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Proton Nuclear Magnetic Resonance (^{1}H NMR) of Flammable Organic Chemicals in Radioactive High Level Supernatant Waste at the Savannah River Site (SRS)

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Proton Nuclear Magnetic Resonance (^{1}H NMR) of Flammable Organic Chemicals in Radioactive High Level Supernatant Waste at the Savannah River Site (SRS)

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ABSTRACT

The Savannah River Site stores approximately 36 million gallons of radioactive and hazardous waste that contains approximately 245 million Curies. The waste is sent through various chemical processes to reduce its volume and to separate various components. Facility plans to replace formic acid (a chemical used to reduce soluble mercury) with glycolic acid. Solutions containing glycolate might be sent to the tank farm where the glycolate breaks down generating hydrogen gas by thermal and radiolytic mechanisms. The current analytical method for detecting glycolate (Ion Chromatography) in supernatant requires a large dilution to reduce interference from the nitrate anions. Hydrogen Nuclear Magnetic Resonance is an analytical method that requires less sample dilution. It takes advantage of the CH_2 group in glycolate. Liquid samples were spiked with four different levels of glycolate to build a calibration line as it is recommended in the Standard Addition Method. The detection and quantitation limits determined were 1 and 5 ppm respectively for 32 scans which is well below the process limit of 10 ppm. In one test, 800 scans of a supernatant spiked with 1 ppm glycolate resulted in a ($-CH_2$) peak with a signal to noise ratio of 36.

ABBREVIATIONS

CPC, Chemical Processing Cell (at DWPF); **CPMGPR1D**, Carr-Purcell Meiboom-Gill pre-saturation one dimension ; **CSTF**, concentration, storage, and transfer facilities; **CST**, crystalline silicotitanate; **DANTE**, Delay alternating with nutation for tailored excitation; **DWPF**, Defense Waste Processing Facility; **EXCEPT-16**, exponentially converging eradication pulse train; **FTIR**, Fourier transform infrared Spectroscopy; **^{1}H NMR**, hydrogen nuclear magnetic resonance; **Reillex^{TM} HPQ**, high capacity poly(4-vinylpyridine), cross-linked, methyl chloride quaternary; **IC**, ion chromatography; **LOD**, limit of detection; **LOQ**, limit of quantitation; **MST**, monosodium titanate; **RF**, radiofrequency; **RCT**, recycle collection tank; **SAM**, standard addition method; **SDM**, standard dilution method; **ZGESGP**, zero go using excitation

sculpting with gradient pulses; **ZGPR,** zero go with a pre-saturation pulse; **ZGCPPR**, zero go using a pre-saturation pulse followed by three 90º pulses.

KEYWORDS: NMR, ^{1}H, solvent suppression, glycolate anion, standard addition method, supernatant.

INTRODUCTION

The Savannah River Site used metallic mercury in nitric acid to catalyze the digestion of spent fuels having aluminum cladding. The digested fuel solution is then contacted with organic solvent (solvent extraction) for the extraction of desirable isotopes (uranium and plutonium). Caustic solution is then added to the strip (or extract) solution (to a pH high enough to prevent aluminum precipitation but low enough to prevent steel corrosion) and then it is sent to the tank farm for temporary storage. Finally, the radioactive waste is sent to the Defense Waste Processing Facility (DWPF) for additional treatment and final vitrification.

The radioactive waste processing at DWPF adds formic acid to the waste to reduce mercuric ion (Hg^{2+}) to the more volatile elemental Hg for steam striping. The drawback of this addition is that under acidic and radioactive conditions, formic acid decomposes and generates hydrogen gas at a rate that may present an explosive condition to the storage facility. The alternative organic reductant, glycolic acid, was found to be stable under acidic conditions [1,2].

Therefore, a low hydrogen gas generation acid flowsheet has been developed utilizing glycolic acid with the benefit of easing the need for headspace monitoring requirements for hydrogen and ammonia gases at the DWPF. Low concentrations of glycolate are conservatively assumed to be in the recycle stream from DWPF that collects in the Recycle Collection Tank (RCT). The DWPF recycle stream collected in the RCT has a distinct pathway to the Liquid Waste System (LWS) tanks that feed the 2H and 3H evaporators. This route involves transfer of the DWPF recycle stream to Tank 22 in the Concentration, Storage, and Transfer Facilities (CSTF) followed by transfer to the LWS tank farm/evaporators.

Glycolic acid is a two-carbon alpha hydroxy carboxylic acid that exists as glycolate in caustic tank waste. The two methylene hydrogens (pKa > 25) [3] and the hydrogen attached to the alcohol (pKa > 15) are visible in the ^{1}H NMR. The CH_2 hydrogens are observed as a single peak at 3.95 ppm in the ^{1}H NMR spectrum. The peak can be quantified by measuring the peak height (or area). The reported pKa of the carboxylic acid is 3.810 in water and will be slightly lower in high ionic strength solutions (up to 0.5 pKa units lower) [4]. The weak acid compound exists as a single anion in alkaline tank waste (pH~14). The glycolate anion is highly soluble in basic solution and is expected to remain soluble in the tank waste supernatant. Under caustic and radioactive conditions, the glycolate anion will decompose and possibly generate hydrogen gas [2].

There is a desire to decrease the detection limits for detecting the glycolate anion (approximately around 1 ppm) in high ionic strength samples (~ 7 M^2) from the tanks feeding the 2H and 3H evaporators as driven by the Documented Safety Analysis (DSA) under development for the Tank Farm. Previously, Savannah River National Laboratory (SRNL) developed, tested, and deployed an ion chromatography (IC) method which performed well for samples with low to moderate ionic strength (0.05 to 2 M sodium). The method has limited success at high molarity (1 M and higher nitrate) due to the interference of the nitrate ion peak with the glycolate anion peak. Several chemical processes and flowsheet at the Savannah River Site (SRS) require analytical methods to detect low levels of soluble organic species, below 10 mg/L, in radioactive liquid samples in support of system management and safety. The Savannah River Site National Laboratory (SRNL) has developed and deployed analytical methods such as Ion Chromatography (IC) that worked well with radioactive supernatant of low to medium ionic strength. At high ionic strength, interference from the nitrate anion limits the use of IC method and diluting deteriorated the Limit of Detection (LOD) and the Limit of Quantitation (LOQ) [5].

