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Glycolate Analysis in Tank 22:

Developing and Testing Analytical Methods for the Savannah River Site Liquid Waste System

T. L. White

D. P. DiPrete

F. F. Fondeur

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REVIEWS AND APPROVALS

AUTHORS:

_____
T. L. White, Analytical Development Date

_____
D. P. DiPrete, Analytical Development Date

_____
F. F. Fondeur, Separation Sciences and Engineering Date

TECHNICAL REVIEW:

_____
B. B. Looney, Environmental Sciences, Reviewed per E7 2.60 Date

APPROVAL:

_____
M. L. Whitehead, Manager Date
Analytical Development

_____
S. D. Fink, Director
Chemical Processing Sciences Manager Date

_____
J. E. Occhipinti, Manager
Engineering Date

_____
T. H. Huff, Manager
Engineering Date

EXECUTIVE SUMMARY

Researchers developed and tested a range of techniques to support a low mg/L Limit of Quantitation (LOQ) of glycolate in radioactive Tank 22 waste solution by Ion Chromatography (IC) and by proton NMR.

- For the IC method, Dionex OnGuard II cartridges were tested as a means of removing alkali earth and transition metals that can interfere during ion chromatography applications especially when analyzing for low-concentration, chelating analytes. Additionally, concentrations of nitrate in the raw Tank 22 sample (5,000 to 10,000 mg/L) were managed by using reasonable levels of sample dilution. The resulting IC performance quality was enhanced by improving the baseline, increasing sensitivity [Limit of Quantitation (LOQ) of 12 mg/L and Limit of Detection (LOD) of 4.0 mg/L], and resolving analytes into well-defined Gaussian peaks when using the Dionex OnGuard II H^+ cartridges to remove matrix interferences.
- High concentrations of nitrate limited the performance of the IC method. To achieve an acceptable baseline, samples with high nitrate content require more dilution, resulting in higher detection limits. Tests on samples with higher concentrations of nitrate (Tank 30 and 32 supernate with approximately 150000 mg/L nitrate) suggested that IC detection limits for glycolate in these samples would be > 500 mg/L. Thus, an LOQ of 12 mg/L is not feasible by this IC method on evaporator feed samples.
- An alternative method of glycolate analysis, using proton nuclear magnetic resonance (H NMR), was developed by the research team. In initial tests, the H NMR technique provided reasonable quantitation of glycolate in Tank 22 conditions by direct observation of the liquid. The H NMR method may provide improved detection limits for solutions with higher nitrate concentrations. We recommend further development of this analysis for high nitrate LWS samples such as evaporator feed and evaporator drop tank content.
- A method for pretreatment of samples using crystalline silicotitanate (CST) was developed and tested. The objective of the pretreatment was to facilitate analysis of samples with higher levels of radioactivity. The pretreatment did not influence the glycolate concentration in solution, and the pretreatment is projected to reduce Cs 137 activity in a sample by a factor of 16,200. The double strike CST pretreatment was demonstrated and would allow milliliters of higher activity samples to be transferred from the Shielded Cells and handled in a containment unit for glycolate analysis.

The various studies validated IC and H NMR methods for glycolate analysis, defined the range of applicability, and demonstrated key supporting analytical protocols. Based on the results, high quality glycolate analysis of Tank 22 is feasible down to approximately 12 mg/L, with the potential for broader applicability of the methods to other conditions in the Savannah River Site Liquid Waste System (LWS).

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LIST OF ABBREVIATIONS

ADS	Analytical Development Section
CPC	Chemical Processing Cell
CST	Crystalline Silicotitanate
CU	Containment Unit
DWPF	Defense Waste Processing Facility
EGC	Eluent Generator Cartridge
H NMR	Proton Nuclear Magnetic Resonance
HLW	High Level Waste
IC	Ion Chromatography
ICS	Ion Chromatography System
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LOD	Limit of Detection
LOQ	Limit of Quantitation
LWS	Liquid Waste System
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance
QA	Quality Assurance
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WATERGATE	Water Suppression by Gradient Tailored Excitation

1.0 Introduction

1.1 Scope

The Defense Waste Processing Facility (DWPF) converts highly radioactive liquid waste from the Savannah River Site (SRS) tank farms into readily storable radioactive glass by way of vitrification. This process uses the reductant formic acid in the DWPF Chemical Processing Cell (CPC) to keep radionuclides in their reduced oxidation states for incorporation into borosilicate glass[1]. The primary benefits of formic acid are 1) reduces mercury in the CPC cell to elemental mercury for steam stripping, 2) acid addition is needed to get the liquid waste to the correct rheology, and 3) maintaining the correct REDOX chemistry in the melter with the addition of the oxidant nitric acid in the correct amount. Flowsheet changes are currently underway to replace formic acid used for reduction reactions with an alternative reductant, glycolic acid. This reductant behaves similar to formic acid with the primary benefit of simplified operation since glycolic acid has been shown to have a lower hydrogen generation rate, and thus requires less vapor space monitoring[2].

When preparing High Level Waste (HLW) for vitrification in the CPC, the glycolic acid is not completely consumed. A relatively small portion of the waste containing glycolate returns to the Liquid Waste System (LWS) as a recycle stream by way of the Tank 22 DWPF Recycle Receipt Tank. Part of managing the liquid waste requires quantifying the concentration of glycolate in Tank 22. This report initially details the development and testing of an Ion Chromatography (IC) method and an H NMR method to quantify glycolate in Tank 22 to low mg/L concentrations. Supplemental testing on radioactive high nitrate/nitrite concentration Tanks 30 and 32 samples was performed to assess the applicability of the developed methods to higher nitrate solutions.

1.2 Strategy

The Limit of Quantitation (LOQ) for Ion Chromatography (IC) analysis of anion analytes is governed by the highest concentration analyte[3] and the dose rate of the sample. For instance, Tank 22 contains nitrate/nitrite near 10,000 mg/L and needs to be diluted at a minimum10-fold to avoid excessive column overload (B) as shown in Figure 1. If the sample is sufficiently diluted for the major analyte (A), the method sensitivity for the remaining analytes is decreased. The IC performance and peak shape for weak acids and similar anions is also impacted by complexation reactions and interactions with solution components such as metal cations. Additionally, the sample should measure below 5 mrem/h whole body for safe handling in a containment unit. To address these multiple constraints, this work focuses on developing glycolate methods that mitigate interferences and support application to the analysis of samples from the SRS Liquid Waste System (LWS). Specifically, this work includes:

- Testing pretreatment cartridges to modify/simplify the solution matrix to improve IC performance
- Testing the developed IC method for Tank 22 conditions to document performance and achievable IC detection limits

- Testing a solution decontamination method[4] using crystalline silicotitanate (CST) to remove cesium 137 and lower dose rate without affecting subsequent glycolate analysis
- Testing the performance of an alternative H NMR method to quantify glycolate
- Testing of the developed IC method on tank samples with higher nitrate (~ 150,000 mg/L) such as Tank 30 and 32 supernate to estimate an LOQ for a more concentrated matrix.

The analyte of interest, glycolate, is highly soluble in water and does not readily extract from water. Some amine ion pairing methods have been reported[5] that pulls glycolic acid into organic solvent with moderately good recoveries (~80%). The glycolic acid would then need to be back extacted into water for IC analysis. Rather than increasing analytical error using a multistep extraction protocol, SRNL Personnel pursued IC analysis of glycolate with limited dilution using Dionex OnGaurd II H^+ or Na^+ cartridges to remove matrix interferences and improve peak shape. A second proton nuclear magnetic resonance (H NMR) method was also tested that will quantify undiluted Tank 22 samples for glycolate using water signal suppression and observing the two hydrogens of the methylene group on glycolate.

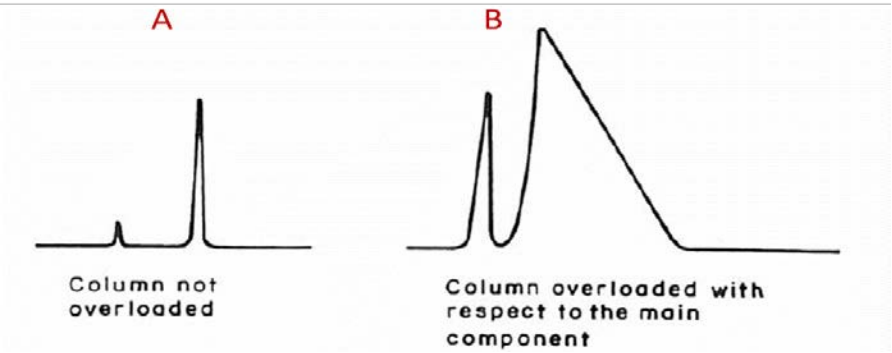


FIGURE 1: Two chromatograms demonstrating acceptable chromatography (A) and excessive column overload (B) of two components

2.0 Experimental Procedure

This study was initiated through the Technical Task Request (TTR)[6]/Task Technical and Quality Assurance Plan (TTQAP)[7] with a Functional Classification of Safety Class. The work and documentation were performed in a manner compliant with QA requirements. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60[8]. For SRNL documents, the extent and type of review was accomplished using the SRNL Technical Report Design Checklist.[9] Records for this work are contained in electronic notebook.[10] Throughout this document glycolate and glycolic acid are used interchangeably although they differ by one acidic proton. The eluent used for the IC analysis is basic KOH and the analyte exists as glycolate. For acidic solutions, the glycolate becomes glycolic acid such as the solution added to the CPC process in DWPF. The pedigree of the glycolate standards used was International Organization for Standardization (ISO) Guide 34, ISO/International Electrotechnical Commission (IEC) 17025 and Certified to ISO 9001 NIST traceable.

2.1 Instrumentation

Analytical samples for glycolate analysis are prepared and analyzed using a Dionex Ion Chromatography System (ICS) 6000[11] under procedure L16.1 ADS 2310[12]. Figure 1 shows the ion chromatography system where the blue shade of the instrument indicates that portion of the instrument housed in a containment unit ready for radioactive sample analysis. Samples loaded into the autosampler are injected into the basic mobile phase, analytes are separated into distinct bands on the analytical column, the mobile phase is neutralized by a suppressor device to increase the signal to noise ratio, and each distinct ion band shows a response on the conductivity detector that is captured on a data acquisition/instrument control system.

