtraction method requires no change to the typical titration procedure; however, it requires the additional analysis of the sample by SRNL Analytical Development using the SVOA method. Using this method, the TiDG concentration is determined by subtracting the TOA concentration as measured by SVOA from the total base concentration determined from the final equivalence point in the titration.

2.2 TOA Spike Method

Ten milliliters of a 0.15 M TOA spike solution was prepared by dissolving 0.53028 g of TOA in isopropanol and diluting to a total volume of 10 mL in a volumetric flask. This solution was then used to spike solvent samples during titration.

In a typical titration, 1.5 mL of solvent sample is dissolved in approximately 30 mL of isopropanol. For the spike method, 10 µL of the 0.15 M TOA solution is added to the dissolved sample. The sample is then titrated as normal using the "NGSBlend" method as described in ITS-0199.[4] This quantity of spike increases the TOA concentration in the sample by 1 mM.

When performing the TOA spike method in comparison to the original titration or SVOA subtraction method, the sample was split, and each titration was run in duplicate. When only a single type of titration is performed, the sample is typically run in triplicate.

2.3 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. Results from the experiments described in this report are documented in SRNL electronic notebooks E7518-00211 and I7563-00188.

3.0 Results and Discussion

As mentioned in the introduction, the non-aqueous titration method has been used for quantification of the TiDG concentration in the NGS since implementation in 2013. The non-aqueous titration method determines the concentration of both suppressors (bases) through the identification of two equivalence points during the titration. Typical titration curves for the scratch blend standard (laboratory blend prepared containing all six solvent components at the nominal concentrations at the time of NGS implementation) and a representative SHT sample from June 2014 are shown in Figure 3-1.[5] The first derivatives (dotted lines) are used to identify the inflection points of the titration curves (solid lines), which indicate an equivalence point in the titration. As can be seen in Figure 3-1, the scratch blend standard has two well-defined peaks in the first derivative curve corresponding to the TiDG (first) and TOA (second) equivalence points. In the SHT sample, the peak in the first derivative corresponding to the TiDG equivalence point is less well defined, but still represents a local maximum that can be identified, allowing for quantification of the TiDG.