The laboratory investigated an alternative analytical method that uses hydrogen nuclear magnetic resonance that can complement and even extend the organic analysis capability of the laboratory for organic species in supernatant.

^{1}H NMR is a spectroscopic technique that uses pulses with bandwidths often in the 10-20 KHz range. Radio waves transmission is significantly attenuated in high ionic strength supernatant [6].

The interaction results in the generation of heat due to the high ionic conductivity (the heat can induce convective motion and even disturb the magnetic field within the sample). The radiofrequency (RF) power loss can be compensated by increasing the 90-degree power level (usually by 10 to 20%). Temperature control (cooling) may alleviate temperature rise in the sample. If the pulsing power is large enough, it may lead to the formation of secondary magnetic fields that result from the formation of induced currents in the receiving coils (a phenomena termed as radiation dampening in the literature) [7,8,9].

Another physical effect of a high ionic strength supernatant is its relatively high viscosity (around 2 to 3 cP that is mostly due to the hydrogen bonding network of the hydroxyls with water) that can slow some of the molecular relaxation of the organic species in solution. [10] This affects the magnetic relaxation of the organic analyte. For example, faster decoherence of the induced transverse magnetization and slower demagnetization of the induced longitudinal magnetization). Supernatant viscosity tends to decrease with increasing temperature. Heating the supernatant from 25 ºC to 40 ºC or cooling it down to 15 ºC did not provided useful signal-to-noise (S/N) improvement. Thus, a second option considered was to reduce the hydroxyl molarity of the supernatant. Reducing the hydroxyl molarity reduces the concentration of hydrogen bonding and therefore, the HOH (or HOD) resonance peak will shift up field and possibly running into the resonance of the analyte of interest. The HOD resonance peak is temperature-dependent (moves up-field with increasing temperature), and care must be taken to minimize peak overlapping in the final spectrum.

The laboratory explored reducing the hydroxyl concentration of the supernatant with the addition of dilute nitric acid for direct reduction of the hydroxyl anions while minimizing reduction of the carbonate and nitrite ions present in the supernatant. Heavy water (D_2O) was also added to increase the concentration of the HOD molecules which have a narrower ^1H NMR peak than the peak from the HOH water molecules. In addition, the addition of heavy water also reduces the radiation damping from H_2O [6, 7, and 8]. The heavy water also helps the NMR spectrometer to lock the magnet from drifting (a source of NMR signal degradation during acquisition).

A third factor that may impact the ^1H NMR method sensitivity for glycolate is the metal chelation ability of glycolate in the supernatant. The chelation or complexation may inhibit the free rotation of the atoms in glycolate. A pretreatment of the supernatant with Agilent 2.5 cc OnGuard II H^+ cartridges, Biotage Silica Thiol (60 mg in 2 mL), and Ethylenediaminetetraacetic acid (EDTA; 25 mg in 2 mL) followed by ^1H NMR analysis showed no significant improvement when compared to the ^1H NMR spectrum of the untreated supernatant. Therefore, the relatively high hydroxyl concentration (or high pH) of the supernatant reduces the concentration of transition, rare earths, and actinide metals available for chelation or complexation, and diminishes any paramagnetic effect on the supernatant.

^1H NMR is a useful tool to verify the presence of organic species in aqueous solutions. One example of this is the detection and quantification of carboxylic acid compounds in water. Several literature articles from the food industry use this method to identify and quantify carboxylic acids [11-16].

The ^{1}H NMR spectrum of aqueous solutions is dominated by the large peak from the water molecules (approximately 4.7 E22 hydrogen atoms in 0.7 mL of aqueous sample) that appears between the 4 to 6 ppm region (position is pH, ionic strength, and temperature dependent) relative to trimethylsilyl propionate (TMSP). The hydrogen signal from the water molecules takes most of the dynamic range available in the detector. The remaining signal, mostly from the target analyte, is almost indistinguishable from the noise. The signal from the water molecules must be reduced or suppressed to observe the target analyte signal. Several pulse programs have been developed to reduce the water signal in the ^{1}H NMR spectra of aqueous (and even non-aqueous) solutions [16-40]. The solvent suppression pulse programs are analogous to establishing a notch filter in Fourier space around the solvent resonance. A further review of the literature revealed that many of the solvent-suppression pulse programs affect the baseline and peaks nearby the suppressed solvent peak requiring fine tuning of the pulse's parameters to minimize these effects. The review also revealed that simple programs like pre-saturation (for example, ZGPR), after optimization, can preserve peaks nearby (within 0.5 ppm) the suppressed peak. We focused on four different solvent-suppressing pulse programs with emphasis on "simple" programs with the fewest pulses such as pre-saturation.

There are several quantitative measurement methods available to the ^{1}H NMR method. These include 1) placing the standard in a narrow tube that is placed inside a bigger diameter tube containing the sample (target analyte) or called "tube-inside-tube" external standard which is ideal for standards that are insoluble in the sample, 2) external standard (run the standard before and after the sample run), and 3) adding a soluble tracer to the sample. And in the case where the target analyte is known, additions of known aliquots of the analyte to the samples is recommended in the Standard Addition Method (SAM) [17].

A modification of the SAM that applies to samples with a high concentration of the analyte is the Standard Dilution Method (SDM) where the sample is diluted with aqueous solution not containing the target analyte [17]. Of these methods, the SAM outputs the concentration of the sample, the variance of the dilution steps and of the NMR measurements, and proof of linearity.

