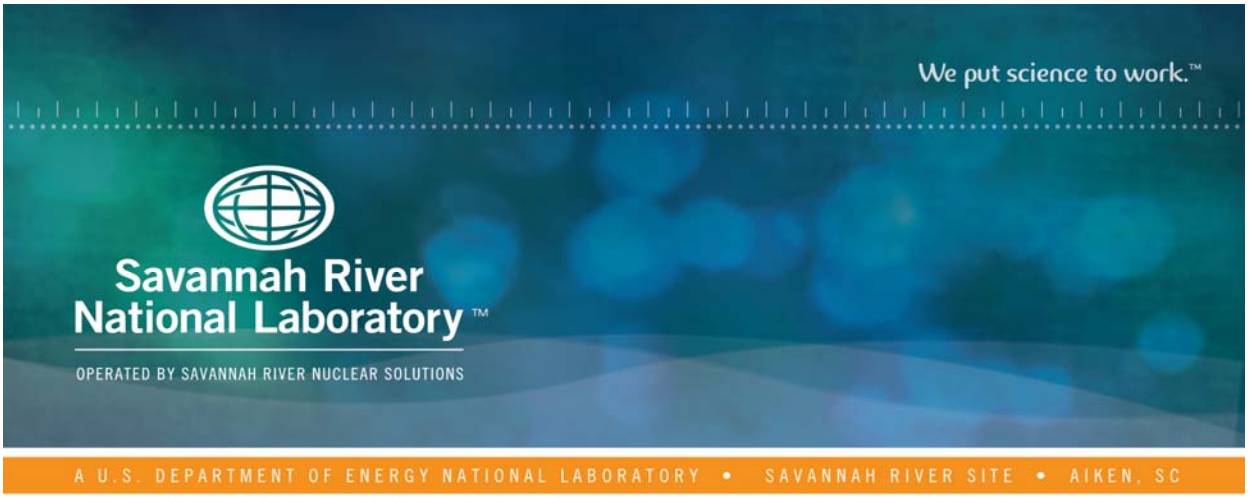

Development of Analytical Methods for Determining Suppressor Concentration in the MCU Next Generation Solvent (NGS)

K. M. L. Taylor-Pashow
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Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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NGS Implementation Project

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) was tasked with identifying and developing at least one, but preferably two methods for quantifying the suppressor in the Next Generation Solvent (NGS) system. The suppressor is a guanidine derivative, N,N',N''-tris(3,7-dimethyloctyl)guanidine (TiDG). A list of 10 possible methods was generated, and screening experiments were performed for 8 of the 10 methods. After completion of the screening experiments, the non-aqueous acid-base titration was determined to be the most promising, and was selected for further development as the primary method. ^{1}H NMR also showed promising results from the screening experiments, and this method was selected for further development as the secondary method. Other methods, including ^{36}Cl radiocounting and ion chromatography, also showed promise; however, due to the similarity to the primary method (titration) and the inability to differentiate between TiDG and TOA (tri-*n*-ocytlamine) in the blended solvent, ^{1}H NMR was selected over these methods.

Analysis of radioactive samples obtained from real waste ESS (extraction, scrub, strip) testing using the titration method showed good results. Based on these results, the titration method was selected as the method of choice for TiDG measurement. ^{1}H NMR has been selected as the secondary (back-up) method, and additional work is planned to further develop this method and to verify the method using radioactive samples. Procedures for analyzing radioactive samples of both pure NGS and blended solvent were developed and issued for the both methods.

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LIST OF ABBREVIATIONS

CI	Confidence interval
CSSX	Caustic-Side Solvent Extraction
ESS	Extraction, Scrub, Strip
FBF	Find-by-formula
FTIR	Fourier transform infrared spectroscopy
HPLC	High performance liquid chromatography
IC	Ion chromatography
LC-MS	Liquid Chromatography – Mass spectrometry
MCU	Modular Caustic-Side Solvent Extraction Unit
NGS	Next Generation Solvent
NMR	Nuclear Magnetic Resonance
RI	Refractive index
RSD	Relative standard deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-volatile organic analysis
TFA	trifluoroacetic acid
THAM	tris(hydroxymethyl)aminomethane
TiDG	N,N',N''-tris(3,7-dimethyloctyl)guanidine
TOA	Tri-*n*-ocytlamine
TOF-MS	Time of Flight Mass Spectrometer
TMS	tetramethylsilane
UV	Ultraviolet

1.0 Introduction

Savannah River Remediation (SRR) is preparing to implement the NGS in the Modular Caustic-Side Solvent Extraction (CSSX) Unit (MCU). The NGS system contains a guanidine derivative (TiDG) as the suppressor, and there is currently no established analytical method for quantifying this component of the NGS. Thus, SRNL was tasked with identifying and subsequently qualifying at least one, but preferably two methods for quantifying TiDG in solvent samples taken during MCU operations. When implemented the NGS will be added to the current inventory of MCU solvent creating a blend with the expected composition shown in Table 1-3. When the solvent needs replenishing, it will be replenished with pure NGS, and eventually all of the current MCU solvent will be depleted. Therefore, the analytical methods need to be able to determine the TiDG concentration in both pure NGS and in the blended solvent.

This work was performed at the request of SRR Engineering[1] and was controlled by a Task Technical and Quality Assurance Plan (TTQAP).[2]

Table 1-1. Composition of Current MCU Solvent

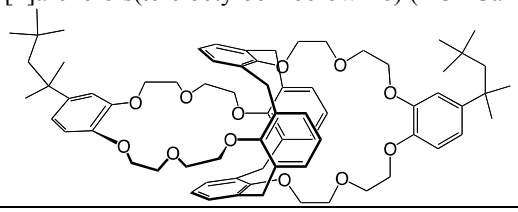
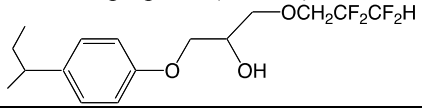
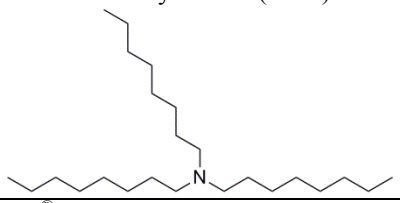
Component	Name/Structure	Concentration
Extractant	Calix[4]arene-bis(*tert*-octylbenzocrown-6) (BOBCalixC6) 	7 mM
Modifier	1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB) 	0.75 M
Suppressor	Tri-*n*-ocytlamine (TOA) 	3 mM
Diluent	Isopar®-L – C_{12}-isoparaffinic hydrocarbon	Balance

Table 1-2. Composition of NGS

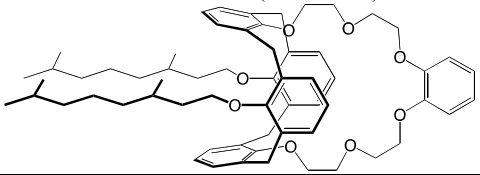
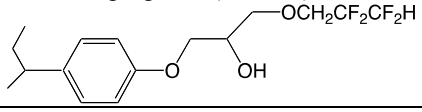
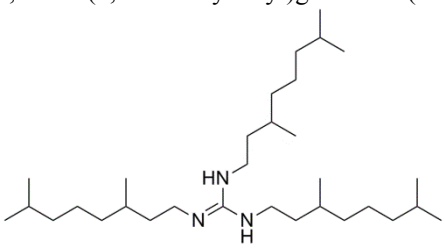
Component	Name/Structure	Concentration
Extractant	1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6 (MaxCalix) 	50 mM
Modifier	1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB) 	0.5 M
Suppressor	N,N',N''-tris(3,7-dimethyloctyl)guanidine (TiDG) 	3 mM
Diluent	Isopar®-L – C_{12}-isoparaffinic hydrocarbon	Balance

Table 1-3. Expected Composition of the Blended Solvent

Component	Concentration
BOBCalixC6	3.5 mM
MaxCalix	46.5 mM
Cs-7B	0.5 M
TOA	1.5 mM
TiDG	3 mM
Isopar®-L	Balance

An initial list of possible methods to be explored was developed and included:

- Acid-base (non-aqueous) titration
- Nuclear Magnetic Resonance (NMR)
  - ^{1}H, ^{13}C, and ^{14}N
- High performance liquid chromatography (HPLC)
  - Use of a refractive index (RI) detector
- Fourier transform infrared spectroscopy (FTIR)
- Raman spectroscopy
- ^{36}Cl radiocounting
- Ion chromatography (IC) for Cl^-
- Liquid Chromatography – Mass spectrometry (LC-MS)
- Treatment with an acid dye followed by spectroscopy
- Kjeldahl method

Early in the discussions, the acid dye and Kjeldahl methods were identified as having the lowest likelihood of success, and were therefore placed on hold while the screening experiments for the

other methods were conducted. Details of the screening experiments performed for the other methods are provided in Section 2.