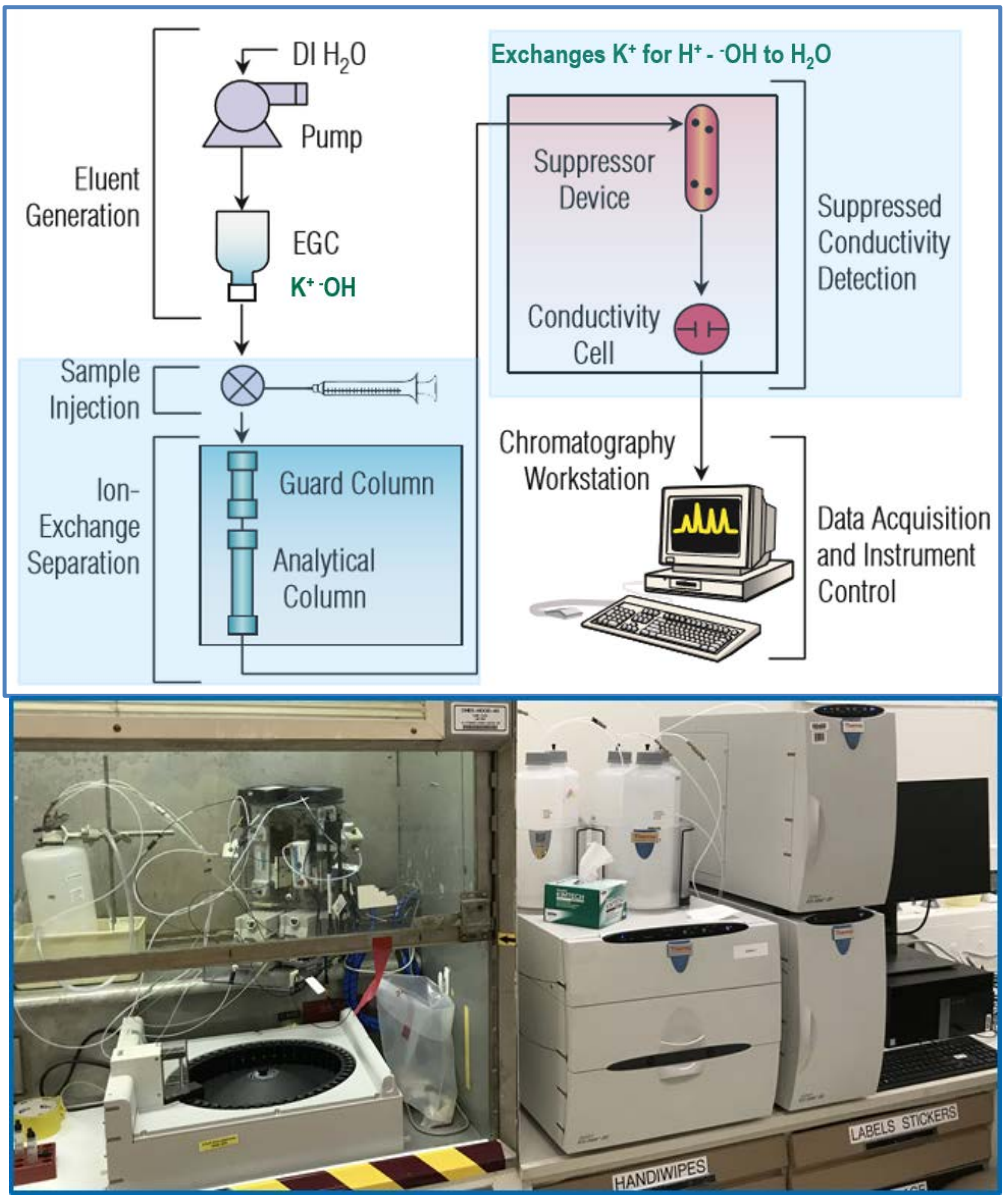


FIGURE 2: Ion Chromatography System (ICS) in a Containment Unit (CU) for radioactive sample analysis (note the blue areas of the schematic housed in the CU)

The Dionex ICS 6000 operating conditions to quantify glycolate are shown in Table 1. The method repeatably and rapidly quantifies glycolate at a retention time of ~4.5 minutes. To keep the analysis time under 20 minutes, the later eluting analytes (nitrite, nitrate, sulfate, phosphate, etc.) historically present in Tank 22 are rapidly flushed from the column by increasing the hydroxide concentration from 5 mM to 30 mM. Other carboxylic acid anions that may be present are formate that elutes 0.5 minutes later (monoacid) and oxalate (diacid) that elutes 12 minutes later.

TABLE 1: Glycolate Ion Chromatography Conditions

Anion Method	
Injection	25 µL
Flow rate	1.1 mL/min
Stop Time	20 min
Guard Column	IonPac AG11-HC-4µm 4x50 mm P/N 078034
Analytical Column	IonPac AS11-HC-4µm 4x250 mm P/N 082313
Suppressor	ADRS 600 Electrolytically Regenerated Suppressor P/N 088666
Mobile Phase	5-30 mM KOH Gradient; Eluent Generator Cartridges (EGC) P/N 075778
KOH conc. at retention time	5 mM at 0 minutes
KOH conc. at retention time	5 mM at 7 minutes
KOH conc. at retention time	30 mM at 7.1 minutes
KOH conc. at retention time	30 mM at 16.5 minutes
KOH conc. at retention time	5 mM at 16.6 minutes
KOH conc. at retention time	5 mM at 20 minutes
Total Time	20 minutes
Quadratic Calibration Curve	0.5 mg/L to 50 mg/L, r = >0.995
Retention Time of Glycolate	4.5 min

A scoping test of proton (H) NMR for quantitation of glycolate at 4.1 ppm was performed using a Bruker 300 MHz NMR. The H NMR experiment WATERGATE (Water Suppression by Gradient Tailored Excitation) was applied to suppress the large water signal at 5.1 ppm in the aqueous samples. This method relies on applying a gradient spin echo technique to separate the water magnetization (by diffusing it with two gradients) from other signals[13]. A hard 90-degree pulse is applied to magnetize the water followed by a 2 ms gradient pulse (a sine-shaped gradient of 50 mT/m was applied to diffuse it) [see Figure 3]. Lastly, a train of pulses set at different angles acts as a 180-degree pulse for everything else in the sample except for water. The delay between the pulses was 355 µs, the spectral width was 72,000Hz, and the time domain was 8K data points (the acquisition time was 56 ms).

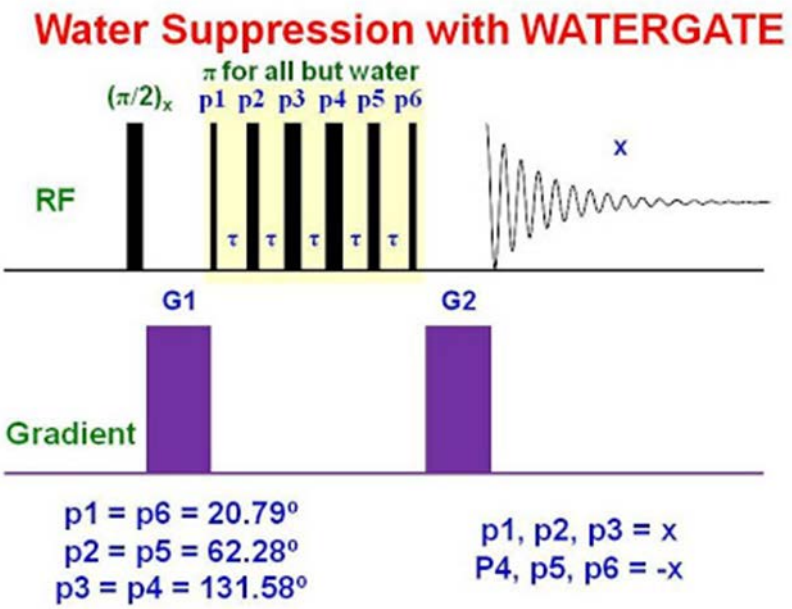


FIGURE 3: Water Suppression by Gradient Tailored Excitation (WATERGATE[11]) H NMR experiment

2.2 Tank 22 preparation and testing on OnGuard II cartridges

SRNL researchers prepared samples using Tank 22 supernate (Project ID: LW-AD-PROJ-190807-5; Cust. ID = HTF-22-18-117-1; Sample ID = W14768) with the two most concentrated IC anions present in the actual waste sample at ~ 10000 mg/L for nitrite and at ~ 5000 mg/L for nitrate. In a containment unit, personnel spiked 10, 25, and 50 mg/L and then diluted (1:10) each sample with deionized water (18 MΩ cm) using calibrated pipettes. Researchers tested both Dionex 2.5 cc OnGuard II H^+ and Na^+ to remove matrix effects. A 10 mL disposable syringe with the OnGuard cartridge attached was charged with 5 mL of diluted sample. The syringe plunger was carefully inserted into the syringe barrel and depressed. The first 2 mL of the sample were not collected while the next 3 mL were collected in an IC 5 mL autosampler vial for analysis. This protocol was developed after following the manufacturer's best practices[14] and some scoping work.

2.3 Tank 22 sample preparation for H NMR

Personnel prepared samples using Tank 22 supernate (Project ID: LW-AD-PROJ-190807-5; Cust. ID = HTF-22-18-117-1; Sample ID = W14768) for analysis by H NMR. In a containment unit, personnel spiked 10, 25, and 50 mg/L of glycolate into Tank 22 supernate to generate a series of glycolate samples differing in concentration for proton nuclear magnetic resonance (H NMR) analysis. Two mL of each sample was directly analyzed using the Bruker 300 MHz NMR as described above.

2.4 Tank 22 testing with crystalline silicotitanite (CST)

Tank 22 supernate (Project ID: LW-AD-PROJ-190807-5; Cust. ID = HTF-22-18-117-1; Sample ID = W14768) was prepared for decontamination by CST. In a containment unit, SRNL personnel spiked 15 mL of Tank 22 supernate with 20 mg/L of glycolate. Two grams of CST were added to

12 mL of sample and filtered. Two more grams of CST were added to the filtrate and filtered. The filtrate was analyzed in conjunction with 3 mL of untreated sample to determine if the CST impacted the glycolate concentration. Two strikes of CST reduced Cs 137 activity in a sample by a factor of 16,200 as determined by gamma spectroscopy with the associated reduction in potential dose. While Cs 137 removal was not needed for this Tank 22 supernate, the double strike CST method would allow milliliters of higher Cs 137 activity samples to be removed from the shielded cells and handled in a containment unit.