MATERIALS AND METHODS

Sample treatment

Solutions with high ionic conductivity, such as SRS supernatant, can affect the nuclear resonance frequency of the hydrogen atoms as well as their magnetic relaxation. To ascertain this effect, several solutions of different ionic strengths were made by diluting a salt simulant (containing 5 M hydroxyl anions, 6.6 M sodium cations, and 0.5 M nitrate anions) with doubled-distilled water. These solutions were then spiked with 50 mg/L glycolic acid. Each solution was tuned and matched in the probe, but difficulties were encountered, especially matching the SRS supernatant. No glycolate signal (at 3.95 ppm from TMSP) was seen in the 5 M and 4 M (sodium hydroxide molarity) solutions (see Figure 1). The spectra in Figure 1 were obtained with the pre-saturation

solvent suppression program (ZGCPPR). Even after increasing the pulse power (< 4.2 dB in the Bruker program) or reducing the pulse width by 50% (7 μs) of the hard 90 degrees pulse while keeping the other parameters the same, the glycolate signal to noise ratio was less than one for the 5 M sodium hydroxide supernatant sample containing glycolate. Thinking that paramagnetic ions (like the transition metal ions) were relaxing the glycolate anion faster than expected, contact tests were conducted with complexing agents (like EDTA) but no improvement in the S/N was observed either. The conclusion of this study, shown in Figure 1, indicates that solutions with a hydroxyl concentration at or less than 0.1 M have minimal effect on the glycolate peak height.

Therefore, for practical and quantitative purposes, it was decided to reduce the hydroxyl concentration of the highly ionic SRS supernatant to approximately 0.1 M. The relaxation of glycolate in supernatant is approximately 1.2 s (as determined by the T1ir program in Bruker) .

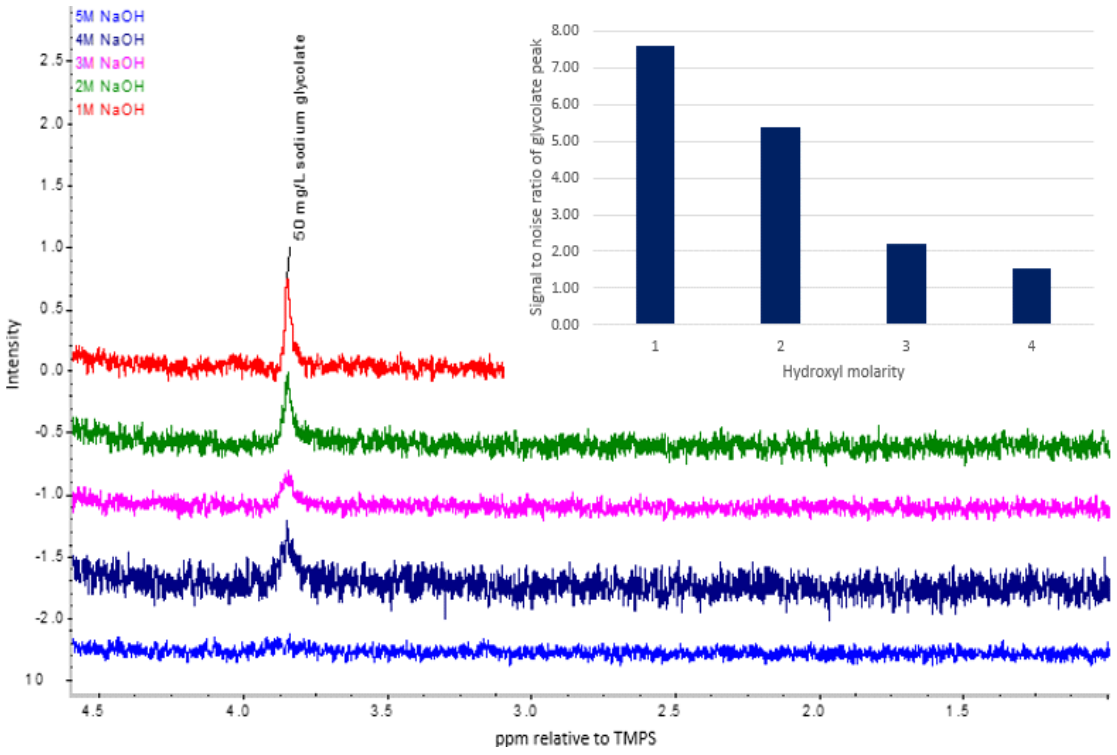

Figure 1. The effect of the hydroxyl concentration in a salt simulant on the signal to noise ratio of the glycolate ^{1}H NMR peak (50 mg/L glycolate was added to the salt simulant). The insert figure shows the calculated signal to noise ratio as a function of hydroxyl concentration in the supernatant.

The sample treatment for reducing the hydroxyl concentration of high molarity supernatant was as follows. The sample first received additions of 3 M nitric acid (3 M nitric was prepared by diluting 14 M nitric acid with 99% deuterated D_2O) to lower the hydroxyl concentration to approximately 0.1 M. If the final deuterium concentration in the sample was too low for detection, additional (99% deuterated) D_2O was added to the sample (typically 100 to 200 micro liters in those cases). The resulting decrease in the sample viscosity typically changes the relaxation spectrum of the analyte (for example, faster tumbling).

The radiation dose rate of the liquid sample was then reduced by contacting the sample with a slurry of inorganic sorbent Crystalline Silico-titanate or Monosodium Titanate (MST) to remove

the trans-uranium isotopes (Pu, Np, Am, and Cm) and 90-strontium, and then, the sample was pumped down-flow into a packed bed of inorganic sorbent crystalline silico-titanate (CST from UOP® IONSIV) to remove 137-Cs [41-45].

Finally, the sample was filtered with 0.45 microns polyether sulfone paper. "As received" samples with low hydroxyl concentration (< 1 M) received ion exchanged treatment only. One benefit of samples with high hydroxide concentration is their low concentration of ions with high magnetic susceptibility like Fe^{2+} and Mn^{2+} which precipitates in caustic solutions [46].

For building a calibration line that can estimate the glycolate concentration, the samples were treated as follows. The treated sample (supernatant) was divided into five portions. Each portion was spiked with a known concentration of glycolate. The five different portions of the treated sample were spiked with 5, 10, 20, and 35 mg/L of glycolate and/or methanol respectively. A calibration line was built with each treated supernatant sample. The calibration line was extrapolated to the concentration axis (at zero NMR signal) to determine the concentration and its error interval at the 95% confidence level. The error interval captures all the sources of noise associated with this method; from sample preparation to the analytical error of the ^{1}H NMR method. This is the reason we chose the SAM over the internal standard method which does not capture the global error associated with sample preparation and analysis of samples with different levels of glycolate concentration.