1.1 Quality Assurance

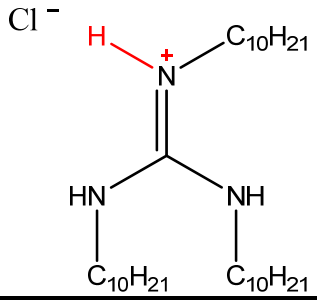
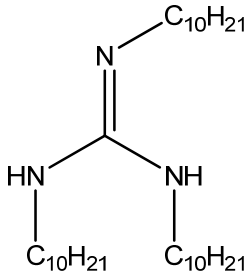
Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

2.0 Method Screening

2.1 Acid-Base (non-aqueous) Titration

Mettler Toledo offers an automatic titration system (model T50) that can be used for non-aqueous titrations when equipped with a DGi116-Solvent pH electrode. The DGi116 electrode is a glass pH electrode that utilizes 1 M LiOH in ethanol as the reference electrolyte. After discussions with the vendor, they agreed to come and demonstrate the equipment to determine if this would be a viable method for measuring TiDG concentration in the NGS. The vendor recommended using a solution of perchloric acid in acetic acid as the titrant solution, and dissolving the sample of NGS in an 80:20 mixture of acetic acid : acetic anhydride. The acetic anhydride is included to react with any residual water that may be present in the sample to ensure an anhydrous system. The NGS solvent is not soluble in the acetic acid : acetic anhydride mixture, and therefore toluene was added as a co-solvent. In preparation for the vendor demonstration several samples of NGS were prepared with varying TiDG concentrations. Since the TiDG is supplied as the HCl salt (guanidinium form), samples of the prepared solvents were also converted to the free base form by contacting the samples with 2 M NaOH. See Table 2-1 for structures of these two forms of TiDG. Initial attempts at titration of these samples (both as-prepared and the free base form) using the acetic acid system proved unsuccessful. The results varied greatly and were not consistent with the expected TiDG concentrations of the samples.

Table 2-1. Guanidinium versus Free Base forms of TiDG.

Guanidinium Form	Free Base Form
	

An alternate titrant/solvent system was then evaluated. This system utilizes a solution of HCl in isopropanol as the titrant with the samples being dissolved in isopropanol. Typical sample sizes are 2-4 grams of NGS solvent dissolved in 30 mL of isopropanol. Initial results from testing with this titrant/solvent system indicated that the as-prepared form (guanidinium) cannot be titrated, and that the TiDG must be in the free base form to allow for titration. Titrations of the free base form that had been prepared by contacting the solvent with 2 M NaOH resulted in TiDG concentrations higher than expected. The titration curves for these samples indicted the possibility of 2 equivalence points, and the zero TiDG control also resulted in the detection of an equivalence point. This additional equivalence point may be indicative of residual NaOH from the conversion to the free base form that is titrated. Based on these results a solvent washing

protocol was developed to convert samples to the free base form, and also remove any residual NaOH prior to titration. The washing protocol developed involves sequential contacts of the solvent with equal volumes of 0.3 M NaOH followed by water. The water washes are repeated until the pH of the wash water is ≤7, which is typically reached after the second wash.

To evaluate the working range of the method a series of NGS solvent samples was prepared with TiDG concentrations of 1, 2, 2.5, 3, 3.5, 4, and 5 mM. The intermediate concentrations were prepared by mixing aliquots of 1 and 5 mM TiDG solvents. A portion of each solvent was then converted to the free base form and washed following the protocol described in the preceding paragraph. Aliquots of these samples (both as-prepared and the free base forms) were also provided for analysis by the NMR and ^{36}Cl radiocounting methods. Each of the samples was then titrated in triplicate with the sample size being varied from 2 – 4 grams of sample dissolved in 30 mL of isopropanol. The measured TiDG concentrations were typically within 5% of the expected value (with 1 exception). There also appeared to be no effect from sample size, indicating that a sample size of 2 g is sufficient. The results are provided below in both tabular and graphical forms. Error bars representing two standard deviations in the triplicate measurements are present in Figure 2-1; however, in most cases they are obscured by the data points.

Table 2-2. Results of Non-Aqueous Titration of 1-5 mM TiDG NGS Samples.

Expected [TiDG] (mM)	Sample Size (g)	Sample Vol (mL)	mL 0.01 M titrant	mmol titrant	mmol guanidine	Calculated [TiDG] mM	% Difference
1	4.009	4.806	0.506	0.0051	0.0051	1.05	5.28%
1	3.007	3.606	0.373	0.0037	0.0037	1.03	3.47%
1	2.014	2.415	0.245	0.0025	0.0025	1.02	1.64%
2	4.006	4.803	0.972	0.0097	0.0097	2.02	1.14%
2	3.025	3.627	0.731	0.0073	0.0073	2.02	0.80%
2	2.016	2.418	0.493	0.0049	0.0049	2.04	2.00%
2.5	4.012	4.811	1.208	0.0121	0.0121	2.51	0.45%
2.5	3.009	3.608	0.906	0.0091	0.0091	2.51	0.47%
2.5	2.017	2.418	0.616	0.0062	0.0062	2.55	1.87%
3	4.003	4.800	1.468	0.0147	0.0147	3.06	1.97%
3	3.005	3.603	1.096	0.0110	0.0110	3.04	1.36%
3	2.000	2.398	0.737	0.0074	0.0074	3.07	2.42%
3.5	4.006	4.803	1.700	0.0170	0.0170	3.54	1.10%
3.5	3.000	3.597	1.283	0.0128	0.0128	3.57	1.93%
3.5	2.013	2.413	0.866	0.0087	0.0087	3.59	2.56%
4	4.010	4.808	1.963	0.0196	0.0196	4.08	2.04%
4	3.011	3.610	1.482	0.0148	0.0148	4.11	2.65%
4	2.015	2.416	0.998	0.0100	0.0100	4.13	3.20%
5	4.001	4.797	2.480	0.0248	0.0248	5.17	3.38%
5	3.010	3.609	1.866	0.0187	0.0187	5.17	3.38%
5	2.007	2.407	1.262	0.0126	0.0126	5.24	4.88%

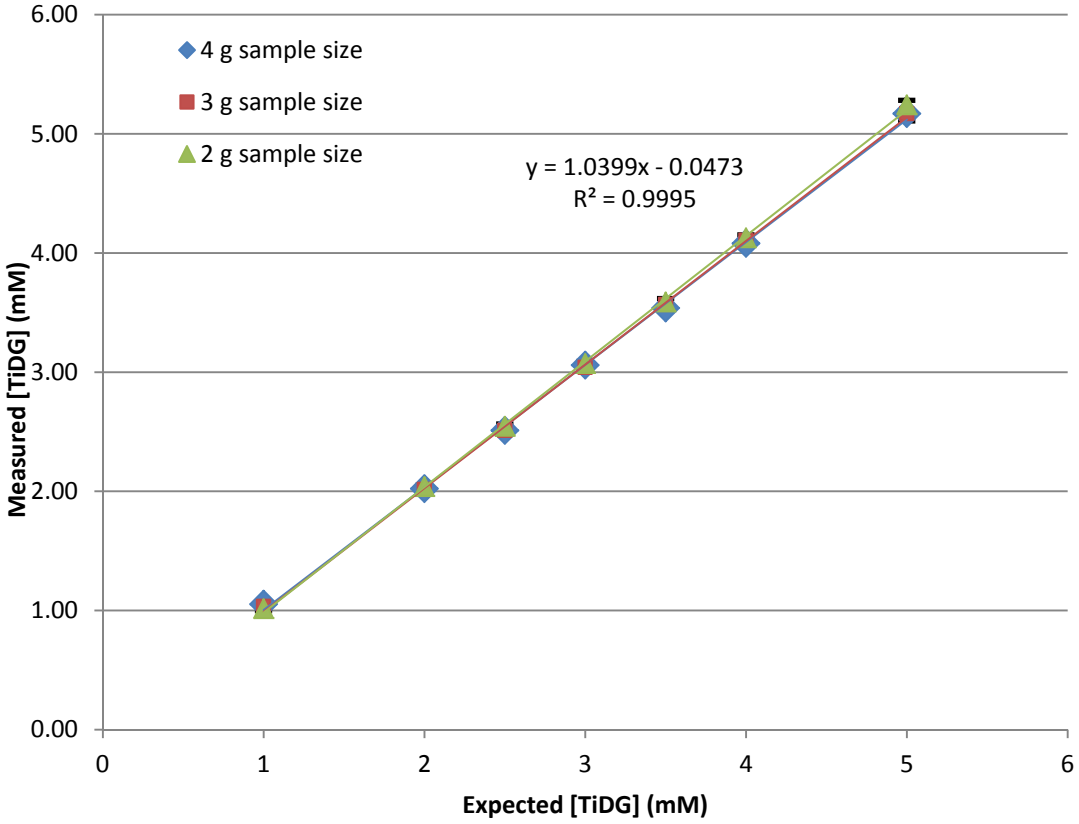


Figure 2-1. Comparison of expected versus measured TiDG concentration in NGS samples.