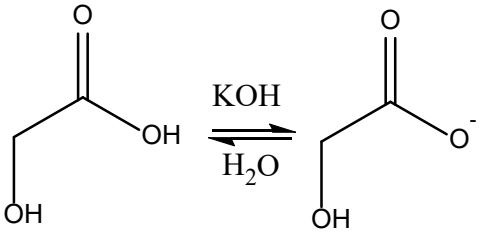
2.5 Tank 30/32 testing with CST

SRNL researchers prepared samples using Tank 30 and Tank 32 high nitrate supernate (Project ID: LW-AD-PROJ-191018-1; Cust. ID = HTF-30-19-91-W1; Sample ID = W15735) for decontamination by CST. In a containment unit, SRNL personnel spiked ~15 mL of Tank 30 supernate with 100 mg/L of glycolate and Tank 32 with 250 mg/L of glycolate. These spike concentrations were based on the lowest concentrations of glycolate concentration that might be achievable considering the high concentration of nitrate and nitrite (~150,000 mg/L) in the actual evaporator feed samples. Two grams of CST were added to 9 mL of sample and filtered. Two more grams of CST were added to the filtrate and filtered. The filtrate was analyzed in conjunction with 3 mL of untreated sample.

3.0 Results and Discussion

3.1 Ion Chromatography of Glycolate

Glycolic acid, shown in Figure 4, is a weak acid[15] (pKa = 3.87) that can chelate[16] through the hydroxyl and carboxylate moieties with metal ions present in Savannah River Site (SRS) radioactive tank waste. This characteristic of glycolate can lead to a non-gaussian peak shape on the IC chromatogram and less than optimal analysis results when analyzing for glycolate at low mg/L concentrations in samples collected from the SRS Liquid Waste System (LWS). Dionex OnGuard II cartridges have successfully been used to correct[17] these matrix effects by removing transition metals and alkali/alkaline earth metals resulting in sharp gaussian peaks[14]. The pretreatment cartridge step allows IC analysis to occur on Tank 22 samples that require little dilution resulting in a lower limit of quantitation (LOQ).



glycolic acid glycolate

FIGURE 4: Glycolic acid and the conjugate base Glycolate is a known chelator of metals

Each OnGuard II cartridge contains ion exchange resin with sulfate groups exposed on the surface to the particle. As liquid sample is passed through the cartridge, the negatively charged sulfate exchanger traps metal cations while the glycolate remains mobile. Figure 5 is a pictorial description of the cartridges and resin.

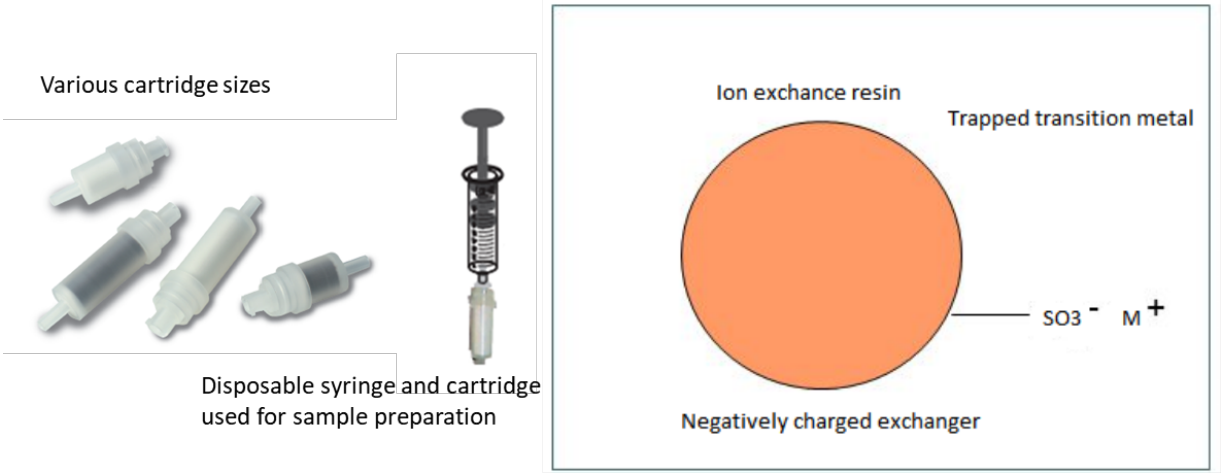


FIGURE 5: Dionex OnGuard II cartridges[14] used to remove matrix effects for low concentration analysis of glycolate

Once glycolate samples have undergone metal removal, glycolate concentration must fall on the calibration curve for optimal quantitation especially since weak acids result in quadratic calibration curves (non-linear). Table 2 lists acid compounds from strongest (lowest pK_a) to weakest (highest pK_a). The strong acids (italicized) with pK_a values below 1 readily dissociate in the IC mobile phase resulting in linear calibration curves. Glycolate is a weak acid ($pK_a = 3.87$)[18] and therefore partially dissociates in the mobile phase. The result is a non-linear calibration quadradic curve where samples higher in concentration than the highest point on the calibration curve are diluted to within the calibration curve range and values below the calibration curve are reported as a less than value of the lowest concentration point on the calibration curve. Figure 6 shows the linear calibration curves for example anions of strong acids (chloride and nitrate) and the nonlinear curve for example anions of weak acids (glycolate and formate).

TABLE 2: Strong acids shown in shaded area at the top of the table[19] form linear calibration curves while weak acids form quadratic curves on the IC instrument

Acid	Formula	pK_a
Hydrochloric	*HCl*	*<0*
Sulfuric	*H_2SO_4*	*<0*
Nitric	*HNO_3*	*<0*
Chloric	*$HClO_3$*	*<0*
Oxalic	$H_2C_2O_4$	1.19
Chlorous	$HClO_2$	1.94
Phosphoric	H_3PO_4	2.15
Nitrous	HNO_2	3.14
Hydrofluoric	HF	3.18
Glycolic	$HOCH_2COOH$	3.87
Acetic	CH_3COOH	4.74
Carbonic	H_2CO_3	6.36
Hydrogen Sulfide	H_2S	6.97
Hydrogen Cyanide	HCN	9.21

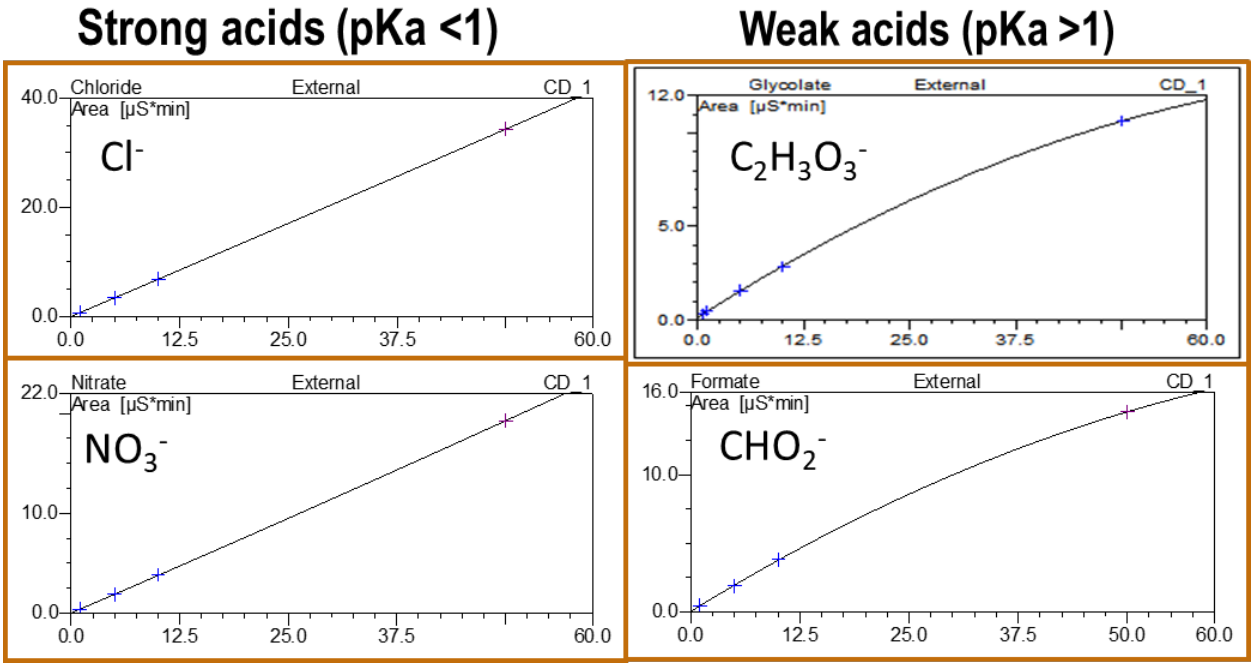


FIGURE 6: Linear IC calibration curve for strong acids on the left and quadratic IC calibration curve for weak acids on the right

3.1.1 Results from Dionex OnGuard II Na^+ cartridge testing

Figure 7 shows a chromatogram of Tank 22 diluted 1:10 spiked with 50 mg/L glycolate. The chromatography is poor, displaying broad, flat-top peaks where a sharp glycolate peak should appear (4 minutes).

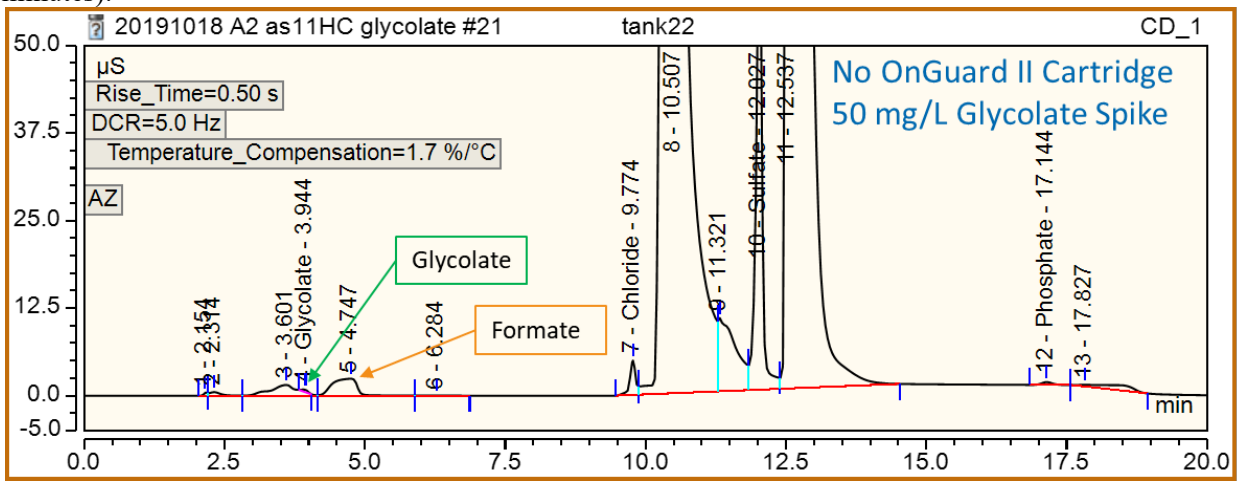


FIGURE 7: A broad, flat-top glycolate peak at 4 minutes in a Tank 22 sample glycolate diluted 1:10

A sharp peak for glycolate is achievable at higher glycolate concentration and/or with more sample dilution to reduce nitrate (e.g., 100-fold dilution and 350 mg/L glycolate) as shown in Figure 8. However, the LOQ in the example becomes 100 mg/L (1 mg/L * 100). To achieve an LOQ of 10-20 mg/L, less dilution in desirable.