Experimental NMR

The treated samples were placed into a 5 mm outside diameter tube (high purity silica from Wilmad Glass, USA). The tube was then placed inside a (Broad-Band Observed or BBO) probe equipped with a Helmholtz coil and a Z-axis gradient (0.5 T/m) unit. Please note that better and

optimum results can be obtained with a BBI probe (Broad Band Inverse with the hydrogen-dedicated coil closest to the sample). The probe resides inside a 7 Tesla magnet from Bruker BioSpin.

Tuning and matching a supernatant containing 7 M NaOH, 2 M $NaNO_3$, and 0.5 M $Na_2Al_2O_4$ to an acceptable matching level was not achieved. The achieved match level was poor (high ionic conductivity). Acceptable matching and tunning numbers were readily obtained when the hydroxide concentration was below 1 M. Heating the supernatant (from 25 to 40 ºC) did not improve the glycolate ^{1}H NMR peak. Therefore, all spectra were collected at 298 °K. All spectra were baseline corrected with the "BAS" command in TopSpin. The BAS performs an automatic baseline correction of the spectrum by subtracting a polynomial. The degree of the polynomial was set at 5. The BAS command first determines which parts of the spectrum contain spectral information and stores the result in the file "*intrng*" (integral regions). The remaining part of the spectrum is considered baseline and used to fit the polynomial function. The glycolate peak was calibrated to be at 3.95 ppm relative to the trimethylsilyl propionate peak (TMSP). Peak integration was done from one side of the peak to the other side of the peak using the integration function available in the TopSpin 2.1 software. The points were chosen based on where the first derivative of the peak reached a zero value (away from the peak center). These points were at least 25 times the peak width at half-height away from the center of the peak to be integrated.

For reducing the signal from the HOD peak, four solvents suppression programs (ZGPR, ZGCPPR, ZGESGP, and CPMGPR1D) were evaluated with the same salt simulant containing 25 mg/L ascorbic acid. The parameters used in each of the four suppression programs are listed

in Table 1. The duration of the pre-saturation pulse used in the ZGPR and ZGCPPR programs was the same as the recycle time (D1) of 7 seconds. The duration of the selective excitation pulse (Sinc function) used in the ZGESGP, and CPMGPR1D (a T_2 filter program) programs was set at 4 ms (their corresponding power level were calculated based on the power level for the hard 90 degrees pulse using the CALCPOWLEV macro in the TopSpin 2.1 Bruker software).

Table 1. Water suppression pulse programs and parameter values used in this work

ZGPR	**ZGCPPR**
D1(s) = 7	D1 (s) = 7
P1 (us) = 14 @ 4.2 dB (18 kHz)	P1 (us) = 14 @ 4.2 dB (18 kHz)
Pre-Sat. Pulse 7s @ 50 dB	Pre-Sat. Pulse 7s @ 50 dB
AQ (s) = 5, TD = 34.5 K, SW(Hz) =3.4K	AQ (s) = 5, TD = 34.5 K, SW(Hz) =3.4K
RG= 287	RG= 287
Resolution (Hz) = 0.2	Resolution (Hz) = 0.2
Excitation Range ~ 0.03 Hz*	Excitation Range ~ 0.03 Hz*
ZGESGP	**CPMGPR1D**
D1(s) = 7	D1 (s) = 7
P1 (us) = 14 @ 4.2 dB (18 kHz)	P1 (us) = 14 @ 4.2 dB (18 kHz)
SP: Sinc1 for 4 ms @ 36.07 dB GP1: Sine.100 @ 155 mT/m GP2:Sine.100 @ 55 mT/m	SP: Sinc for 4.1 ms @ 4.2dB Pre-Sat. Pulse 7s @ 50 dB
AQ (s) = 5, TD = 34.5 K, SW(Hz) =3.4K	AQ (s) = 5, TD = 34.5 K, SW(Hz) =3.4K
RG = 4096	RG= 596, 4 echoes, d20 = 2 ms
Resolution (Hz) = 0.2	Resolution (Hz) = 0.2
Excitation Range ~ 2.5 kHz[#]	Excitation Range ~ 2.4 kHz[#]

*Calculated as 0.2/(pre-sat pulse width) for the uniformly-excited region by a rectangular pulse but the entire excited region is ~ 2/(pre-sat pulse width).

[#]For soft pulses, the uniformly-excited region was calculated as 10/(pulse width). Theoretically the 4π/(pulse width) includes the entire excited region.

The distance between the water and the glycolate peaks was 225 Hz and the water peak width at the baseline was ~ 150 Hz.

All FIDs were processed with an exponential multiplication (LB = 1) and filled one time (SI = TD).

The C-H peak of the furan ring in ascorbic acid was calibrated at 4.5 ppm relative to the trimethylsilyl propionate peak (TMSP). Peak integration was done from one side of the peak to the other side of the peak. These points were chosen based on where the first derivative of the peak reached a zero value (away from the center of the peak), and these points were at least 2.5 times the peak width at half-maximum away from the center resonance of the peak to be integrated.

RESULTS AND DISCUSSION

Initial scoping of the water suppression programs chosen in this study was to estimate the degree of attenuation of the HOD peak resonance and of nearby resonances. For this purpose, 25 mg of ascorbic acid (a molecule with at least one hydrogen resonance at 0.5 ppm away from the HOD peak) was dissolved in salt simulant containing 6 M sodium, 2 M hydroxide, and 100 microliters of 99% deuterated D_2O. The ^1H NMR spectra of this solution from four different solvent suppression methods are shown in Figure 2. In Figure 2, the -CH group in the furan ring of the ascorbic molecule has a peak at 4.5 ppm which is approximately half a ppm away (up field) from the HOD resonance at 4.9 ppm. The ratio of the peak height at 4.5 ppm (labeled "A" in Figure 2) to the peak height at 4.2 (labeled "B" in Figure 2) gives an indication of the attenuating effect of the parameters used in the water suppression pulse program used in this study. The insert plot in Figure 2 shows the ratio of the -CH peak (4.5 ppm) to the HOD peak (4.2 ppm). In general, all the water suppression pulse programs can reduce the HOD peak to acceptable levels. We did not optimize the selective pulse's parameters used in the excitation sculpting program (ZGESGP) or in the CPMGPR1D program but use parameters that Bruker recommends in their training manual [47]. When parameters are properly optimized, these pulse programs can provide acceptably mitigated HOD peak with minimal attenuation of nearby peaks. Figure 2 shows that the pre-saturation pulse program (ZGCPPR) can provide acceptable results (minimal attenuation

of signals 0.5 ppm away from the HOD peak and acceptable baseline distortion) with minimal parameter adjustment. Another group reached similar conclusions based on acceptable results with the ZGCPPR pulse program [28].