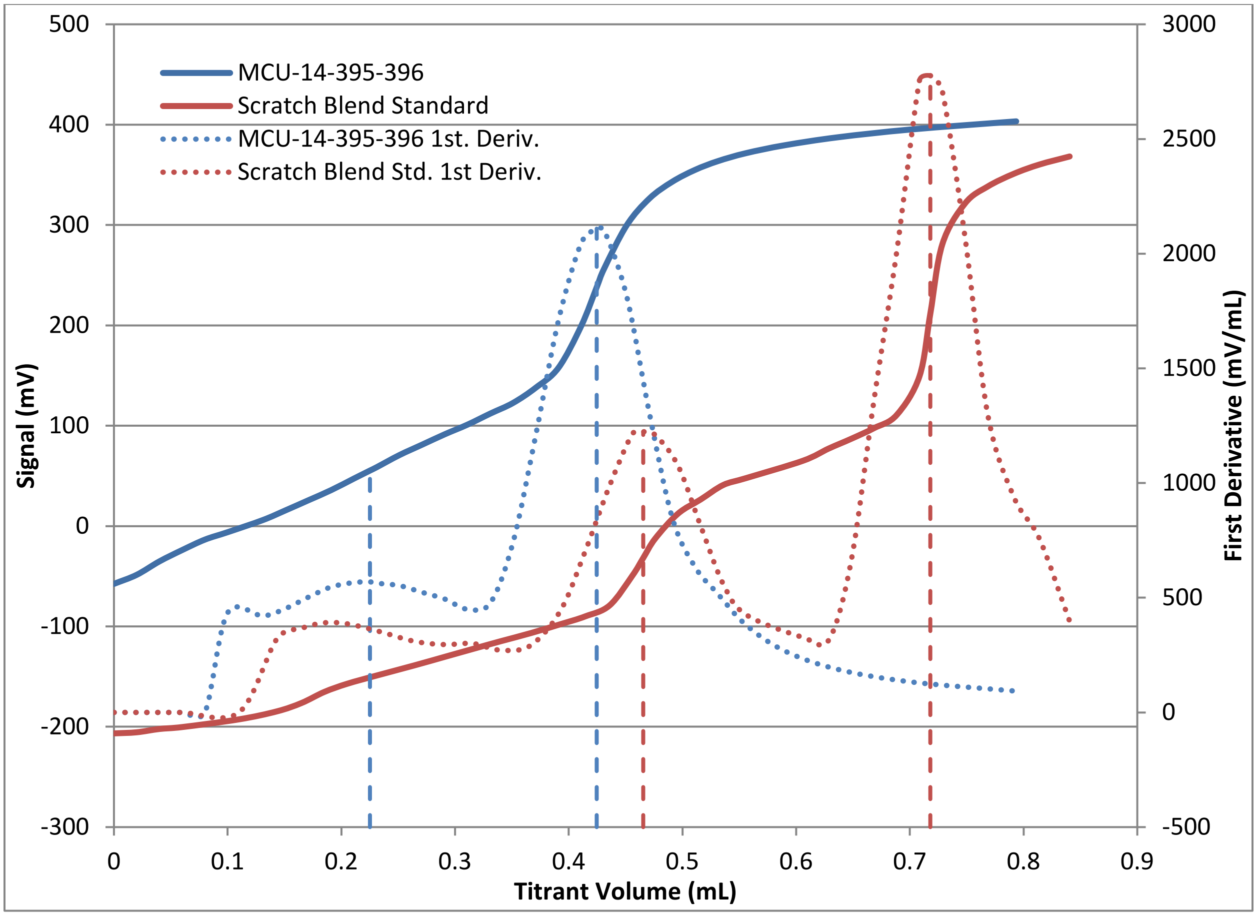

Figure 3-1. Titration curves (solid lines) and first derivatives of titration curves (dotted lines) of a representative SHT sample (blue) from June 2014[5] and a scratch blend standard sample (red). The vertical dashed lines represent the identified equivalence points.

The distance between the TiDG and TOA equivalence points corresponds to the TOA concentration, i.e., the additional titrant consumed by the TOA. Therefore, as the TOA concentration decreases over time, these two equivalence points become closer together and more difficult to resolve. Figure 3-2 shows a titration curve for a sample from May 2016 (MCU-16-701, 702, 703) where the TiDG equivalence point could not be identified from the data.[3] In order to determine the TiDG concentration in this sample the total amount of base in the sample was first calculated, using the volume of titrant required to reach the second and final equivalence point, which represents the sum of the TiDG and TOA. The TOA concentration in the sample was then determined by SVOA analysis, and that value was subtracted from the total base concentration to yield the concentration of TiDG in this sample. This is a viable method; however, it does introduce additional uncertainty, especially as the reported method uncertainty for SVOA is 20%. After the two samples from May 2016 (SHT-16-701, 702, 703 and SHT-16-710, 711, 712) the TiDG equivalence point became identifiable again for a period of time. During this time, TiDG concentrations obtained by both methods (direct titration and the SVOA subtraction method) were reported. This allowed for comparison of the two methods.