To complete the method screening a sample of blended solvent was prepared and analyzed using this method. The solvent was prepared with the nominal concentrations expected in the blended solvent, i.e., 3 mM TiDG and 1.5 mM TOA. The blend sample was treated with the same washing protocol developed for the pure NGS samples, to ensure the TiDG was in the free base form. Titration of the sample was then performed in triplicate. Two equivalence points were observed as expected, the first for the TiDG and the second for the TOA. The measured TiDG concentrations for this sample were within 5% of the expected value, while the TOA concentrations measured higher than expected. The results are provided in Table 2-3. The presence of TOA makes the equivalence point for TiDG less defined, but still detectable (Figure 2-2). Although the equivalence point for the TiDG is not as defined in the presence of TOA, the uncertainty in the measurement appears to be consistent with that of pure NGS samples; however, the uncertainty in the TOA concentration is much greater. This method is acceptable for quantification of TiDG in the blended solvent, and both TiDG and TOA in pure solvents (NGS and the current solvent, respectively), but not for TOA in the blended solvent. In order to better define the uncertainty for TiDG measurement in the blended solvent, additional experiments should be performed with a series of blended solvent samples prepared with varying TiDG concentrations, as was done for the pure NGS samples.

Table 2-3. Results from analysis of a sample of blended NGS.

Sample Mass (g)	1st Eq. Pt. – Vol. of Titrant (mL)	2nd Eq. Pt. – Total Vol. of Titrant (mL)	Calculated [TiDG] (mM)	% Difference	Calculated [TOA] (mM)	% Difference
2.0783	0.7135	1.2570	2.86	-4.56%	2.18	45.4%
2.0103	0.7555	1.1835	3.13	4.48%	1.78	18.4%
2.0148	0.6985	1.1535	2.89	-3.62%	1.88	25.6%

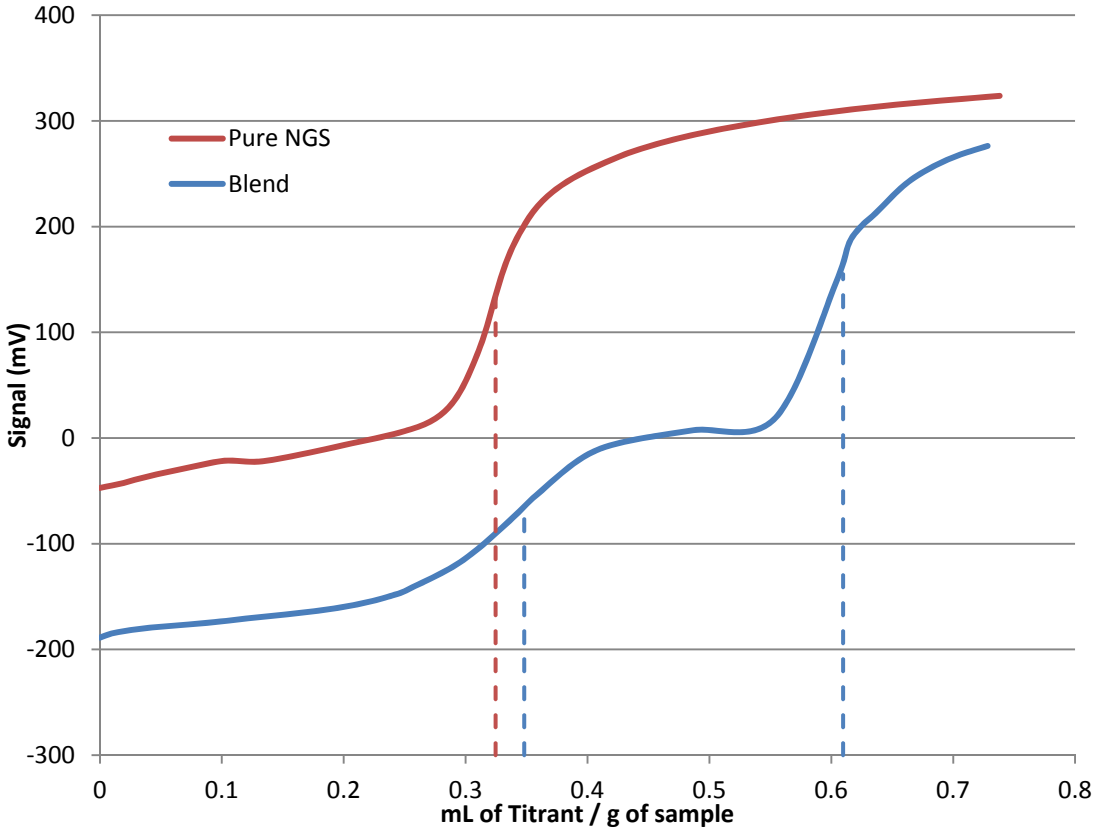


Figure 2-2. Typical titration curves for a sample of pure NGS and a sample of blended solvent. The vertical lines indicate the location of the detected equivalence points. For the blend sample, the first equivalence point is for the TiDG, and the second for the TOA.

2.2 Nuclear Magnetic Resonance (NMR)

The TiDG molecule contains atoms such as carbon, hydrogen, and nitrogen that have nonzero spin angular momentum (nuclear). That makes these atoms magnetic and the quantized nature of their magnetic energy (energy that is proportional to the magnetic field applied to the molecule and their molecular environment) permits the detection of residual magnetism emitted by these atoms after they are irradiated with radio waves.

The radio wave absorbed by these atoms is influenced by the net shielding (diamagnetic and paramagnetic) effect of their orbiting electrons. Electrons are involved in the bonding of the individual atoms to make up the molecule (covalent, ionic, and metallic bonding). Molecular structure is defined by the electron circulation around the atoms. Thus, the molecular structure of substances can be determined with NMR spectroscopy. The C-NH, C=N-R, and C=NH-R (R=alkyl) atom fragments of the TiDG are unique to the suppressor in the NGS solvent system

and these fragments can be observed in the ^{1}H, ^{13}C, and ^{14}N NMR spectra if the sensitivity is sufficient.

2.2.1 *^{1}H NMR*

For the ^{1}H NMR experiments, the equipment (spectrometer and probe) were set at the highest frequency (300.13 MHz). Initial screening experiments indicated that due to the low concentration of suppressor in the samples, the samples needed to be run neat, as opposed to being diluted in a deuterated solvent. A set of NGS samples prepared with varying TiDG concentrations from 1-5 mM were analyzed on the NMR. Samples in both the as-prepared (guanidinium form) and the free base form were analyzed (See Table 2-1 for structures). From these experiments it was determined that quantification using the guanidinium proton would provide the best results. A method was developed to protonate any samples received not in the guanidinium form by simply contacting the sample with an equal volume of 10 mM HCl.

For quantification, the collected data was baseline corrected (linearly) and the peak associated with the C=NH-R proton (located at 4.8 ppm) was integrated. Representative spectra are shown in Figure 2-3. Although a relatively minor peak in the spectrum, the peak area as a function of TiDG concentrations appears linear over the range studied (See Figure 2-4). However, the noise in the method (derived from sample preparation, collection, and data treatment) was sufficient to reduce the square of the correlation coefficient (r^2) to 0.97. For a given analyte range, the recommended r^2 value between measurement and the actual analyte concentration should be at least 0.99. For the TiDG concentration range studied, the ^{1}H NMR signal strength (peak area and height) was insufficient to meet the statistical criteria. To estimate the uncertainty with the ^{1}H NMR data, the individual 95% confidence curve is used as shown in Figure 2-4.

The method's linearity and prediction must be corroborated with radioactive samples where degraded material and interferences from foreign substances are likely. In addition to quantifying the suppressor concentration the ^{1}H NMR can also quantify, with more certainty, the extractant, modifier, and diluent.