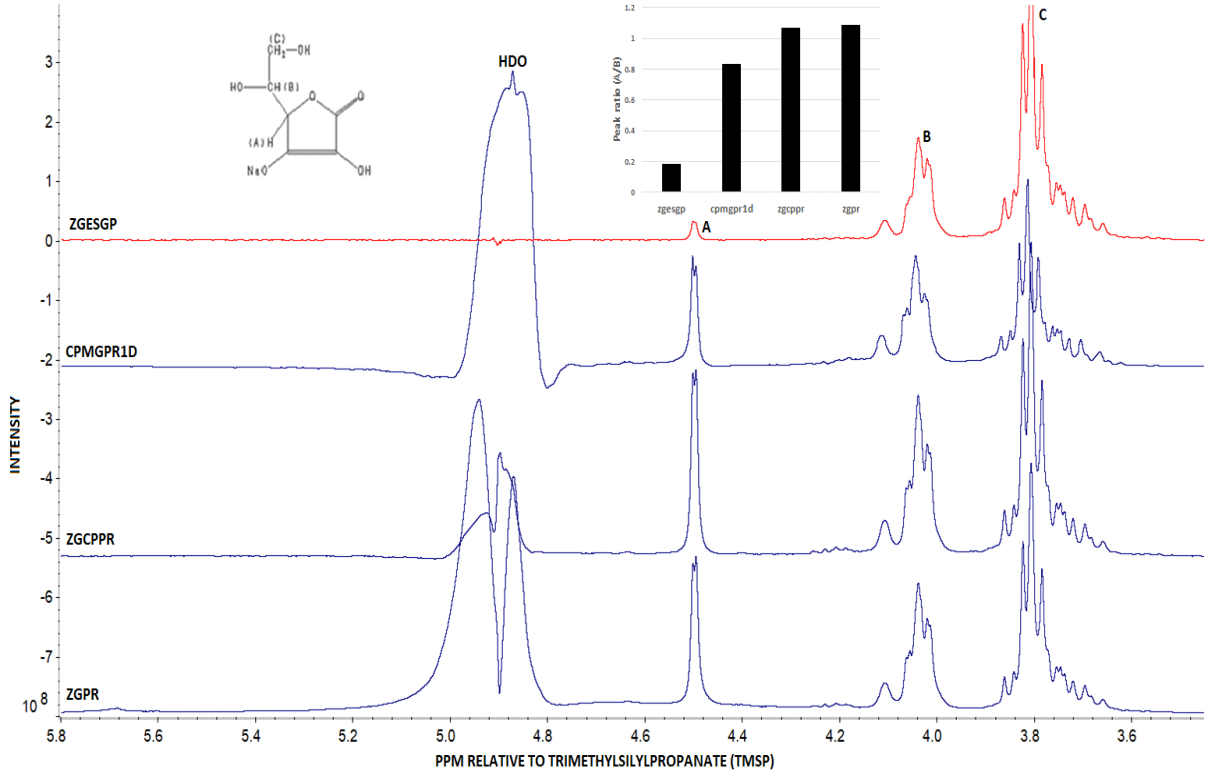

Figure 2. The ^{1}H NMR spectra of ascorbate in caustic supernatant obtained with the ZGESP, CPMGPR1D, ZGPR, and ZGCPPR programs. The insert plot shows the ratio of the peak labeled "A" to peak labeled "B".

Both the pre-saturation and excitation sculpting pulse sequences (as well as other solvent suppression programs such as for example WATERGATE [28]) can be used to build calibration lines for any resonance. Since our objective was to select a "simple to apply" solvent suppression program that can give a LOQ near 1 mg/L in salty and radioactive supernatant, work continue with the ZGCPPR program. The ZGCPPR program allows us to run samples "unlocked" without the need for adding deuterated water to the supernatant and still be able to quantify 1 mg/L glycolate.

The radioactive supernatants were evaluated for two target organics known to pose a flammability hazard: Methanol and glycolate. Glycolate is expected to be present in the radioactive supernatants from the recycle stream of a chemical process flowsheet (to be implemented in the near-future) at the Defense Waste Processing Facility (DWPF is where vitrification of radioactive supernatant is done) that uses glycolic acid to reduce Hg^{2+} to metallic mercury (metallic mercury is then steam-stripped from acidic solutions). Methanol is a natural byproduct from the radiolysis of organic already present in the radioactive supernatant.

Glycolate analysis by the SAM

Samples of low ionic strength supernatant from Tank 22H were spiked with different concentrations of glycolate as recommended in the SAM. The ^{1}H NMR solvent suppression of these samples are shown in Figure 3. A linear relationship between the ^{1}H NMR peak height of the -CH_2-OH group and the concentration of glycolate in Tank 22H supernatant was obtained as shown in Figure 3. The ^{1}H NMR spectrum from each sample is shown in the insert figure.

A second set of samples, this time a high ionic strength supernatant from Tank 38H supernatant, was nitric acid treated as discussed in the experimental section and spiked with different levels of sodium glycolate as recommended by the SAM. A linear relationship was also observed between the peak height of the glycolate and the concentration spiked glycolate as shown in Figure 4. Extrapolating back to zero, the confidence interval includes the origin indicating no glycolate is detected by this method in this sample. The collected spectrum for the sample spiked with 1.24 mg/L of sodium glycolate (lower number of scans was collected) was a bit noisier.