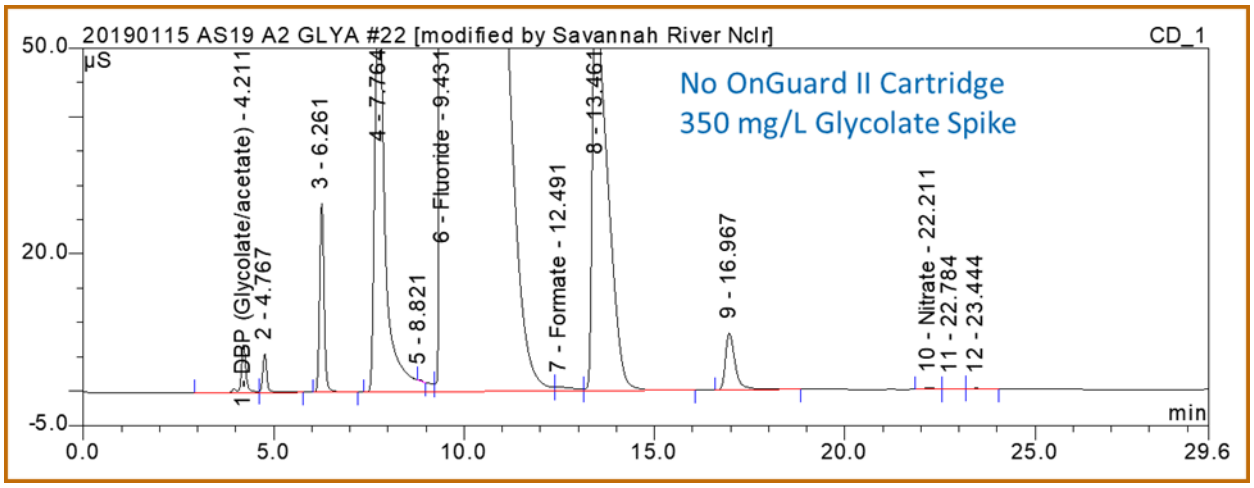


FIGURE 8: Sharp peak at 4.2 minutes for glycolate in a Liquid Waste Sample (LWS) diluted 1:100

OnGuard II Na^+ cartridge pretreatment of Tank 22 supernate with slight dilution (1:10) did not yield usable chromatography as seen in Figure 9. These cartridges are not recommended for use on Tank 22 samples.

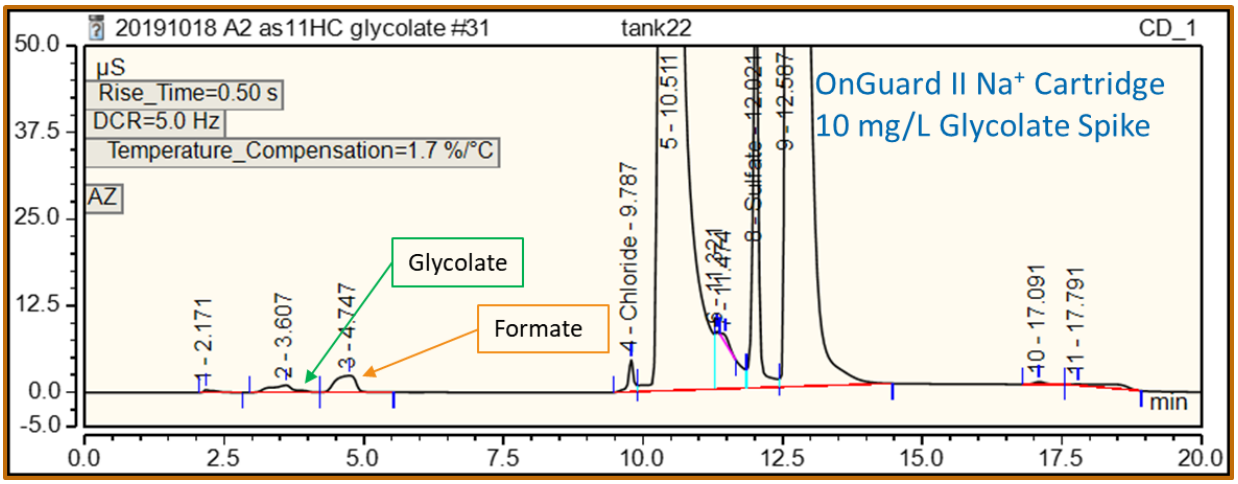


FIGURE 9:Tank 22 sample using OnGuard II Na^+ cartridge pretreatment resulting in poor chromatography illustrating OnGuard II H^+ (next section) are the correct cartridges to use

3.1.2 Results from Dionex OnGuard II H^+ cartridge testing

As shown in Figure 7, poor chromatography of glycolate spiked into Tank 22 at 50 mg/L is observed. The use of OnGuard II H^+ cartridges greatly improved the peak resolution and reasonable data is achieved. No interferences are shown in the blank chromatogram but a trace amount of an interferent does result from the use of the OnGuard II H^+ cartridge. Figure 10 shows the analysis of the deionized water used to dilute the samples (blank), 5 mL of the blank water put through the cartridge and analyzed, and 5 mL of Tank 22 put through the cartridge and analyzed. Both cartridge samples show an interferent where glycolate elutes that quantifies at (n=3) 4.92 mg/L.

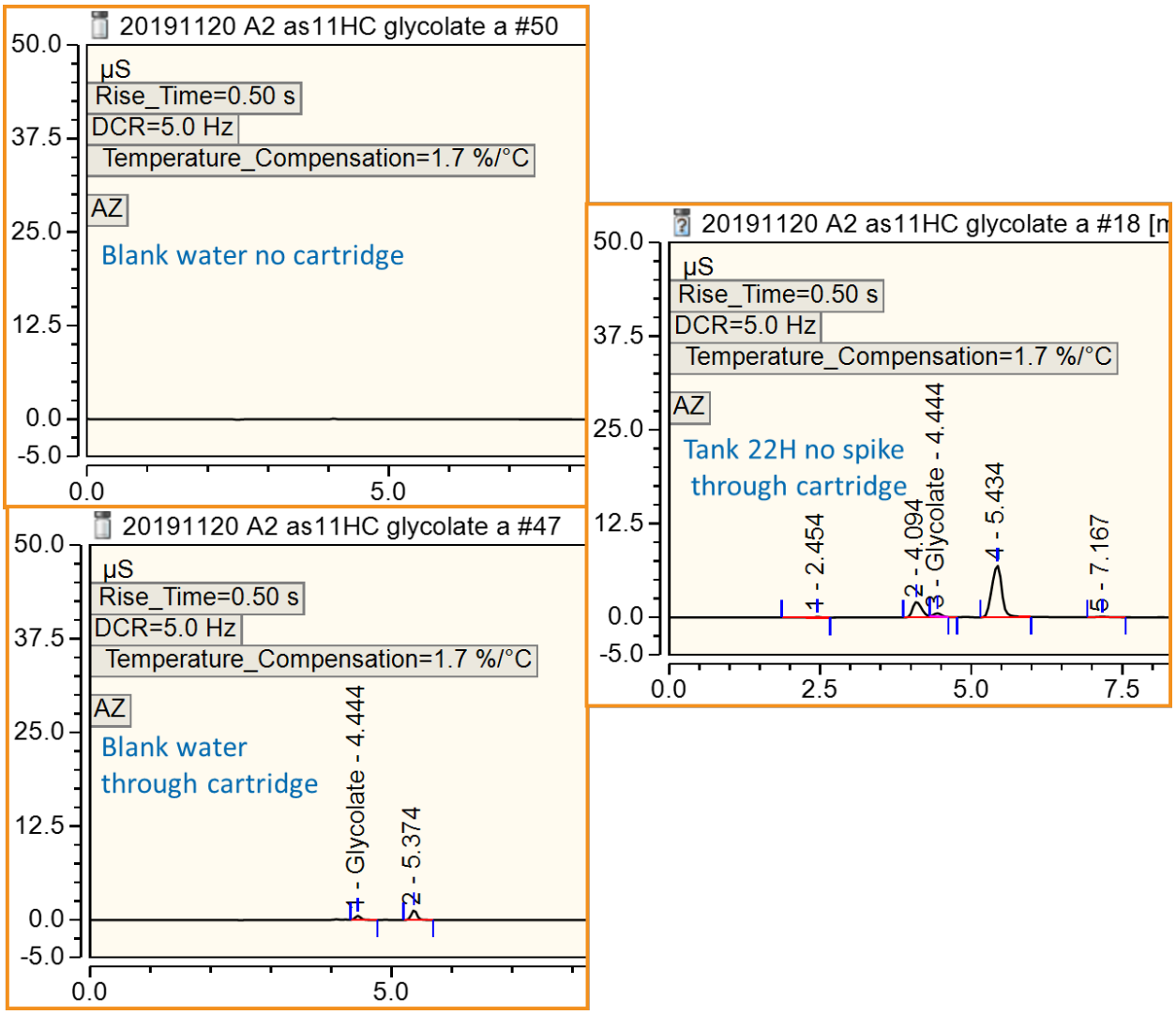


FIGURE 10: Deionized or blank water used for IC analysis shows no interference where glycolate elutes (4.2 minutes) while blank water and Tank 22 material passed through the cartridge (5 mL) shows a low-concentration interferent at 4.2 minutes

The interferent is minimized by rinsing the column with 10 mL of sample prior to sample collection as shown in Figure 11. Cartridge blanks should be analyzed with each set of samples.