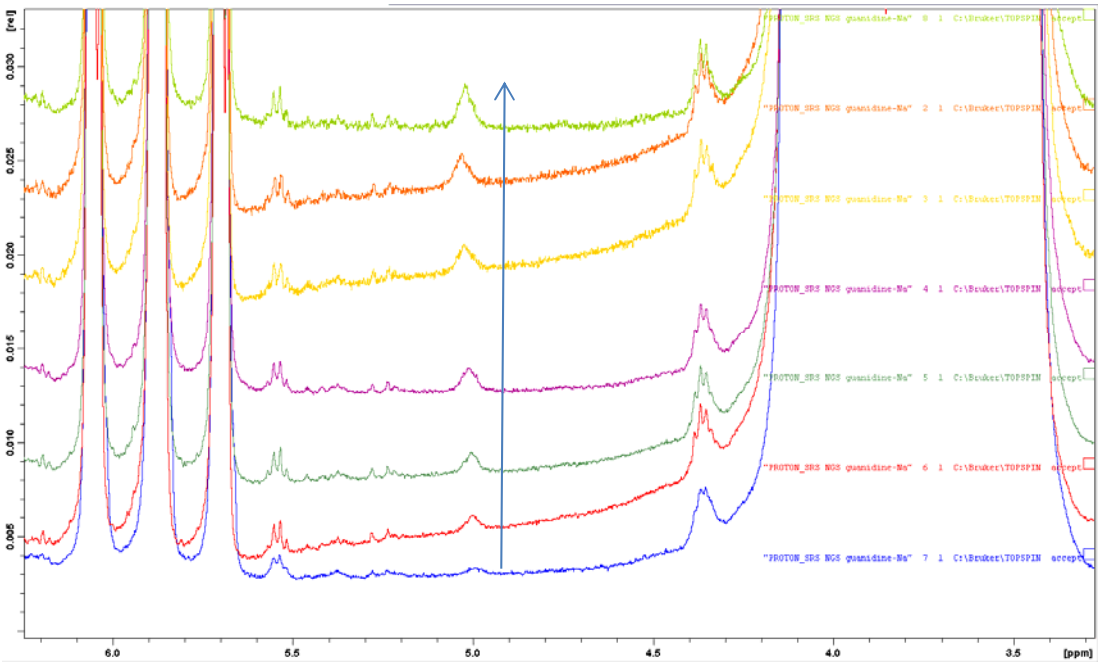


Figure 2-3. ^{1}H NMR spectra of NGS samples with varying concentrations of TiDG. The arrow indicates the location of the C=NH-R peak and also indicates the direction of increasing TiDG concentration from 1 mM to 5 mM. Spectra are calibrated relative to TMS.

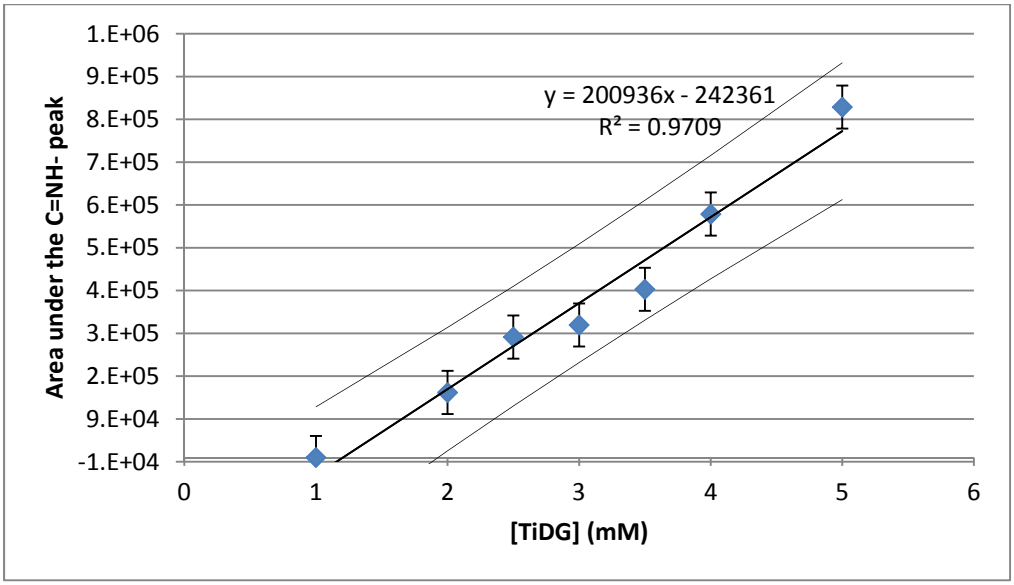


Figure 2-4. Area under the C=NH-R peak as a function of TiDG concentration in NGS. The error bars represent one sigma uncertainty. The upper and lower lines are the 95% individual confidence interval (CI). The CI interval provides the uncertainty associated with the ^{1}H NMR data.

2.2.2 *^{13}C NMR*

The same samples evaluated using ^{1}H NMR spectroscopy were also analyzed using ^{13}C NMR. The ^{13}C NMR method may detect the C=N peak expected to appear between 157 to 160 ppm (or 13,849 to 14,073 Hertz). As can be seen in Figure 2-5, the spectrum of nominal NGS and the spectrum of NGS without TiDG are similar and no new peak can be assigned to the TiDG. Therefore, it was concluded that the TiDG concentration is below the limit of detection (LOD) of the ^{13}C NMR method.

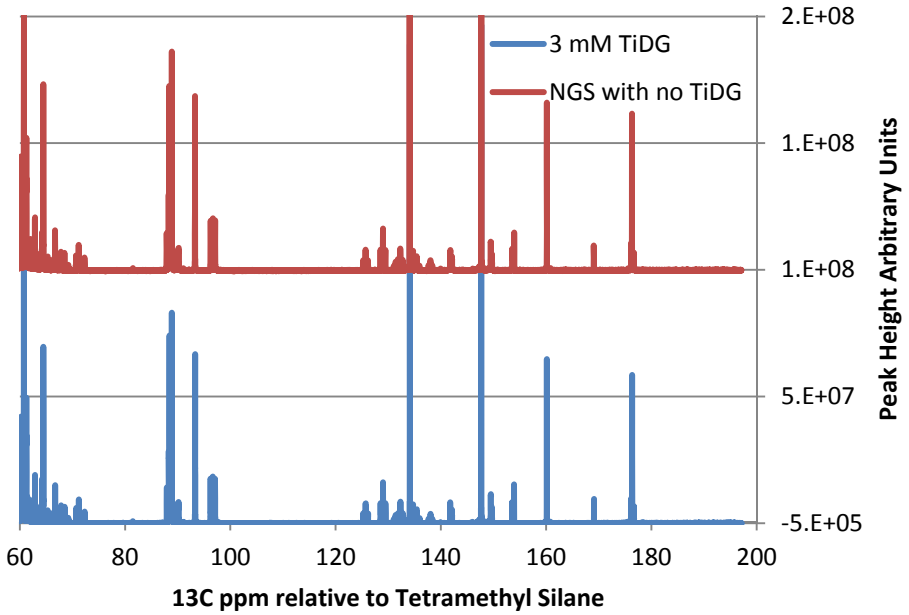


Figure 2-5. The ^{13}C NMR spectra of NGS without (red) and with 3 mM (blue) TiDG. There is no visible peak in the spectra associated with the TiDG.

2.2.3 *^{14}N NMR*

The samples analyzed by ^{1}H NMR were also analyzed by ^{14}N NMR. Only one peak was observed in the sample containing 5 mM TiDG (out of two magnetically different nitrogen atoms). No peaks were observed in the samples containing less than 5 mM TiDG. Therefore, it was concluded that this method is not viable for the TiDG concentration range of interest (below 5 mM).

2.3 High Performance Liquid Chromatography (HPLC)

The guanidine moiety of TiDG contains a single C=N bond that interacts with the short wavelength region (190 nm – 200 nm) of the ultraviolet (UV) spectrum.[3] Most common organic mobile phases that would be used for the separation of TiDG from the other components absorb in this region restricting the use of a UV detector for analysis. A RI detector was installed in place of a UV detector on the HPLC and a series of TiDG samples were examined. Separation and quantitation was attempted using normal phase and reversed-phase chromatography. Neither method provided a strong TiDG response in the 1-5 mM range for quantitation.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was performed on several samples containing varying concentrations of the TiDG. Figure 2-6 shows the spectra obtained after subtracting the spectrum of a sample

containing no TiDG. There is some signal observed for the TiDG near 1600 cm^{-1}; however, the signal to noise ratio is not sufficient to allow for quantification of TiDG at these levels (i.e., 1 – 5 mM).