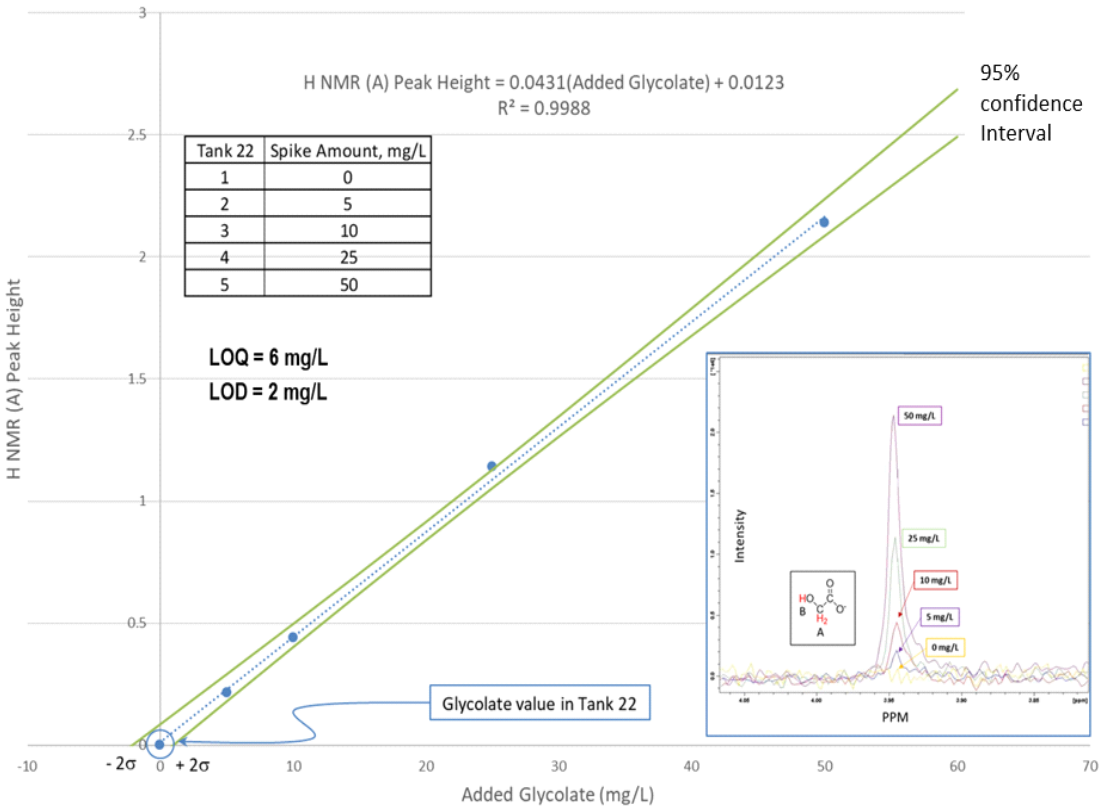

Figure 3. Standard addition method ^{1}H NMR analysis (32 scans and recycle delay of 9 seconds) for Tank 22H supernatant. The insert figure shows the ^{1}H NMR glycolate spectra for different levels of glycolate in the Tank 22H supernatant

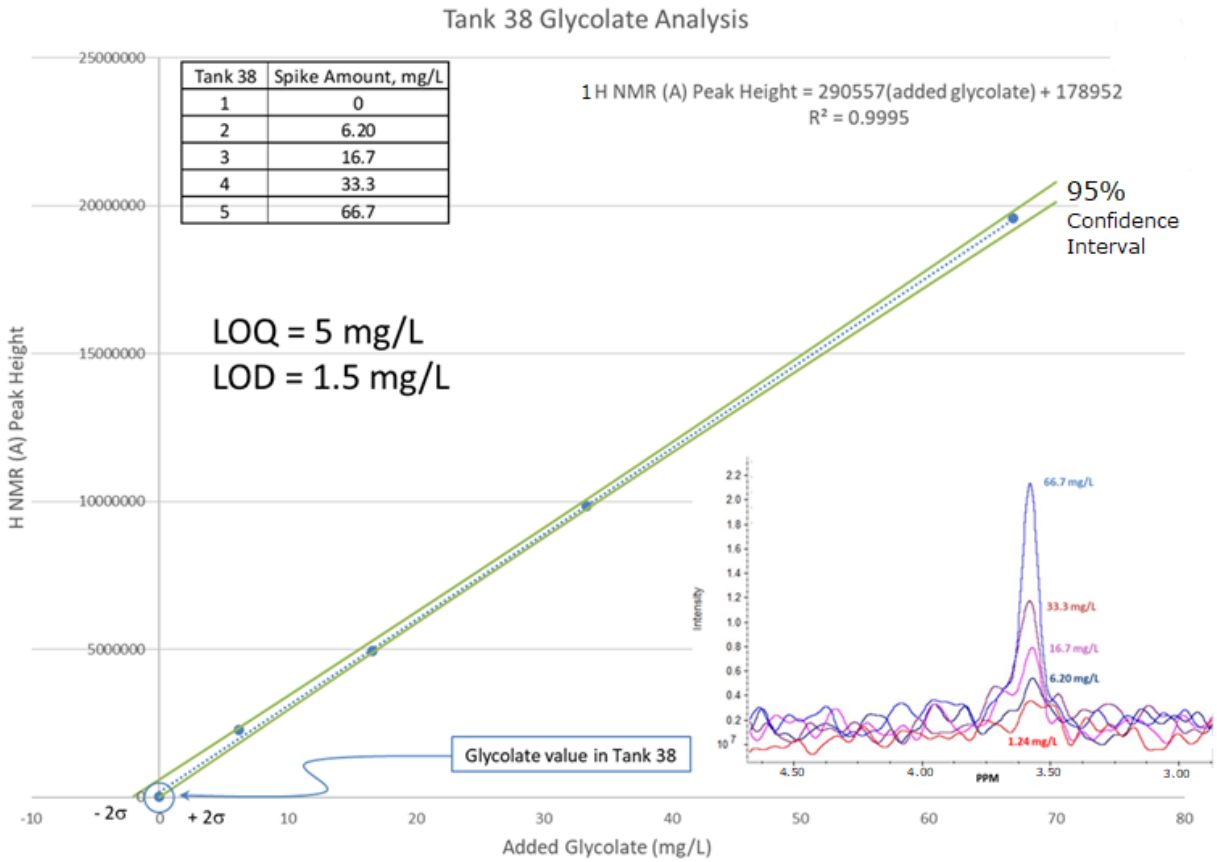

Figure 4. Standard addition method ^{1}H NMR analysis (32 scans and recycle delay of 9 seconds) for Tank 38H supernatant. The insert figure shows the ^{1}H NMR glycolate spectra for different levels of glycolate in the Tank 38H supernatant.