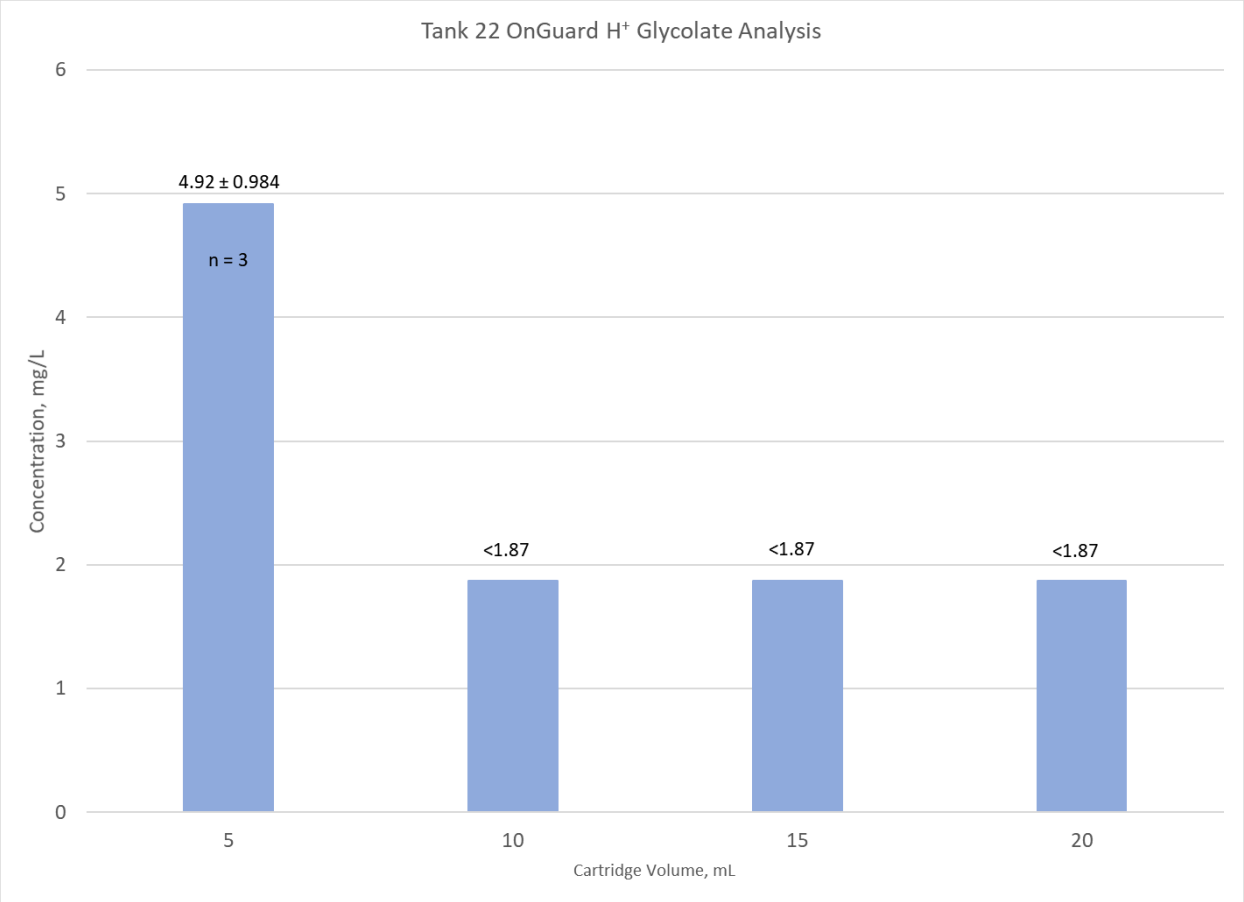


FIGURE 11: Interferent from column in Tank 22 sample that levels out at 10 mL of cartridge volume

We recommend cartridge blank subtraction from the samples as shown in Figure 12. Blanks should be passed through the OnGuard II H^+ cartridge using the same sample protocol as the sample. Tank 22 was spiked at three different concentrations (50, 25, and 10 mg/L) with glycolate. The top orange line shows a positive bias that is reduced especially at the low standard of 10 mg/L when the cartridge blank is subtracted from the sample result as shown by the bottom blue line. At 25 and 50 mg/L, the benefit of the blank subtraction becomes less due to subtracting a relatively large concentration value from a small concentration value. The lines are both linear due to the cartridge step in the sample preparation improving chromatography peak shape. Note that these samples were measured using a low volume (less than 10 mL, providing minimal cartridge rinse), demonstrating the viability of the method for situations where available sample volume is limited. The data highlight the need to analyze cartridge blanks that are prepared the same as the associated samples, and demonstrates the value of subtracting the cartridge blank in generating the highest quality data for Tank 22 samples especially when glycolate is near 10 mg/L in concentration

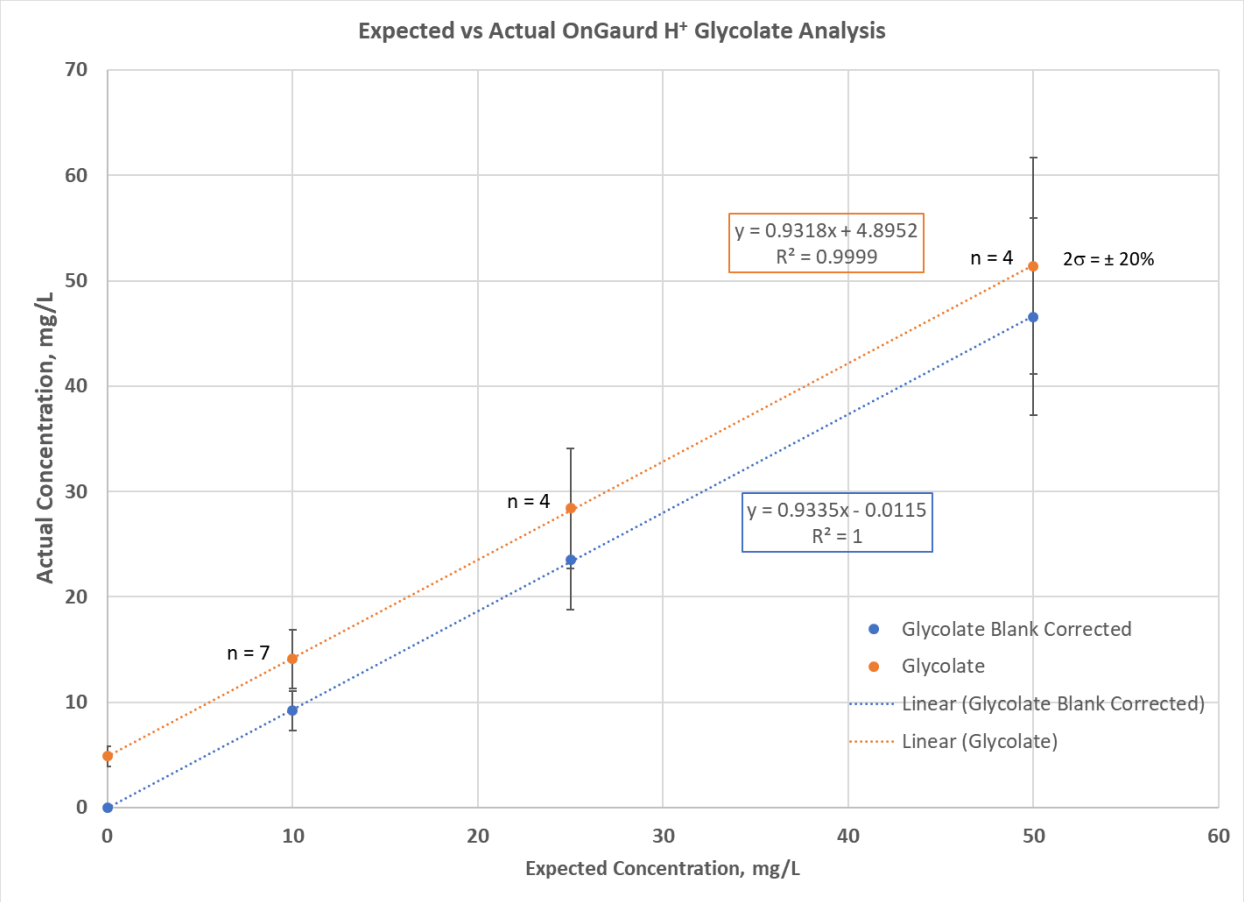


FIGURE 12: Glycolate spiked in Tank 22 at 50, 25, and 10 mg/L showing raw data (top line) and cartridge blank subtracted data (bottom line)

Figure 13 is a summary of the chromatograms showing the improved gaussian glycolate peak at 10, 25 and 50 mg/L using OnGuard II H^+ cartridges. In addition, Limit of Detection (LOD) and Limit of Quantitation (LOQ; 3.3 * LOD) were determined by analyzing a low-concentration glycolate (10 mg/L) spike in the tank 22 sample. Seven 5 mL Tank 22 waste samples were spiked at an amount under ten times the estimated DL (~3 mg/L). The samples were passed through cartridges where the first 2 mL of eluent was discarded, and the last 3 mL of eluent was put into sample vials for analysis. A blank sample was treated the same way and subtracted from the tank 22 glycolate result. The LOD was calculated using the Student's t-value and spiked tank 22 standard deviation value[20]. The Limit of Detection (LOD) is 4 mg/L and the LOQ was determined to be 12 mg/L.