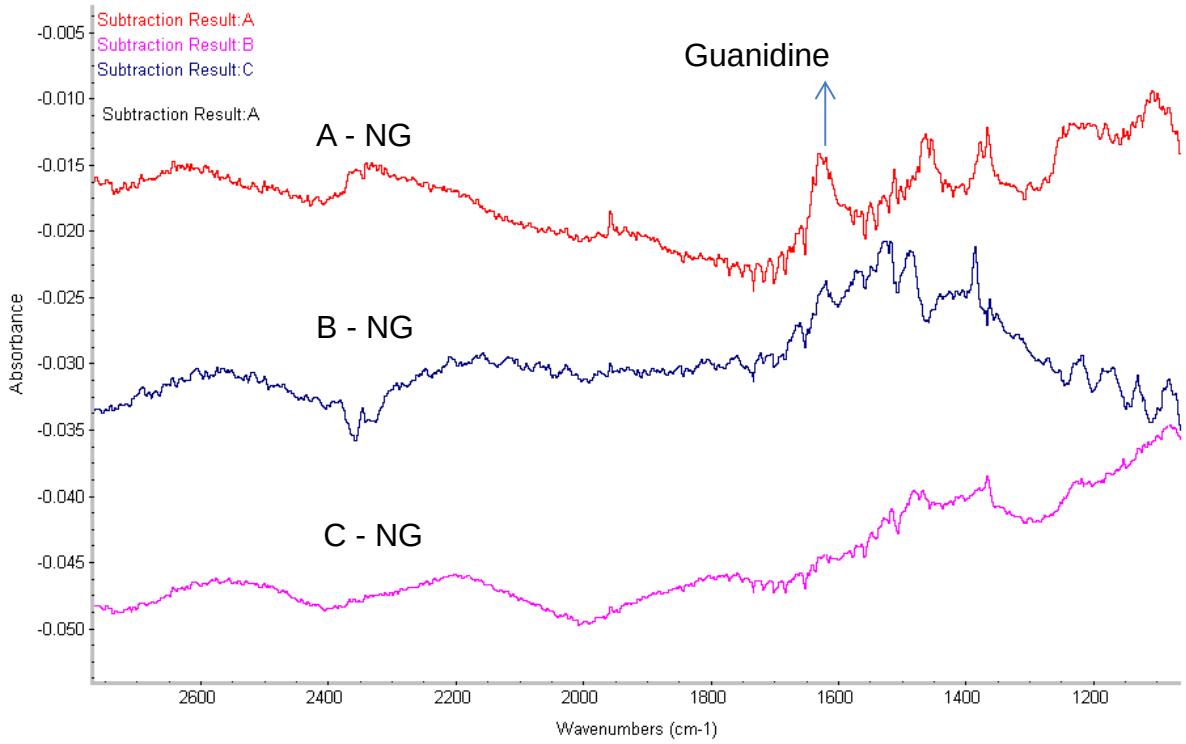


Figure 2-6. FTIR spectra of samples A – C containing varying amounts of TiDG after subtraction of the spectrum of a sample of NGS containing no TiDG.

2.5 Raman Spectroscopy

Single scattering Raman spectroscopy was conducted on several samples of NGS with varying concentrations of TiDG (0 to 5 mM). The results from this test revealed no difference in the spectral information obtained from the sample with no TiDG and those samples containing TiDG. The expected emission peaks due to the C-N stretch in the 1020 to 1250 cm^{-1} region and due to the C-N-H wagging in the 720-785 cm^{-1} region were not observed above the method's noise.

An initial scoping experiment was also performed using silver nanoparticles to perform surface enhanced Raman spectroscopy (SERS); however the method has yet to detect TiDG in NGS. The silver nanoparticles are prepared with a surfactant on the surface that serves to stabilize the particles against aggregation. In order to obtain the SERS enhancement the TiDG must displace the surfactant present on the surface of the particles. Additional research could be performed in this area to find a surface stabilizing agent that is more labile, and could be displaced by the TiDG molecule. A more promising area is to precipitate silver nanoparticles in NGS-alcohol blends where the TiDG molecules can selectively interact with and cap the silver nanoparticles. This method is still in the development stage.

2.6 ^{36}Cl Radiocounting

Samples of NGS prepared with varying TiDG concentrations from 0 – 5 mM were analyzed using this method. Samples of the solvent were contacted with an equal volume of 0.01 M HCl that had been spiked with ^{36}Cl. The samples were contacted by vortexing for 30 seconds, standing for 5 minutes, and then vortexing for an additional 30 seconds. The samples were then left standing overnight to allow the aqueous and organic phases to separate. Samples of both the organic and aqueous phases were then added to Ultima Gold™ AB scintillation cocktail and were analyzed by liquid scintillation analysis to determine the distribution of ^{36}Cl. A sample of known TiDG concentration was then used as a reference for correlating the radiocounting results to TiDG concentration. The ^{36}Cl counts will be proportional to the TiDG concentration. Each sample was analyzed in triplicate. The results from these experiments are shown in Table 2-4.

Table 2-4. Results from ^{36}Cl Radiocounting Method

Expected [TiDG] mM	Calculated [TiDG] mM	Relative Standard Deviation	% Difference
0	0.0243	21.8%	
1	1.51	10.0%	51.0%
2	2.49	0.7%	24.5%
2.5	2.91	8.3%	16.4%
3	3.25	8.5%	8.3%
3.5	3.75	5.2%	7.1%
4	3.80	13.4%	-5.0%
5	4.61	12.6%	-7.8%

Since the TiDG is received as the HCl salt, it was expected that better results could be obtained using the free base version of the solvent. Therefore, the screening experiments were repeated using samples of solvent of varying TiDG concentration that had been converted to the free base form and washed according to the solvent washing protocol described in Section 2.1 that was developed for the non-aqueous titration procedure. Results from these experiments are shown in Table 2-5.

Table 2-5. Results from ^{36}Cl Radiocounting Method Using Free Base/Washed Samples

Expected [TiDG] mM	Calculated [TiDG] mM	Relative Standard Deviation	% Difference
1	1.07	2.50%	7.00%
2	2.01	0.40%	0.50%
2.5	2.50	0.00%	0.00%
3	3.04	1.00%	1.33%
3.5	3.52	4.60%	0.57%
4	4.00	only 1 run conducted	0.00%
5 (used as standard)	5.00	4.50%	0.00%

This method appears promising for determination of TiDG concentrations in NGS solvent samples. The precision of results obtained from this method are similar to those of the non-aqueous titration method (Figure 2-7). However, one drawback to this method is that it can only provide a total base number and will not be able to differentiate between TiDG and TOA in the blended solvent. If this method were to be used for the blended solvent, the TOA concentration would have to be determined using another method (SVOA is currently used) and subtracted from the results of the ^{36}Cl method to determine the TiDG concentration in a given sample. In addition, other radioisotopes (e.g. ^{137}Cs) may need to be separated from the sample prior to ^{36}Cl counting.

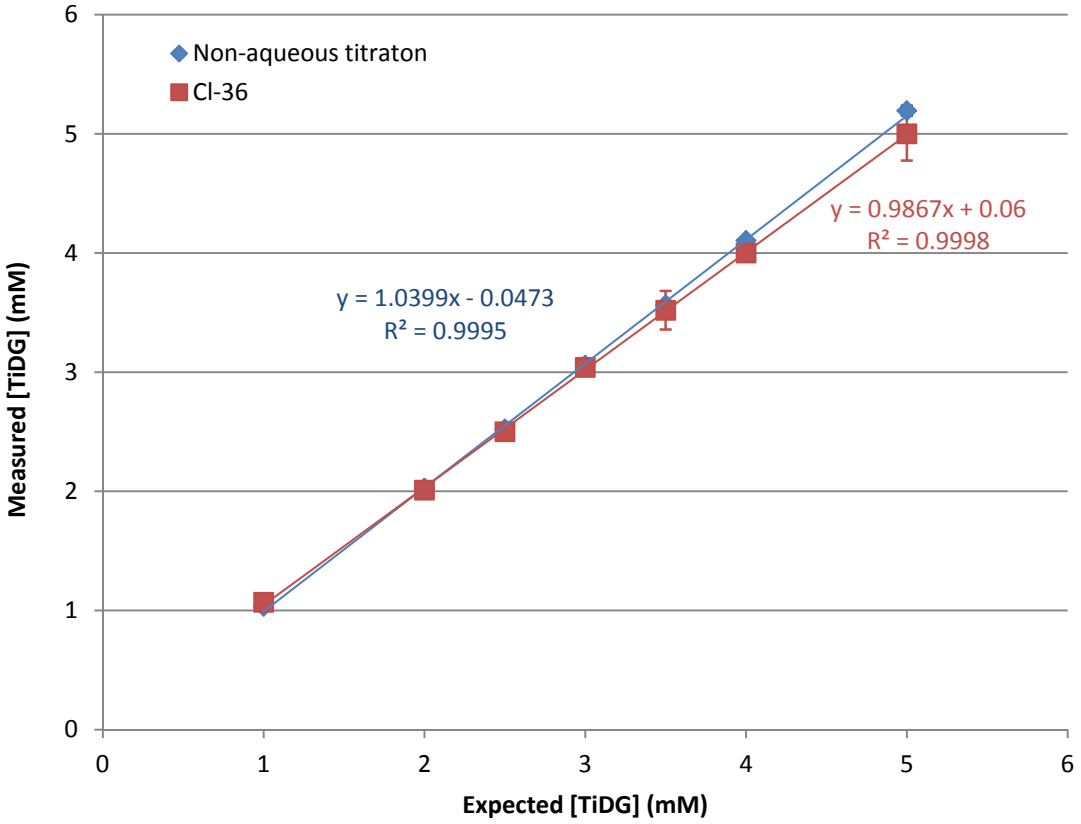


Figure 2-7. Comparison of results obtained from non-aqueous titration and ^{36}Cl methods. The error bars represent the standard deviation in the measurements.