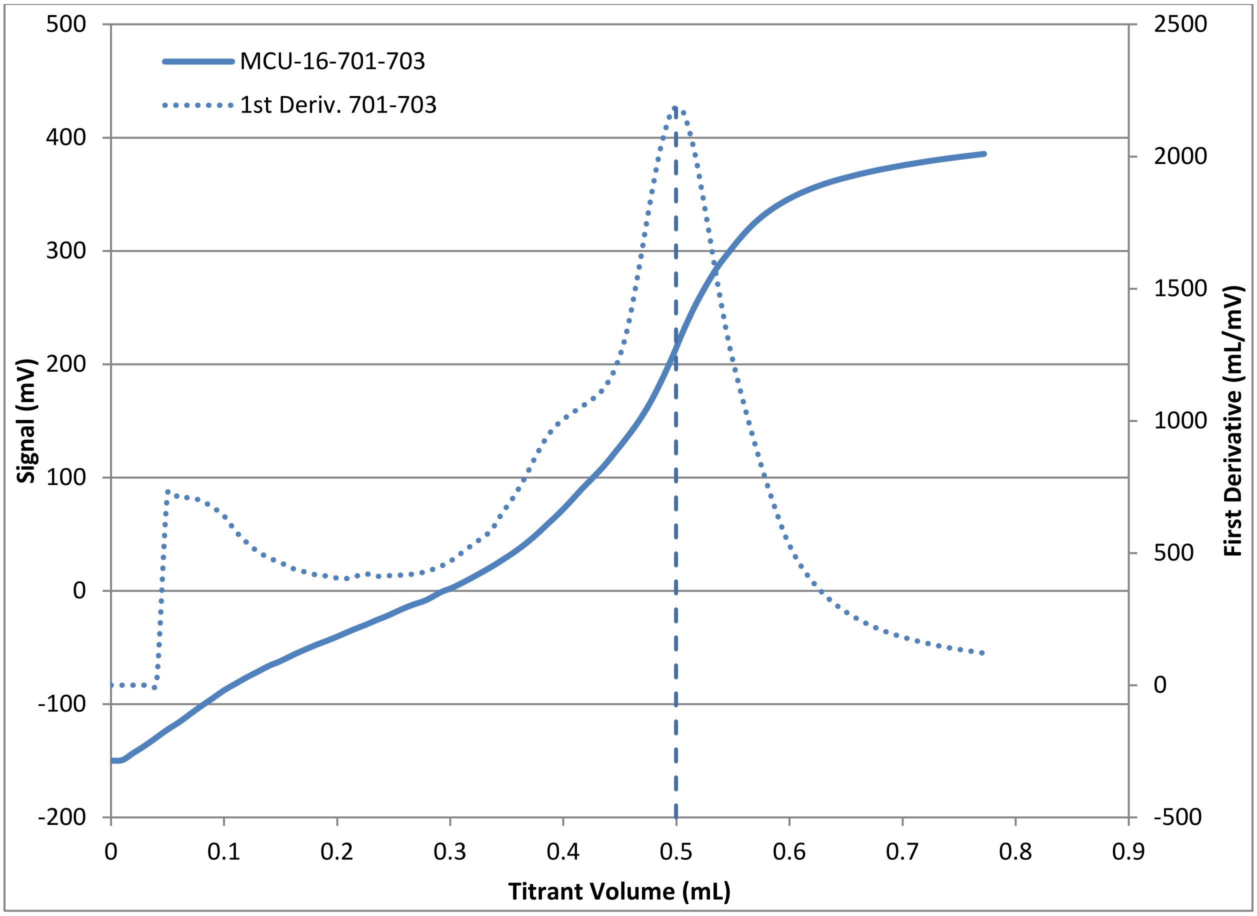

Figure 3-2. Titration curve (solid line) and first derivative of titration curve (dotted line) for the first SHT sample where the TiDG equivalence point could not be identified.[3] The vertical dashed line represents the single identified equivalence point (total base).

Table 3-1 shows a comparison of the TiDG concentrations determined by both direct measurement by titration, where an equivalence point for TiDG could be identified, and the SVOA subtraction method results. As can be seen from the data, there was reasonable agreement (< 15% difference) between the two methods when the TiDG concentration was greater than 1.5 mM; however, larger differences were seen when the TiDG concentration was below 1.5 mM. At low TiDG concentrations, the SVOA subtraction method gave higher values for the TiDG concentration. Since the TOA concentration is expected to either remain constant or decrease (since it is not being replenished), it appears the titration method may be biased low when the TiDG concentration is low, resulting in higher TOA concentrations as measured by titration.

Table 3-1. Comparison of [TiDG] measured directly by titration vs the TOA-SVOA Subtraction Method

Sample ID	Titration Data		SVOA		% Difference in [TiDG]
	[TiDG] (mM)	[TOA] (mM)	[TOA] (mM)	[TiDG] (mM) by subtraction	
MCU-16-934-936	2.107	0.461	0.452	2.132	1.2%
MCU-16-991-993	1.908	0.504	0.368	2.044	6.9%
MCU-16-1033-1035	1.655	0.629	0.396	1.888	13.2%
MCU-16-1247-1249	1.076	0.623	0.339	1.359	23.2%
MCU-16-1317-1319	0.705	0.712	0.452	0.964	31.0%
MCU-17-86-88	1.803	0.465	0.565	1.595	12.2%

In order to improve the titration method so that the TiDG equivalence point can be determined directly, a method was developed that involved the addition of a 1 mM spike of TOA to the sample to further separate the two equivalence points. As described above, a 0.15 M solution of TOA was prepared in isopropanol. This solution was then used to spike the titration samples. Samples were spiked with a 10-µL aliquot, which represents 1 mM TOA in the standard 1.5-mL sample size. The method was first demonstrated using two batches of scratch blend standard that had been converted to the free base form at different times, and therefore, had expected different TiDG concentrations due to aging in the deprotonated form. Note that unused scratch blend standard does not experience this aging, as it is stored with TiDG in the protonated form. Both samples were run with and without the additional TOA spike, and results are shown in Table 3-2. As can be seen from the data, the agreement was excellent between the TiDG measured with and without the spike of additional TOA. After subtracting out the 1 mM TOA spike, the agreement in the TOA concentration between the two measurements was also excellent.