Since most administrative operational limits for flammables in radioactive supernatant are more concern with 1 mg/L, a sample of Tank 38H supernatant was spiked with 1.24 mg/L sodium glycolate and scanned for over 4 hours, the signal to noise ratio of the glycolate peak improved by 30 times.

Methanol Analysis by SAM

Methanol is a byproduct from the radiolysis of soluble organic chemicals in supernatant. Methanol has a very low flash point (9 ºC) and an explosive limit of 6-36 % in air [48].

This means very small amounts of ignition material can possibly cause fire. Tank 50H contains the decontaminated supernatant coming from the Salt Waste Processing Facility (SWPF) where

liquid-liquid extraction is used to remove 137-cesium. Residual organic from the liquid-liquid extraction operation also ends up in Tank 50H. Safety requirements for continuous storage states the concentration of methanol shall be below 1 mg/L (including the measurement uncertainty). A solvent-suppression ^{1}H NMR analysis revealed a methanol peak in the Tank 50H sample that measured 0.22 mg/L at a signal to noise ratio of 3.6 relative to the 12 mg/L of TMSP added to the sample as shown in Figure 5. Also shown in Figure 5 is the Tank 50H supernatant with 20 mg/L of methanol added in for easier visual location of the methanol peak. The ratios in signal-to-noise ratio (SNR) before and after standard addition allow an estimation of the methanol in the original Tank 40H sample. This shows that the ^{1}H NMR solvent suppression method can detect and measure levels of flammable species in radioactive supernatant.

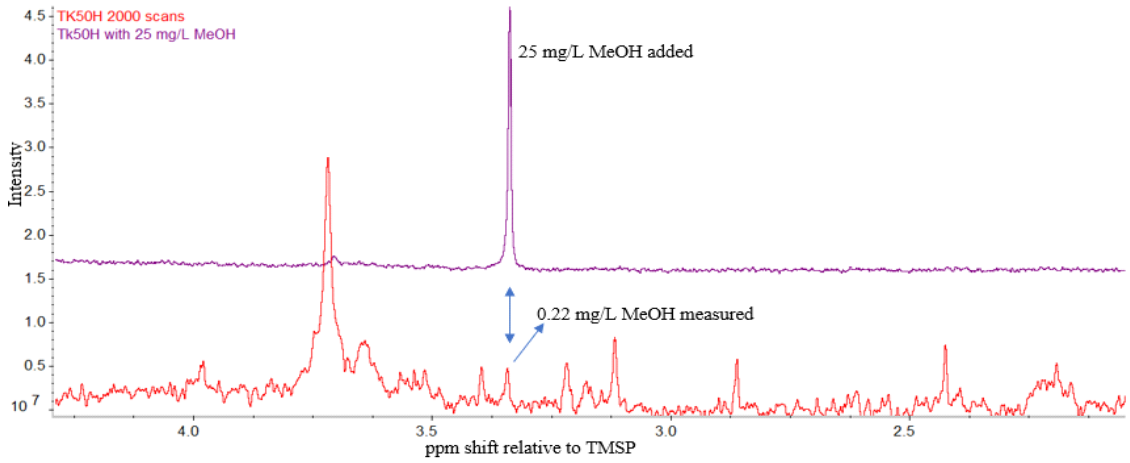

Figure 5. ^{1}H NMR spectra (solvent suppression) of Tank 50H supernatant showing the methanol peak (~ 0.22 mg/L methanol with a signal to noise ratio of 3.6 obtained with 2000 scans). Also shown a spectrum of Tank 50H supernatant with 25 mg/L methanol added is also shown for peak location.

Acid Stripping of Plutonium-Loaded Reillex™ HPQ Resin

Detection of organic species leached from an ion exchange resin used in plutonium processing is another application of solvent-suppressed ^{1}H NMR. Plutonium-loaded HPQ™ Reillex resin is treated with 0.3 M nitric acid to strip the plutonium (IV) from the resin [49]. The eluate was analyzed by the solvent suppression ^{1}H NMR method to determine the presence of organic species and it revealed that the resin released organics including Para substituted aromatic species containing the NO_2 groups (see Figure 6) and confirmed by FTIR (1554 cm^{-1} and 1322 cm^{-1} in Figure 7 as well as other oxidation products). The liquid might pose a hazard to downstream processes at the site. However, liquid calorimetry measurements of this liquid revealed the thermal properties and decomposition reaction rates were not energetic.