2.7 Ion Chromatography (IC) for Cl^-

IC analysis for Cl^- concentration is based on the same principles as the ^{36}Cl radiocounting method described in Section 2.6. However, instead of using ^{36}Cl spiked HCl and radiocounting to determine Cl^- concentration, the Cl^- ion is back extracted from the organic solvent and measured using IC. For these screening experiments, samples of the as-prepared solvent with varying amounts of TiDG were contacted with 0.01 M HCl. After allowing the phases to separate, the aqueous layer was removed, and the organic layer was contacted with 0.06 M NaOH to extract the Cl^- from the solvent. This aqueous layer was then analyzed using IC. A correlation was observed between expected TiDG concentration and the Cl^- concentration measured by IC (Figure 2-8). Although not completely linear, it is believed this method could be improved and would be viable; however, since it is similar to two of the other methods (titration and ^{36}Cl radiocounting) which had already shown promising results, it was not pursued further. In addition, this method would be subject to similar limitations as the ^{36}Cl method, in that it would not be able to differentiate TiDG and TOA in the blended solvent.

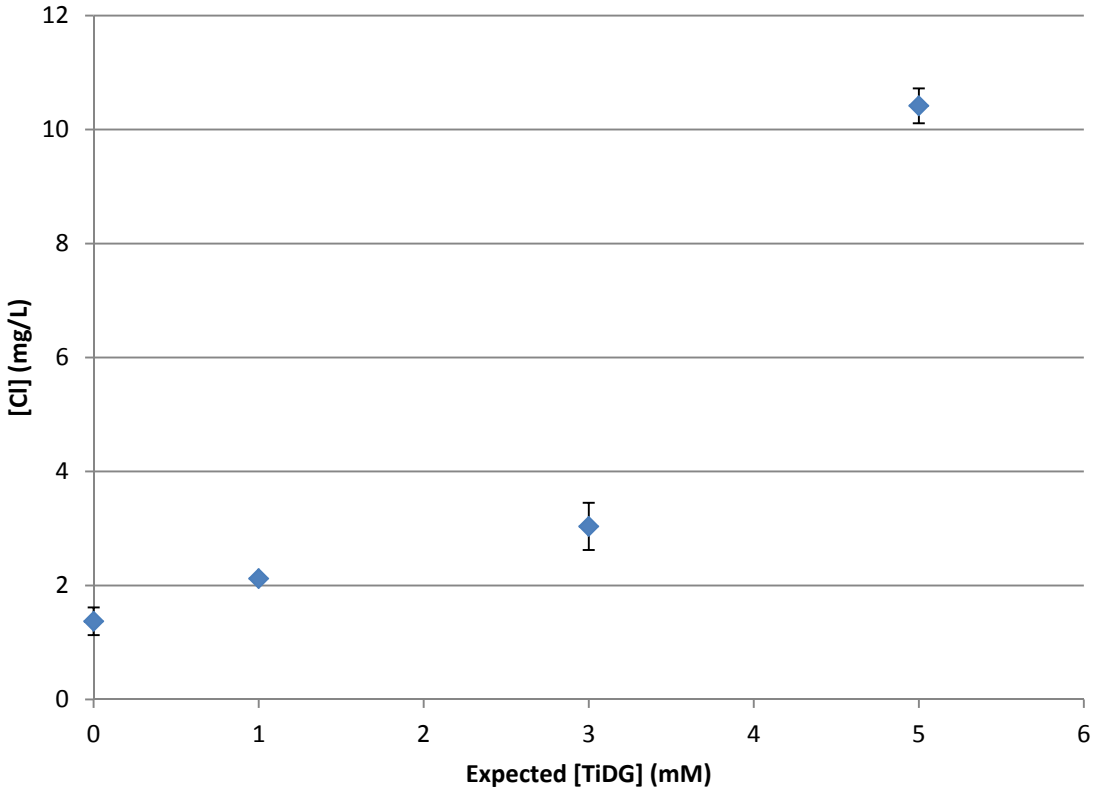


Figure 2-8. Results of IC analysis of Cl^- back extracted from NGS samples that had been contacted with 0.01 M HCl. The error bars represent the standard deviation of replicate samples.

2.8 Liquid Chromatography – Mass Spectrometry (LC-MS)

LC-MS is the method currently being used by Parsons for measurement of TiDG concentrations in the NGS. Although SRNL currently does not have capabilities to analyze radioactive samples on an LC-MS at SRNL, a clean LC-MS was available in the Environmental Biotechnology group at SRNL for some initial screening experiments. An advantage to this method is that all solvent components (extractant, modifier, and suppressor) can be measured simultaneously. A sample of as-prepared NGS at nominal concentrations was used to evaluate this method.

An Agilent Liquid Chromatograph 1260 equipped with a Hilic column was used to separate the compounds of interest in a gradient from 95% H_2O with 0.1% trifluoroacetic acid (TFA) to 95% acetonitrile with 0.1% TFA. The sample was introduced into an Agilent Accurate Mass Time of Flight Mass Spectrometer 1624 (TOF-MS). Retention times for the compounds, i.e., extractant – MaxCalix, modifier – Cs-7SB and suppressor – TiDG, were 0.94, 0.82, and 0.79 minutes respectively, based on a flow rate of 0.2 mL/min. The TOF-MS was set in positive mode with a dual electrospray ionizer and other appropriate settings to properly ionize the compounds for detection. Dilutions of the solvent (100x, 1,000x, 2,000x, 5,000x, 10,000x, and 50,000x) were prepared in isopropanol and were analyzed in triplicate. The algorithm used to identify the compound was "Find-by-formula" (FBF), which calculates an exact mass from a formula and mines the chromatograph for all possible adducts formed. Although complex analysis confirmed the identity of the compounds by TOF-MS, a single Quad instrument would be adequate for this analysis. Purchasing of a Quad instrument for analysis of radioactive samples over a TOF-MS

would result in considerable cost savings. Instead of using FBF, a simple unit mass ion profile extraction shows that the background is clean enough to detect the compounds of interest (especially at higher concentrations). A 10,000 fold dilution is suggested for an adequate detection limit and decrease in background for TOF. An Accurate Mass device is not ideal for quantification because not all of the compounds of interest are sent to the detector; yet the device did show linearity with parts per million concentrations (See Figure 2-9 through Figure 2-11). The error bars in these figures show the standard deviations in triplicate measurements of each dilution factor. The dilutions with the large error bars are outside of the optimal concentration range for ionization and detection.

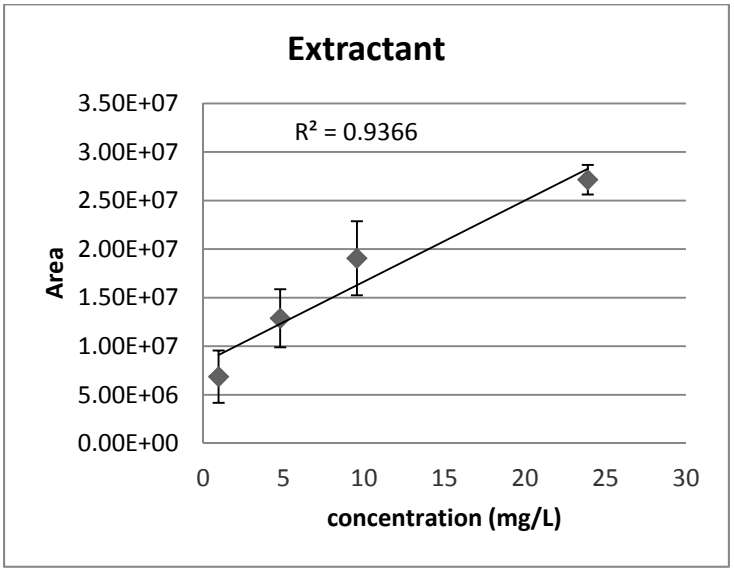


Figure 2-9. Quantification of Extractant Using LC-MS.