Table 3-2. Comparison of Data with TOA Spike Method

Sample ID	Without Spike (mM)		With 1 mM TOA Spike (mM)			% Difference	
	[TiDG]	[TOA]	[TiDG]	[TOA]	[TOA] minus spike	TiDG	TOA
Recent Scratch Blend	2.397	1.881	2.311	2.819	1.819	3.6%	3.4%
Aged Scratch Blend	1.553	2.112	1.499	3.093	2.093	3.5%	0.9%

This method was then tested on actual MCU SHT monthly samples. For these samples, titrations were run both with and without the TOA spike. A representative titration curve with and without the TOA spike is shown in Figure 3-3. In all samples tested, the TiDG equivalence point could not be identified without the TOA spike. The total base amounts from the runs without the TOA spike were used to determine the TiDG concentration by the SVOA subtraction method. A comparison of those results to those obtained using the TOA spike method is provided in Table 3-3. The TiDG concentrations determined by the two methods agree well, with percent differences ranging from 1 to 13.6%. The TOA concentrations were less consistent with percent differences ranging from 34 to 66%. This is attributed to the potential error in pipetting the small quantity (10 µL) of TOA spike solution into the sample. The exact amount of TOA added will have no impact on the TiDG concentration determined by this method; however, since the 1 mM spike must be subtracted back out from the measured TOA concentration, any deviation from the 1 mM amount will cause a significant error in the calculated TOA concentration. An alternate method to calculate the TOA from titration is to perform two titrations, one with and one without the TOA spike. The titration without the TOA spike will give the total base concentration, and the titration with the TOA spike will provide the TiDG concentration. The TiDG concentration can then be subtracted from the total base to give the TOA concentration. This method was demonstrated with the samples tested for the TOA spike method. The results are shown in Table 3-4, and in all cases, the TOA concentrations calculated by this method were much closer to the TOA concentrations determined by SVOA. This further confirms that the TOA concentration measured by the TOA spike method is likely impacted by uncertainty in the TOA spike measurement.