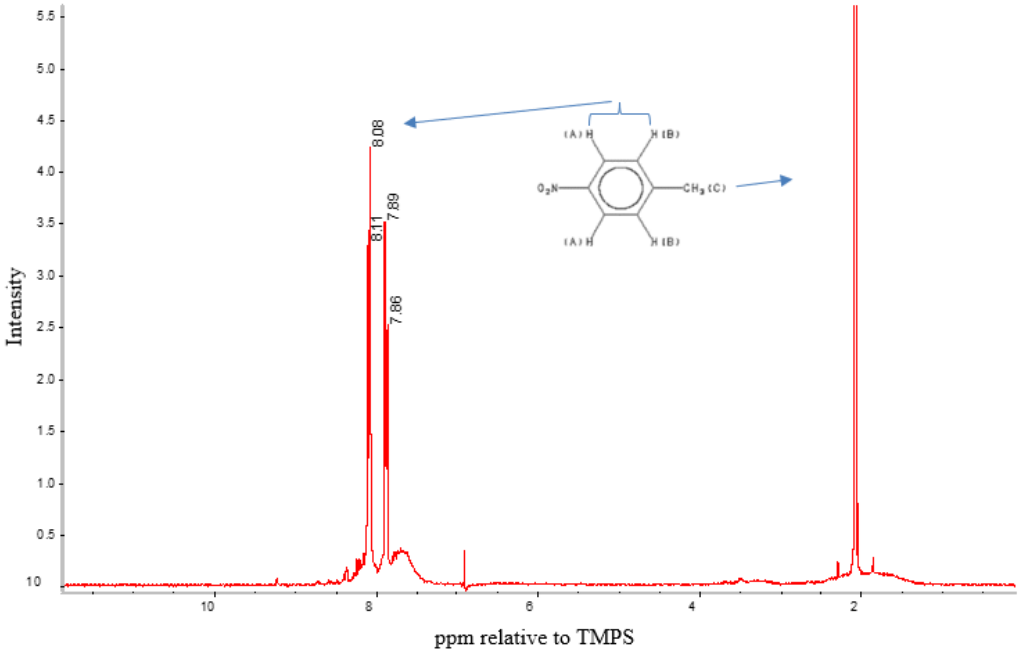

Figure 6. ^{1}H NMR spectrum (solvent suppressed) of a 0.3 molar acid solution that stripped Plutonium from a Reillex™ HPQ resin.

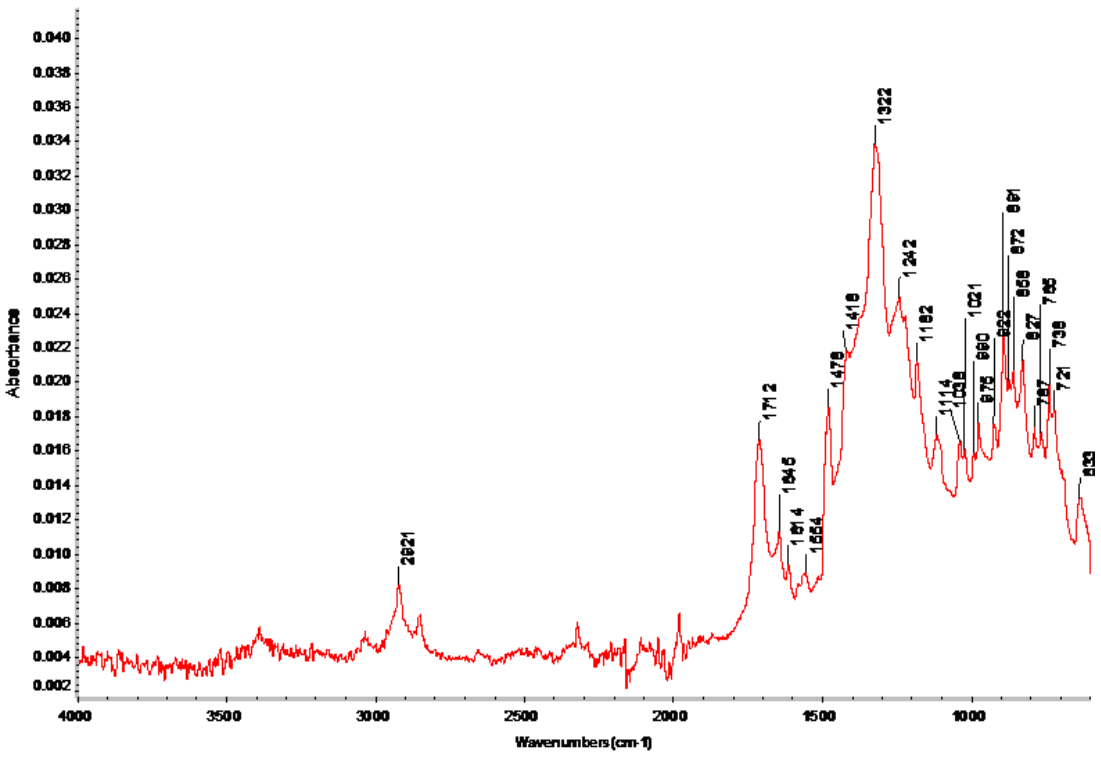

Figure 7. FTIR of a 0.3 M nitric acid solution (same solution as in Figure 6) that stripped plutonium from a Reillex™ HPQ resin. The 1554 cm^{-1} and the 1322 cm^{-1} peaks might indicate the presence of nitro groups

CONCLUSIONS

This work extended the analytical capabilities for glycolate analysis in high ion strength LWS samples by ^{1}H NMR techniques and a novel sample preparation protocol involving pH adjustment, locking agent addition, and ion exchange decontamination protocol. The method allows the user to directly view glycolate in LWS samples with minimal dilution. When compared to ion chromatography, this method achieved lower LOQ and LOD values for high ionic strength samples. Additionally, the method may be used to directly view undiluted/slightly diluted tank waste to identify other-select organic compounds. This analytical protocol and analysis are not rapid and requires hands-on intensive labor when compared to ion chromatography. Thus, the most appropriate application of the ^{1}H NMR method should target determining glycolate at concentration levels below 10 mg/L in tank waste samples during transitional or process changes. A summary of the analysis of the samples presented in this work is shown below.

No glycolate was detected in Tank 22H supernatant (low ionic strength < 0.2 M^2) and in Tank 38H supernatant (high ionic strength~ 6.0 M2) at the LOD of 2 mg/L.

Approximately 0.2 ppm of methanol was found in the supernatant from Tank 50H which is below the safety guidance for continuous storage.

Para-substituted aromatic rings were found in the dilute nitric acid solution (0.3 M) that had eluted plutonium-loaded Reillex™ HPQ resin.

Future work could explore other state-of-the-art water suppression approaches [50] to the water stream effluents from the final polishing processes at the Savannah River Site that is sent to the environment for final discharge. Also, SRS supernatant contains a high concentration of acetate and formate anions that are readily measured by Ion Chromatography-Anions and those measurements can be used as internal standard for the measurement of organic in the supernatant by the ^{1}H NMR method. Finally, better sensitivity and better results can be obtained if a higher magnetic field is used like a 11.7 Tesla magnet with either a liquid nitrogen or liquid helium-cooled cryoprobe.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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