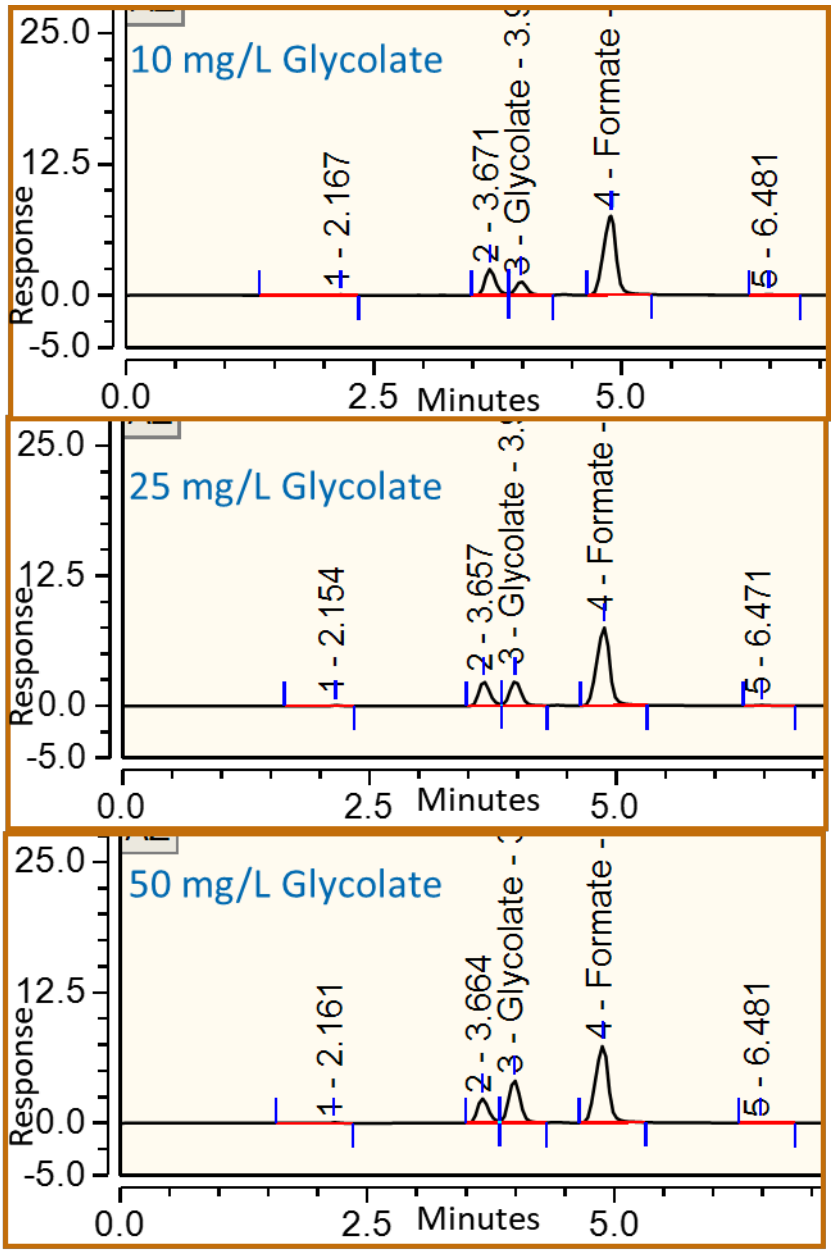


FIGURE 13: Chromatograms showing Tank 22 with 50, 25, and 10 mg/L of glycolate

3.1.3 H NMR analysis of Tank 22 spiked with glycolate

Researchers examined undiluted Tank 22 supernate solutions to assess the viability of H NMR for glycolate quantitation. Figure 14 shows the raw data for an initial method development measurement using a 200 mg/L glycolate standard and a 10 mg/L glycolate spike into Tank 22 supernate. The signals for the two methylene hydrogens (A) and the alpha hydroxide hydrogen (B) is observable in the Tank 22 sample spectrum and match the standard. Additionally, the methylene (A) hydrogens (two hydrogens) were chosen to quantify because of higher peak intensity than peak B (one acid hydrogen). A second test was executed where Tank 22 solution was spiked with 3 concentrations of a glycolate standard. As shown in Figure 15

(inset), the Cauchy-Laurentzian peak shapes that were observed in the methylene signal traces are generally as expected for spectral lines. Using the peak heights measured for the different concentration, the final linear calibration graph for glycolate spiked Tank 22 ranging from 0 to 50 mg/L was well behaved with the intercept near 0 and with a high degree of correlation ($r^2 = 0.998$). The data suggest that the H NMR is an alternative method that can both identify and quantify glycolate at low concentrations (10 -50 mg/L). The glycolate standard was used to identify methylene hydrogens (A) in the Tank 22 sample and help avoid miss identification of the H NMR peak due to some other potential organic interferents.

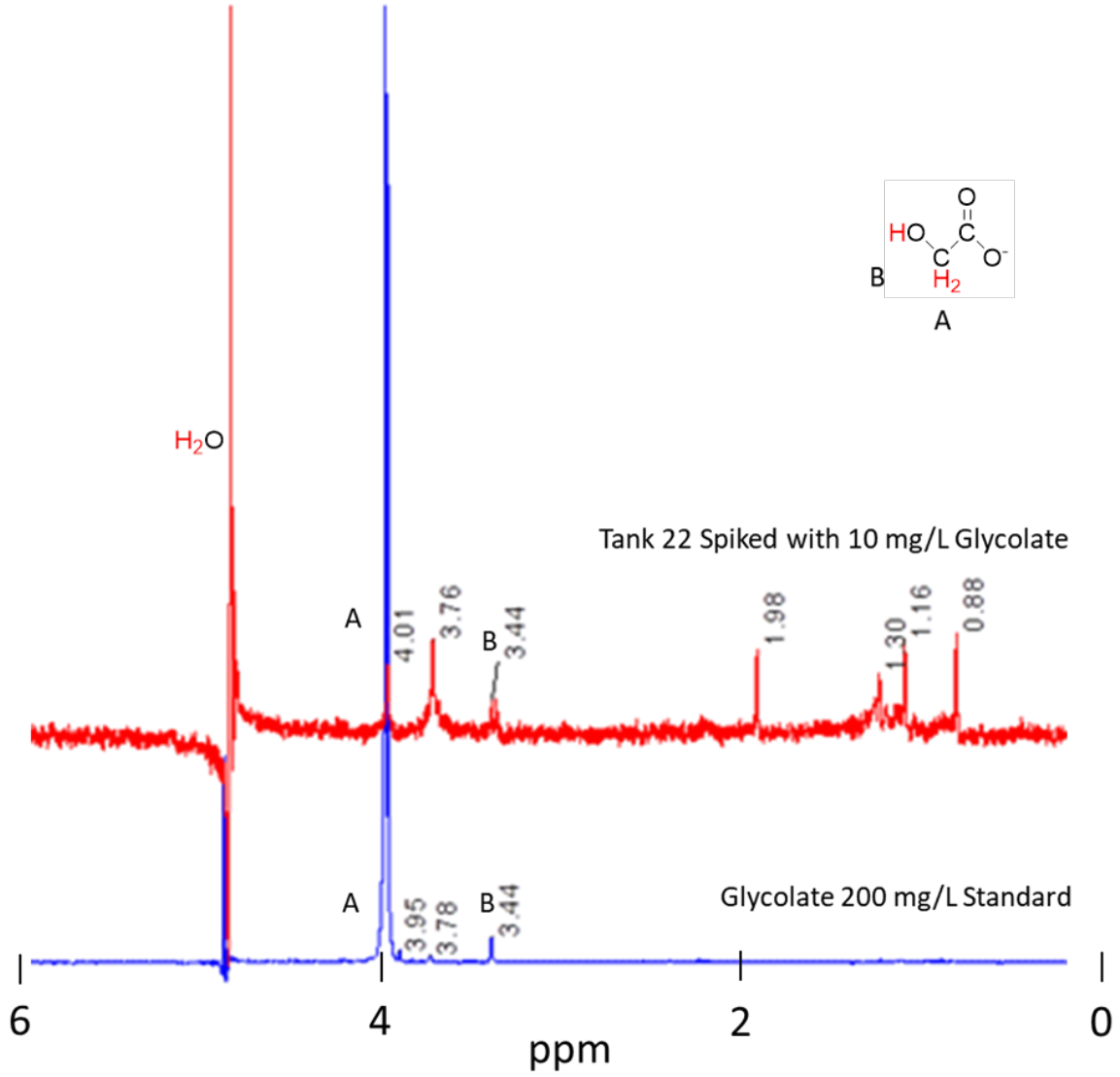


FIGURE 14: H NMR Overlay of 10 mg/L glycolate in Tank 22 and 200 mg/L glycolate standard to ensure correct peak assignment for the methylene hydrogens

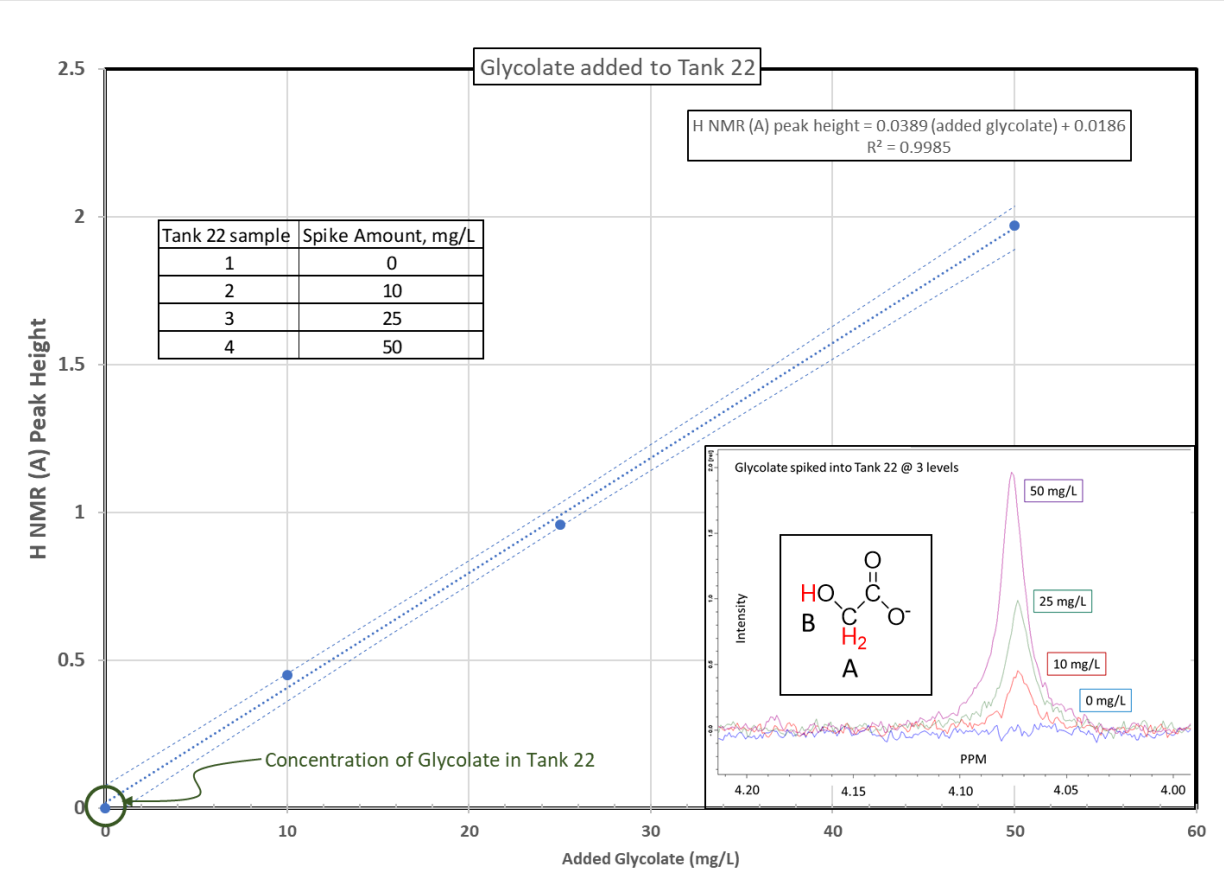


FIGURE 15: Glycolate spiked into Tank 22 at 10 mg/L, 25 mg/L and 50 mg/L analyzed by H (A) NMR

Using standard addition, the developed method was applied to a simulated condensate with properties similar to Tank 22 supernate (see Figure 16). The solution concentration was estimated by projecting the standard addition regression line to the x axis (estimated glycolate concentration = - x intercept). This resulting value, 29 mg/L (2σ ± 14%) glycolate, matches the concentration determined by Ion Chromatography of 33 mg/L (2σ ± 20%) using an OnGaurd II H^+ cartridge, external calibration curve, and blank subtraction.