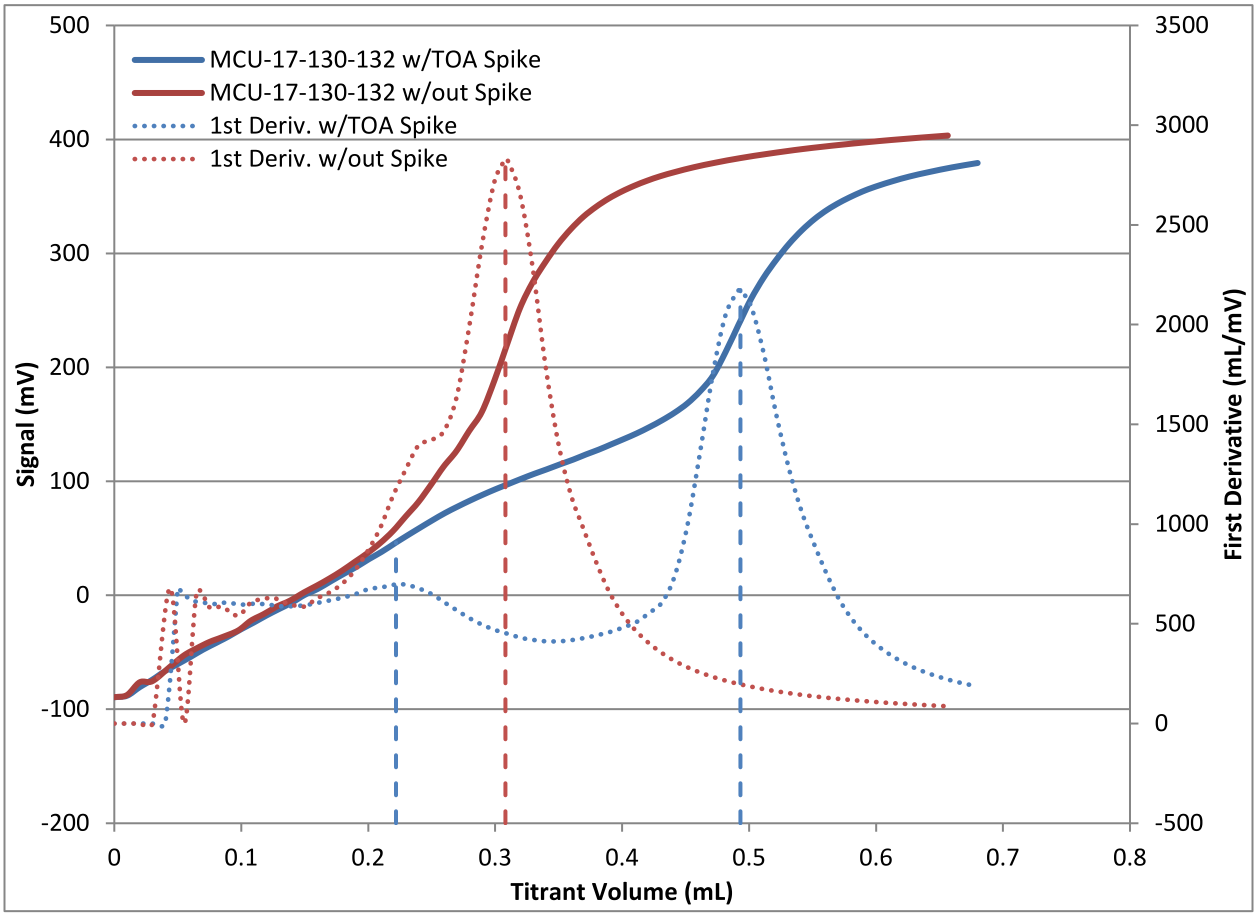

Figure 3-3. Titration of MCU-17-130-132 with (blue) and without (red) a 1 mM TOA spike addition.

Table 3-3. Comparison of SVOA Subtraction Method to TOA Spike Method

Sample ID	SVOA Subtraction Method		TOA Spike Method		% Difference	
	[TOA] (mM)	[TiDG] (mM)	[TOA] (mM)	[TiDG] (mM)	TOA	TiDG
MCU-17-119-121	0.537	1.330	0.347	1.422	43.0%	6.7%
MCU-17-122-124	0.368	1.637	0.729	1.428	65.8%	13.6%
MCU-17-130-132	0.537	1.379	0.758	1.393	34.1%	1.0%

Table 3-4. Comparison of TOA Concentration Determined by SVOA and Titration

Sample ID	SVOA [TOA] (mM)	Titration TOA (mM)*	% Difference
MCU-17-119-121	0.537	0.446	18.5%
MCU-17-122-124	0.368	0.576	44.1%
MCU-17-130-132	0.537	0.524	2.45%

*This value was determined through two titrations, one without the TOA spike to determine the [total base], followed by one with the TOA spike to determine the [TiDG]. The [TiDG] was then subtracted from the [total base] to determine the [TOA].

4.0 Conclusions

Due to the difficulty of resolving the TiDG equivalence point in recent MCU SHT samples due to the relatively low concentration of TOA, a new method has been developed. This method involves adding a spike of TOA to the SHT sample, then titrating following the normal titration procedure. The additional TOA moves the TOA equivalence point further out, thereby increasing the separation between the two equivalence points, allowing for identification of the TiDG equivalence point. Due to the error introduced in adding additional TOA to the sample, this method is not ideal for quantification of TOA in the SHT samples. However, this can be overcome by performing two titrations, one without the TOA spike to determine the total base concentration, and one with the TOA spike to determine the TiDG concentration. The TiDG concentration can then be subtracted from the total base to determine the TOA concentration.

5.0 Recommendations

It is recommended that the titration procedure for quantification of TiDG in the MCU SHT samples be modified to include the TOA spike addition. Based on the data presented here, this method appears viable, and it is recommended to use this method as the primary method for TiDG quantification. In addition, this method, in combination with the original titration method without the TOA spike, can be used to determine the TOA concentration by subtraction if desired.

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[2] T. B. Peters, F. F. Fondeur, K. M. L. Taylor-Pashow, “Results from the Salt Disposition Project (SPD) Next Generation Solvent (NGS) Demonstration Plan” SRNL-STI-2014-00101, Rev. 0, April 2014.

[3] F. F. Fondeur and D. H. Jones, “Solvent Hold Tank Sample Results for MCU-16-701-702-703: May 2016 Monthly Sample and MCU-16-710-711-712: May 2016 Superwashed Sample” SRNL-STI-2016-00419, Rev. 0, August 2016.

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[5] F. F. Fondeur and K. M. L. Taylor-Pashow, “Solvent Hold Tank Sample Results for MCU-14-395-396 and MCU-14-497/498: June and July 2014 Monthly Samples” SRNL-STI-2014-00417, Rev. 0, September 2014.

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