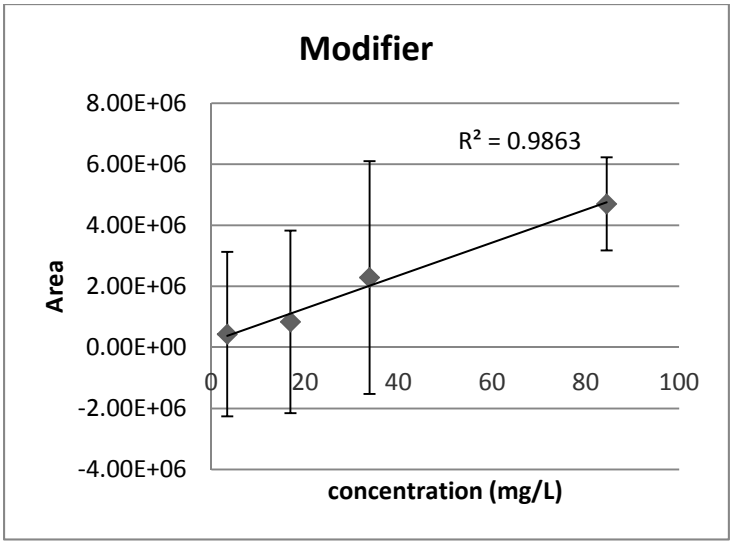


Figure 2-10. Quantification of Modifier Using LC-MS.

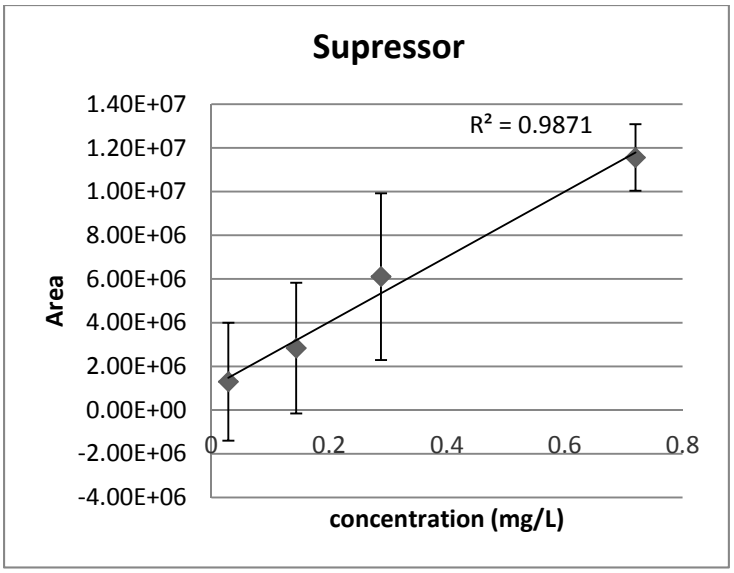


Figure 2-11. Quantification of Modifier Using LC-MS.

3.0 Method Development

After screening all of the methods described in Section 2, the team determined that the non-aqueous titration method was the most promising, and selected it as the primary method for TiDG analysis in the NGS system. The ^{1}H NMR method was also selected for further development as a back-up method. Additional samples, including radioactive samples, were analyzed, and procedures were developed for these two methods.[4,5] The following sections describe the results from the additional analyses performed for further method development.

3.1 Acid-Base (non-aqueous) Titration

3.1.1 *Standards*

The titrant solution used for the non-aqueous titrations is 0.01 M HCl in isopropanol. The solution is prepared by diluting the appropriate volume of concentrated HCl (12.1 M) in isopropanol. This titrant solution must be standardized against a primary standard in order to obtain a precise concentration that will be used for determining the TiDG concentration in the unknown samples. A commonly used primary standard, tris(hydroxymethyl)aminomethane (THAM), was selected for standardization of the titrant solution. This compound has limited solubility in isopropanol, and therefore, absolute ethanol will be used to dissolve the THAM for HCl titer determination. The titer value of the titrant will be determined by titrating triplicate samples of THAM. The %RSD for this triplicate measurement must be ≤ 3%.

In addition to standardization of the titrant solution, a standard of known TiDG concentration will be analyzed along with the unknown samples. The standard will be a sample of solvent (either pure NGS or blended solvent) prepared with a known concentration of TiDG. Analysis of the standard will occur at the beginning and end of analyses of unknown samples. The acceptability of the standard is set to be within 10% of the expected value. Based on these limits, the uncertainty for the method is set at 10%.

3.1.2 *Non-Radioactive Process Samples*

Samples from the V-05 and V-10 contactor testing performed at the SRNL Engineering Development Lab (EDL)[6] were analyzed by the titration method. Samples of both the feed

solvent and a sample of the solvent taken after processing (post-coalescer) were analyzed. The feed solvent is the blended solvent containing both TiDG and TOA, with expected concentrations of 3 mM and 1.5 mM, respectively. Both samples were taken through the solvent washing sequence described in Section 2.1 to ensure the samples were in the free base form. The samples were then diluted (3.0 mL of sample into 30 mL of isopropanol) and titrated with 0.01 M HCl. The results are summarized in Table 3-1 and Table 3-2. The feed sample was determined to have a TiDG concentration of 3.16 ± 0.005 mM, 5.3% above nominal, and a TOA concentration of 1.89 ± 0.038 mM, 26% above nominal. The concentration of TiDG was found to decrease in the post-coalescer sample, while the TOA concentration increased. The TiDG concentration decreased to 2.94 ± 0.050 mM, while the TOA concentration increased to 1.97 ± 0.110 mM. The two samples had a similar amount of total base, with a percent difference of only 2.6%. The uncertainties reported represent one standard deviation from triplicate analyses of the same sample; however, the method uncertainty could be as high as 10%.

If the differences between the feed sample and post-coalescer sample are real, and not due to method uncertainty, a possible explanation for the decrease in TiDG concentration with a corresponding increase in TOA concentration could be the degradation of TiDG to form primary amines, which have previously been identified as degradation products of the suppressor.[7] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine), making the equivalence points coincide.[*8]

Table 3-1. Results from Titration of EDL Feed Sample.

Sample Vol (mL)	Expected mM TiDG	Calculated [TiDG] mM	% Difference	Expected mM TOA	Calculated [TOA] mM	% Difference	mM Total Base
3.0	3	3.16	5.25%	1.5	1.85	23.04%	5.00
3.0	3	3.16	5.29%	1.5	1.89	25.97%	5.05
3.0	3	3.15	4.98%	1.5	1.92	28.08%	5.07
	Ave	3.16			1.89		5.04
	SD	0.005			0.038		0.034
	%RSD	0.16%			2.01%		0.68%

Table 3-2. Results from Titration of EDL Post-Coalescer Sample.

Sample Vol (mL)	Expected mM TiDG	Calculated [TiDG] mM	% Difference	Expected mM TOA	Calculated [TOA] mM	% Difference	mM Total Base
3.0	3	2.99	-0.29%	1.5	2.09	39.41%	5.08
3.0	3	2.94	-1.91%	1.5	1.88	25.17%	4.82
3.0	3	2.89	-3.64%	1.5	1.94	29.10%	4.83
	Ave	2.94			1.97		4.91
	SD	0.050			0.110		0.149
	%RSD	1.71%			5.60%		3.04%

3.1.3 *Radioactive Samples*

In order to validate the method for radioactive samples, and to determine if any interferences are introduced from the extraction, scrub, and strip (ESS) processes associated with MCU, several samples of solvent used in real waste ESS tests were analyzed.[9] The samples consisted of pure NGS, a cold blend prepared by adding NGS cocktail to unused CSSX solvent, and two samples of

[*]For example, the pKa of ethylamine (primary amine) is 10.63 and the pKa of triethylamine (tertiary amine) is 10.65.

a hot blend which were prepared by adding NGS cocktail to a sample of used CSSX solvent from the facility. Sample TS175-12-C-111001 was prepared with the October 2012 MCU SHT quarterly samples, while sample TS175-12-D-111002 was prepared with the January 2013 MCU SHT quarterly samples. The samples ranged in age from 3 – 7 months at the time of titration. All titrations were performed in June 2013; preparation dates are shown in Table 3-3.