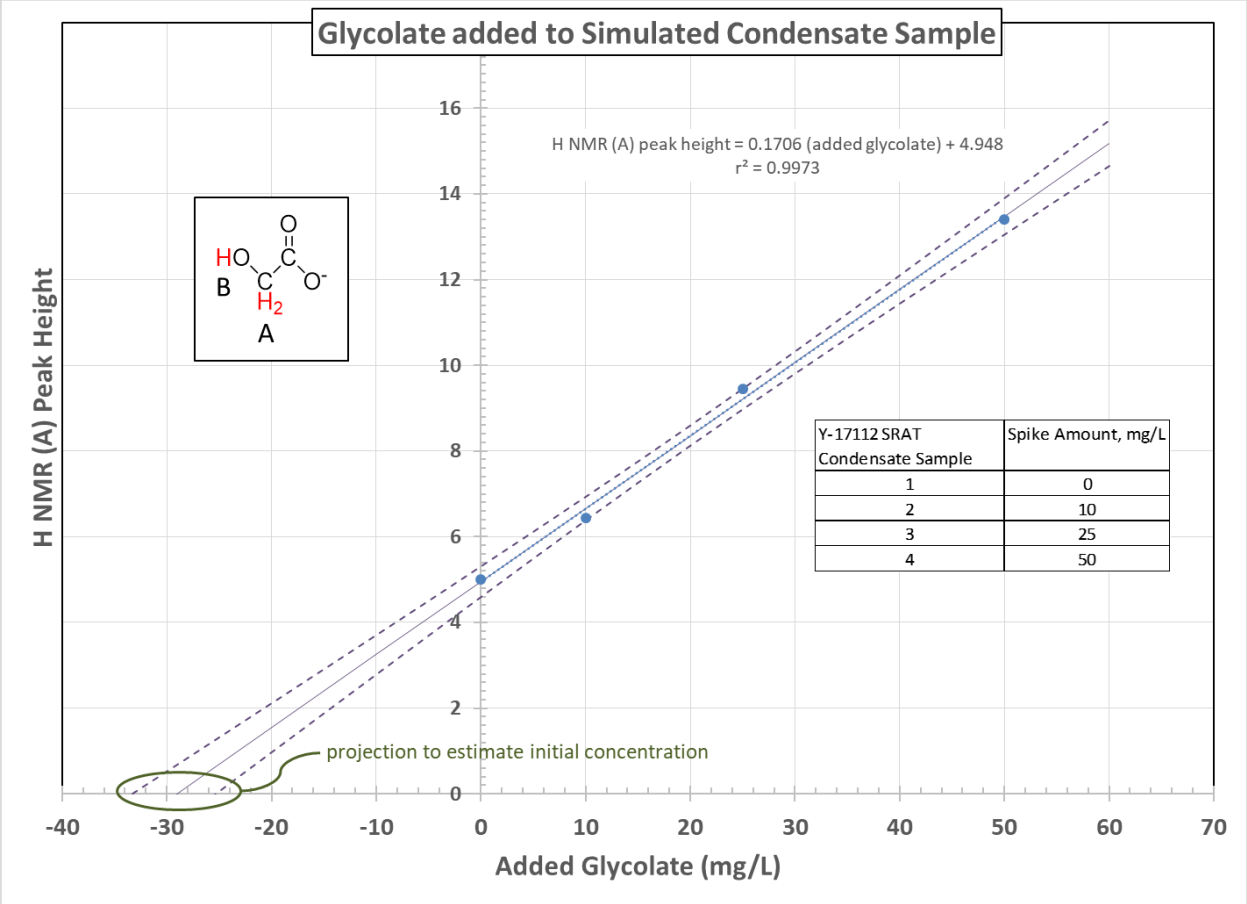


FIGURE 16: Standard addition approach with H (A) NMR to determine glycolate in simulated Tank 22 solution

3.1.4 Results of CST testing to lower radioactivity of Tank 22 supernate

A double strike of CST did not affect measured concentrations of glycolate – there was no statistical difference in the results between untreated and CST treated aliquots of a 20 mg/L spike solution. This methodology is available to lower the radioactivity of Tank 22 samples for handling in containment units without dilution. Figure 17 shows the results of analyses of Tank 22 spiked with 20 mg/L before and after CST treatment. The bars on the left represent the raw data and the right result bars are the data after blank subtraction. These samples (n =5) fall within the ± 20% 2σ uncertainty of the method demonstrating the viability of a CST strike for dose control on Tank 22 samples for glycolate analysis.

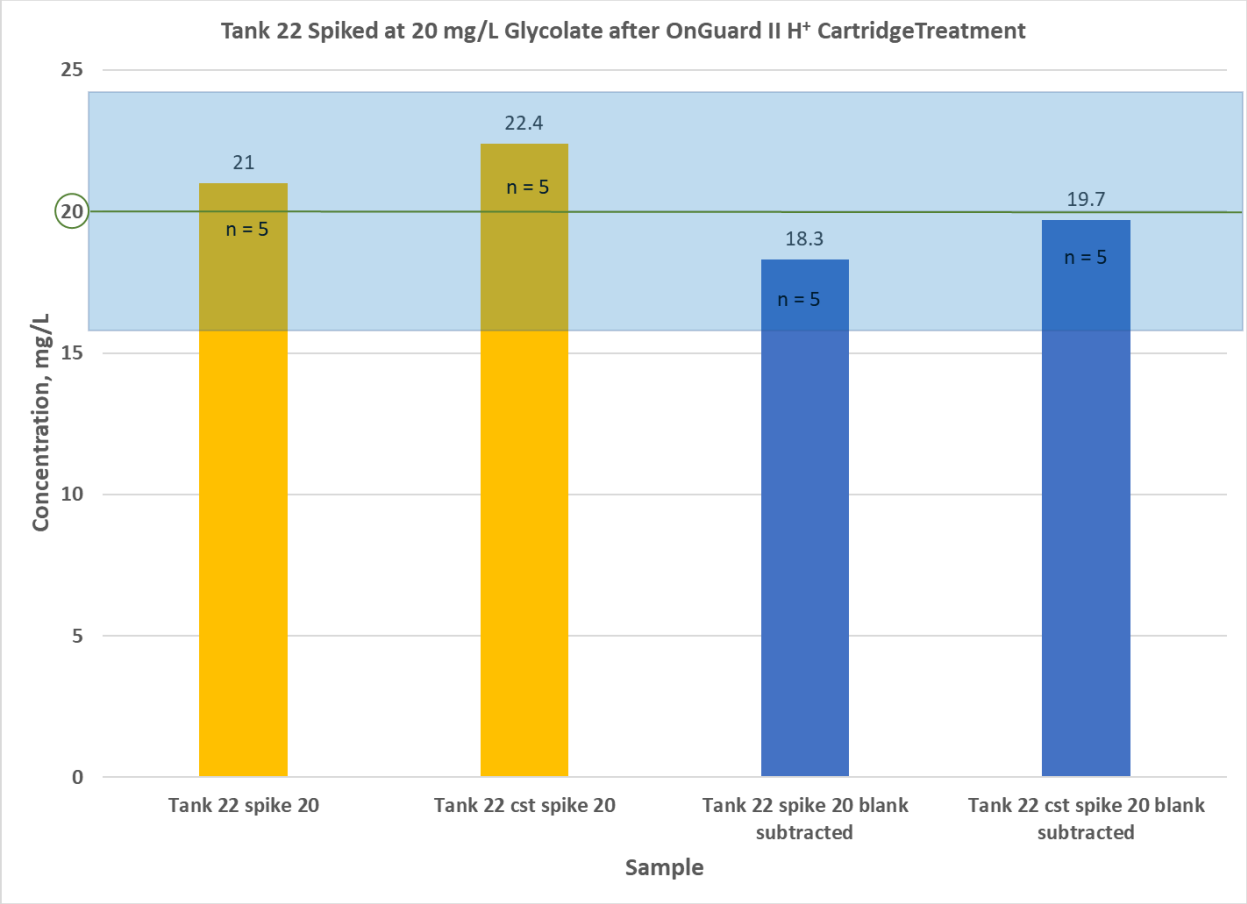


FIGURE 17: Tank 22 spiked with 20 mg/L glycolate with and without CST strike using blank subtraction

3.1.5 Results of CST testing to lower radioactivity of Tanks 30 and 32 supernate

Some initial scoping studies were carried out using Tank 30 and 32 supernate that contains high concentrations of nitrate (~150000 mg/L). Samples spiked with 100 and 250 mg/L glycolate were diluted 1 to 200, treated with CST, and passed through OnGuard II H^+ cartridges, followed by ion chromatography. This protocol did not yield usable data primarily due to the high nitrate and nitrite content of the samples as shown in Figure 18. These samples would need to be diluted 500 to 1000-fold to achieve reasonable ion chromatography which would give a limit of quantitation of 500 to 1000 mg/L. Based on the data, we recommend consideration, and further development, of H NMR as an alternative protocol that may have application to high nitrate samples such as CST treated supernate from Tanks 30 and 32.

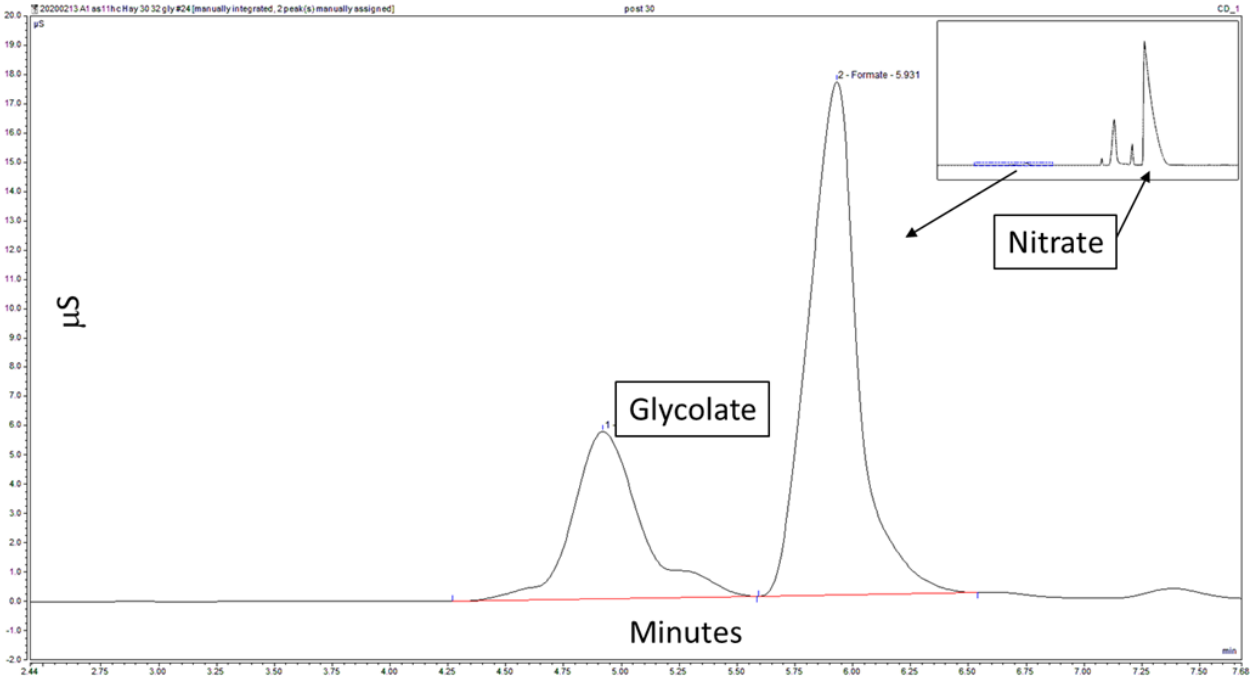


FIGURE 18: Tank 30 sample passed through an OnGuard II H^+ cartridge demonstrating a poor peak shape for Glycolate.

4.0 Conclusions

An IC method has been developed using OnGuard II H^+ cartridge sample preparation prior to analysis that can quantify glycolate down to 12 mg/L ($2\sigma \pm 20\%$) in Tank 22 conditions with an LOD of 4 mg/L. The use of CST to lower radioactivity prior to analysis did not affect the glycolate concentration. When the IC protocol was tried on Tank 30/32 radioactive samples with elevated nitrate concentrations, the method did not resolve glycolate at 250 mg/L. It is estimated glycolate would need to be present in the sample > 500 mg/L to be observed using the IC protocol. A secondary method using H NMR on undiluted Tank 22 was also developed and tested. The H NMR determined glycolate to approximately 10 mg/L and was successfully tested on simulated SRAT condensate that was low in nitrite/nitrate concentration like Tank 22 in matrix composition. Following additional tests, the H NMR method may be applicable to higher nitrate solutions.

5.0 Recommendations

- OnGuard II H^+ cartridges should be used to measure glycolate in Tank 22 samples. Analytical cartridge blanks should follow the sample cartridge protocol and blank values should be subtracted from the glycolate result. Without blanks subtraction, glycolate concentration values near 10 mg/L will be biased high.
- CST strikes can be used to lower the dose rate to personnel handling of Tank 22 samples.
- For LWS samples found in the Chemical Processing Cell (CPC)[21] where glycolate is greater than 2500 mg/L, OnGaurd II H^+ cartridges are not necessary but will not have a deleterious effect on the data.

- SRNL personnel should evaluate the H NMR as a process check (in conjunction with IC) for determination of glycolate in Tank 22 during process sampling events.
- SRNL personnel should develop and expand the matrices analyzed by the H NMR protocol for high nitrate samples such as supernate from evaporator feed and drop tanks. Specifically, follow on work should determine the detection sensitivity regarding glycolate in high nitrate supernate.

6.0 Reference

1. Williams, M. S.; Jantzen, C. M.; Burket, P. R. *Corrosion Testing of Monofrax K-3 Refractory in Defense Waste Processing Facility (DWPF) Alternate Reductant Feeds*; 2016; pp 1-28.

2. Bricker, J. M.; Fellinger, T. L.; Hutsell, D. J.; Hopkins, R. C.; Pickenheim, B. R.; Hansen, E. K.; Peeler, D. K.; Stone, M. E.; Kot, W. K.; Brandys, M.; Mohr, R. K.; Pegg, I. L.; Pasieka, H. K.; Joseph, I.; Diener, G. A., Process Enhancements to Improve Overall Throughput in the Defense Waste Processing Facility at the Savannah River Site. In *Waste Management*, Pheonix, AZ, 2011; pp 1-12.

3. Meyer, V. R., *Practical High-Performance Liquid Chromatography*. Wiley: West Sussex, England, 1988; p 1-376.

4. Miller, J. E.; Brown, N. E. *Development and properties of crystalline silicotitanate (CST) ion exchangers for radioactive waste applications*; Sandia national laboratories: Sandia national laboratories, 1997; pp 1-61.

5. Asci, Y. S.; Incl, I., Extraction of glycolic acid from aqueous solutions by amberlite LA-2 in different diluent solvents. *Journal of Chemical Engineering Data* **2009,** *54*, 2791-2794.

6. Chen, G.; Clark, M. C. *Evaluation of Chemical Additives for Glycolate Mitigation*; Savannah River Site: Aiken, SC, 2018; p 5.

7. Lambert, D.; Peters, T.; Nash, C.; Williams, M. *Task Technical and Quality Assurance Plan for Evaluation of Chemical Additives for Glycolate Mitigation*; Savannah River National Laboratory: Aiken, SC, 2018; p 15.

8. Manual E7 2.60 Rev. 18 *Technical Reviews*; Savannah River National Laboratory: 2019.

9. Savannah River National Laboratory *Technical Report Design Check Guidelines*; Savannah River National Laboratory: 2004; pp 1-19.

10. Savannah River National Laboratory *Electronic Laboratory Notebook*; 2019.

11. White, T. L.; Brown, L. W. *Installation of Dionex ICS 6000 and 5000 Instruments in B-134*; 2019; pp 1-5.

12. Savannah River National Laboratory *Analysis of Ions in Solution Using an Ion Chromatography System*; L16.1 ADS-2310; Savannah River Site, 2019; pp 1-23.

13. Liu, M.; Mao, X.; Ye, C.; Huan, H.; Nicholson, J. K.; Lindon, J. C., Imporved WATERGATE pulse sequence for solvent suppression in NMR Spectroscopy. *Journal of Magnetic Resonance* **1998,** *132* (1), 125-129.

14. Thermo Scientific *Product Manual for Dionex OnGuard II Cartridges*; 2015; pp 1-34.

15. Portanova, R.; Lajunen, L. H.; Tolazzi, M.; Piispanen, J., Critical evaluation of stability constants alpha-hydroxycarboxylic acid complexes with protons and metal ions and the accompanying

enthalpy changes part II. aliphatic 2-hydroxycarboxylic acids. *International Union of Pure and Applied Chemistry* **2003,** *75* (4), 495-540.

16. Karraker, R. H. Stability constants of some rare-earth-metal chelates. Iowa State University, Ames, Iowa, 1961.

17. Kuo, C., Improved application of ion chromatographic determination of carboxylic acids in ozonated drinking water. *Journal of Chromatography A* **1998,** *804*, 265-272.

18. Sillen, L. G.; Martell, A. E., *Stability constants of Metal-Ion Complexes*. Burlington House: London, England, 1964.

19. SeQuant, A Practical Guide to Ion Chromatography. In *SeQuant AB*, SeQuant, Ed. SeQuant AB: Umea, Sweden, 2007; pp 1-26.

20. Electronic Code of Federal Refulations - Title 40 - Chapter 1 - Subchapter D - Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 2, www.ecfr.gov (accessed 4/2020).

21. White, T. L.; Lambert, D. P.; Zamecnik, J. R.; Riley, W. T. *Ion Chromatography (IC) Analysis of Glycolate in Simulated Waste*; Savannah River National Laboratory: Aiken, SC, 2015; p 41.

Distribution:

cj.bannochie@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
Brenda.Garcia-Diaz@srnl.doe.gov
connie.herman@srnl.doe.gov
dennis.jackson@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
Amy.Ramsey@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
eric.skidmore@srnl.doe.gov
michael.stone@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
Records Administration (EDWS)
david.diprete@srnl.doe.gov
fernando.fondeur@srnl.doe.gov
Anthony.Howe@srnl.doe.gov
dan.lambert@srnl.doe.gov
brian02.looney@srnl.doe.gov
chris.martino@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
whitney.riley@srnl.doe.gov
edward.sadowski@srnl.doe.gov
Matthew.Siegfried@srnl.doe.gov
thomas02.white@srnl.doe.gov
Mary.Whitehead@srnl.doe.gov
Wesley.Woodham@srnl.doe.gov
robin.young@srnl.doe.gov

MARIA.RIOS-ARMSTRONG@SRS.GOV
Anthony.bell@srs.gov
Kevin.Brotherton@srs.gov
Grace.Chen@srs.gov
thomas.colleran@srs.gov
joseph.copeland@srs.gov
Richard.Edwards@srs.gov
Daniel.Eitreim@srs.gov
Curtis.Gardner@srs.gov
robert.hoeppel@srs.gov
bill.holtzscheiter@srs.gov
Pauline.Hang@srs.gov
Thomas.Huff@srs.gov
john.iaukea@srs.gov
Spencer.Isom@srs.gov
Vijay.Jain@srs.gov
Jeremiah.Ledbetter@srs.gov
roger.mahannah@srs.gov]
Andrew.Marvel@srs.gov
john.occhipinti@srs.gov
jeff.ray@srs.gov
thomas.temple@srs.gov

Christine.Ridgeway@srs.gov

patricia.suggs@srs.gov