All of the samples were taken through the washing sequence described in Section 2.1 to ensure the TiDG was in the free base form prior to titration. The results of these analyses are shown in Table 3-3 and Figure 3-1. The vertical lines in Figure 3-1 indicate the equivalence points as detected by the titration software.

Table 3-3. Results from titration of solvent samples from real waste ESS testing.

Sample ID	Description	Date Prepared	Expected [TiDG] (mM)[9]	Measured [TiDG] (mM)	Expected [TOA] (mM)[9]	Measured [TOA] (mM)
TS175-12-A-110999	Pure NGS	Dec. 2012	2.77	1.71	None	n/a
TS175-12-B-111000	Cold Blend	Dec. 2012	3.25	2.18	1.5	1.63
TS175-12-C-111001	Hot Blend	Jan. 2013	2.94	2.00	1.5	1.71
TS175-12-D-111002	Hot Blend	Mar. 2013	3.05	3.02	0.637	1.11

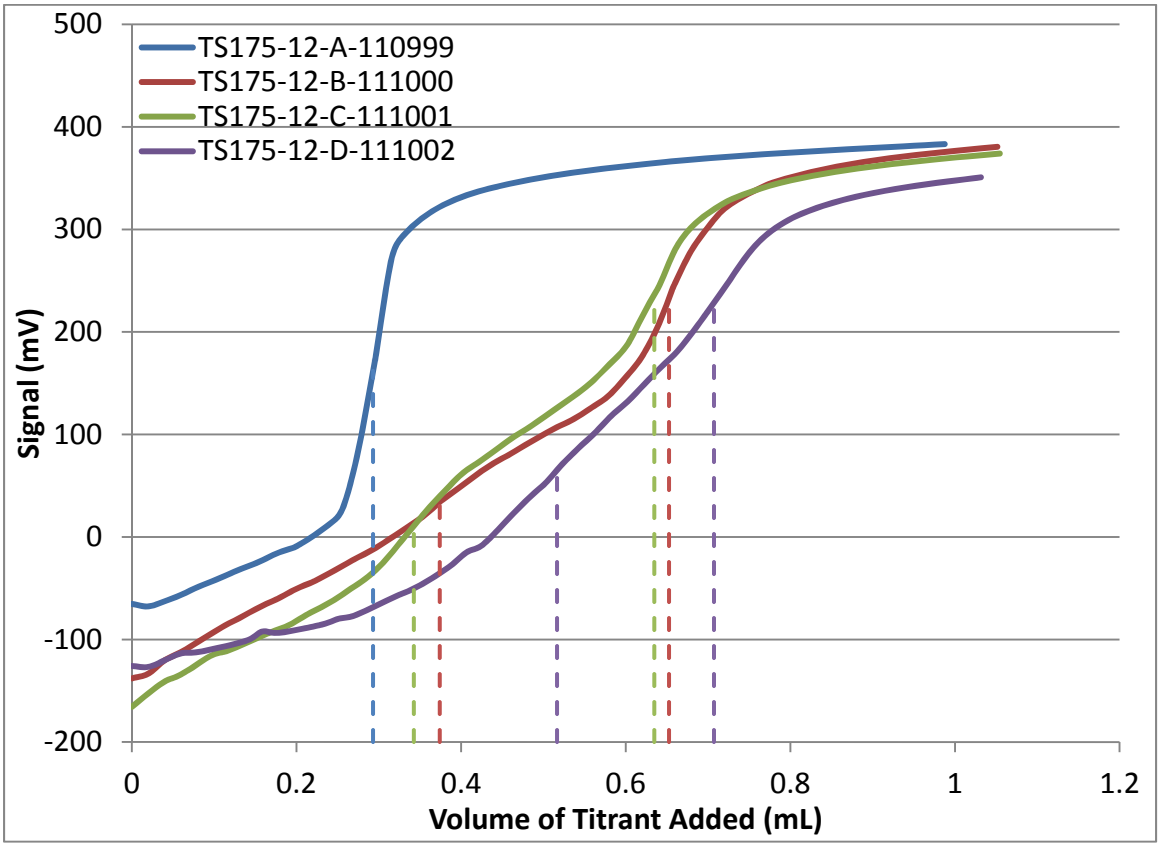


Figure 3-1. Titration curves from analysis of solvents samples from real waste ESS testing.

Results indicated that all samples, with the exception of Sample TS175-12-D-111002, were less than expected in TiDG concentration. The TOA concentration was higher than expected in all cases; although, as described in Section 2.1, there is a large error associated with quantifying TOA in the blended solvent. These results are consistent with TiDG degradation to form primary amines as described in Section 3.1.2. Since sample TS175-12-D-111002 was the most recently prepared sample, the results are consistent with this sample having the least TiDG degradation, and results closest to the expected values. Overall, these results indicate that the method is viable for analysis of radioactive process samples. The expected number of equivalence points were detected in all cases.

3.2 ^{1}H NMR

3.2.1 *Standards*

A standard of known TiDG concentration will be analyzed along with the unknown samples. The standard will be a sample of pure NGS solvent prepared with a known concentration of TiDG. Analysis of the standard will occur at the beginning and end of analyses of unknown samples. The results from analysis of the standard will be tracked over time to look for obvious deviations in the measurement. Due to the nature of the method, there will be some variation in the raw data obtained each time the standard is analyzed. The standard and the samples will be run during the same session to ensure there is no instrument variability between the standard and sample runs. Whenever is possible, at least three standards containing different TiDG concentrations (1 mM, 2 mM, and 3 mM) will be run and analyzed to construct a calibration line. The TiDG concentration of the unknown sample will be estimated from this calibration line. In the case that only one standard is analyzed, the results from that analysis will be used to calculate the unknown sample TiDG concentration using the formula shown in Equation 1. Based on the results of analysis of a series of samples with TiDG concentrations ranging from 1 to 5 mM, the limit of detection was determined to be 1 mM TiDG.

$$\frac{Sample\ Peak\ Area}{Standard\ Peak\ Area} = \frac{([sample] - 1mM)}{2\ mM} \qquad Eq.1$$

3.2.2 *Non-Radioactive Process Samples*

The samples from the V-05 and V-10 contactor testing performed at EDL were also analyzed using the ^{1}H NMR method. The feed solvent was measured directly without any washing being performed. The peak area was compared to the peak areas of 1 mM TiDG and 3 mM TiDG standard solvent solutions. The post-coalescer sample required acidification by contacting a sample of the solvent with an equal volume of 10 mM HCl prior to analysis, as described in Section 2.2.1. The feed solution was determined to have a TiDG concentration of 2.85 ± 9%, while the post-coalescer sample was determined to have a TiDG concentration of 2.79 ± 11%. These results are the same as those determined by titration, within the method uncertainties, and therefore, are in good agreement.

4.0 Conclusions

Ten methods were identified as candidates for quantifying the guanidine suppressor in the NGS system. Screening experiments were performed for 8 out of the 10 methods identified. Based on the screening experiments, the non-aqueous titration demonstrated good precision and ability to measure the TiDG at the desired levels in both the pure NGS and blended solvents. This method was selected for further development, and has been evaluated using both non-radioactive and radioactive process samples obtained from other areas of the SNRL testing program for NGS.

Based on these results the non-aqueous titration has been selected as the primary method for TiDG quantification in NGS. The ^{1}H NMR method also showed promising results, and has been selected for further development as a secondary method for quantifying the TiDG. Analysis of non-radioactive process samples from other SRNL testing has been completed, and good agreement was obtained between the two methods. Additional development experiments, including analysis of radioactive samples, is planned and will be reported in a later revision to this report.

Procedures have been developed and issued for both methods outlining the protocols for analyzing radioactive MCU solvent samples of both pure NGS and blended solvent, containing both TiDG and TOA suppressors. In addition, the procedures outline the standards to be used for verifying the method during sample analysis. The non-aqueous titration method utilizes a primary standard, THAM, for standardizing of the titrant solution. NGS or NGS-Blend samples of known TiDG concentrations are also titrated as standards along with the unknown samples to confirm the method is working as expected. For the ^{1}H NMR method, samples of NGS with known TiDG concentrations will be used as standards for determining the TiDG concentration in the unknown sample(s).

5.0 Path Forward

Additional method development is in progress for the ^{1}H NMR method and will be included in a later revision to this report. Planned testing includes confirming the validity of the method using radioactive samples, where degradation products may provide interferences. Modifications made to the NMR procedure will be tested on the blend sample expected in mid to late September after the NGS concentrate is blended with the BOBCalixC6 based solvent at MCU.

In addition, analysis of additional blended solvent samples with varying TiDG concentrations is recommended to further define the method uncertainty for analysis of blended solvent using the titration method.

6.0 References

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