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Title page

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Analysis of Glycolate in Radioactive Waste by Ion Chromatography (IC) and Proton Nuclear Magnetic Resonance (H NMR)

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Abstract

In preparation for implementing the Nitric-Glycolic (NG) acid flowsheet for the Savannah River Site (SRS) Liquid Waste System (LWS), analytical methods for determining glycolate at low concentration, below 20 mg/L in radioactive samples, were developed to support system management and safety. To accommodate the wide range of LWS matrix conditions, two alternative methods were developed, refined, and demonstrated for glycolate analysis in radioactive waste samples: ion chromatography (IC) and a proton nuclear magnetic resonance (H NMR). Investigators validated IC and H NMR methods for glycolate analysis, defined the range of applicability, and demonstrated key supporting analytical protocols. The deployed IC method is applicable in low to moderate ionic strength samples and requires sample pretreatment using a Dionex OnGuard II H^+ cartridge. The deployed H NMR method is more labor intensive but provides options for a broader range of matrices. Based on the results, high quality glycolate analysis of the Defense Waste Processing Facility (DWPF) condensate in Tank 22 is feasible by IC down to approximately 12 mg/L. Using H NMR, glycolate may be determined to 8 mg/L or lower depending on the run time with the potential for broader applicability of the method to higher ionic strength conditions in other tanks of the SRS LWS.

Keywords

Ion Chromatography, Proton Nuclear Magnetic Resonance, Glycolate in Radioactive Waste

Introduction

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) reducing mercury in the CPC cell to elemental mercury for steam stripping, 2) improving the rheology of the liquid waste for processing, 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 like formic acid with the primary benefit of simplified operation since glycolic acid has been shown to have a lower hydrogen generation rate under DWPF acid operating conditions, 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 DWPF recycle before transfer to the LWS waste tanks. Under caustic tank waste conditions found in the LWS, researchers at SRNL demonstrated thermolytic degradation of glycolate leading to the evolution of hydrogen not seen with formic acid [3]. A permanganate oxidation process has been developed to treat and reduce the concentration of glycolate in the recycle stream prior to transfer the Concentraion, Storage, and Transfer Facilities (CSTF). Analytical techniques for the

determination of glycolate in low mg/L concentrations are required to support the Nitric-glycolic (NG) acid flowsheet.

Ion chromatography is currently used to analyze anions at DWPF and the LWS and the application [4,5] of the method to the analysis of glycolate at low concentrations is explored in this work. Additionally, H NMR is a useful tool to verify the presence of carboxylic acid compounds in water. Several literature articles [6-8] from the food industry use this method to identify and quantify carboxylic acids. For application using radioactive waste, a possible protocol would be to use 1) a mixture of titanate ion-exchangers, crystalline silicotitanate (CST) and monosodium titanate (MST), added to the sample to lower the dose rate, 2) standard addition method (SAM) using glycolate [9], and 3) H NMR analysis to identify organic compounds (e.g. methanol, glycolate, aromatics, etc.) and quantify glycolate. In addition to ion chromatography, this paper examines using Water Suppression by Gradient Tailor Excitation (WATERGATE) [10,11] to suppress a large water signal in the spectrum and quantifying the resulting H NMR glycolate peak using SAM.

Experimental

Chemicals and materials

Traceable glycolate (1000 mg/L) was purchased from High-Purity Standards (HPS) and used to generate calibration curves, spikes, and quality control standards. Monosodium titanate (MST) was purchased from Harrell Industries [12] while crystalline silicotitanate (CST) was purchased from Honeywell UOP LLC as IONSIV™ R9120-B. For the Ion Chromatography System (ICS), Dionex OnGuardTM II H 2.5 cc cartridges were procured from Thermoscientific along with IonPac AG11 and AS11 HC 4 mm columns. Norell Select Series 5 mm NMR tubes were purchased from Sigma-Aldrich for use with the Bruker 300 MHz Ultrashield AVANCE Spectrometer.

Dionex Ion Chromatography System (ICS) 6000

Analytical samples for glycolate analysis are prepared and analyzed using a Dionex Ion Chromatography System (ICS) 6000. Figure 1 shows the ion chromatography system

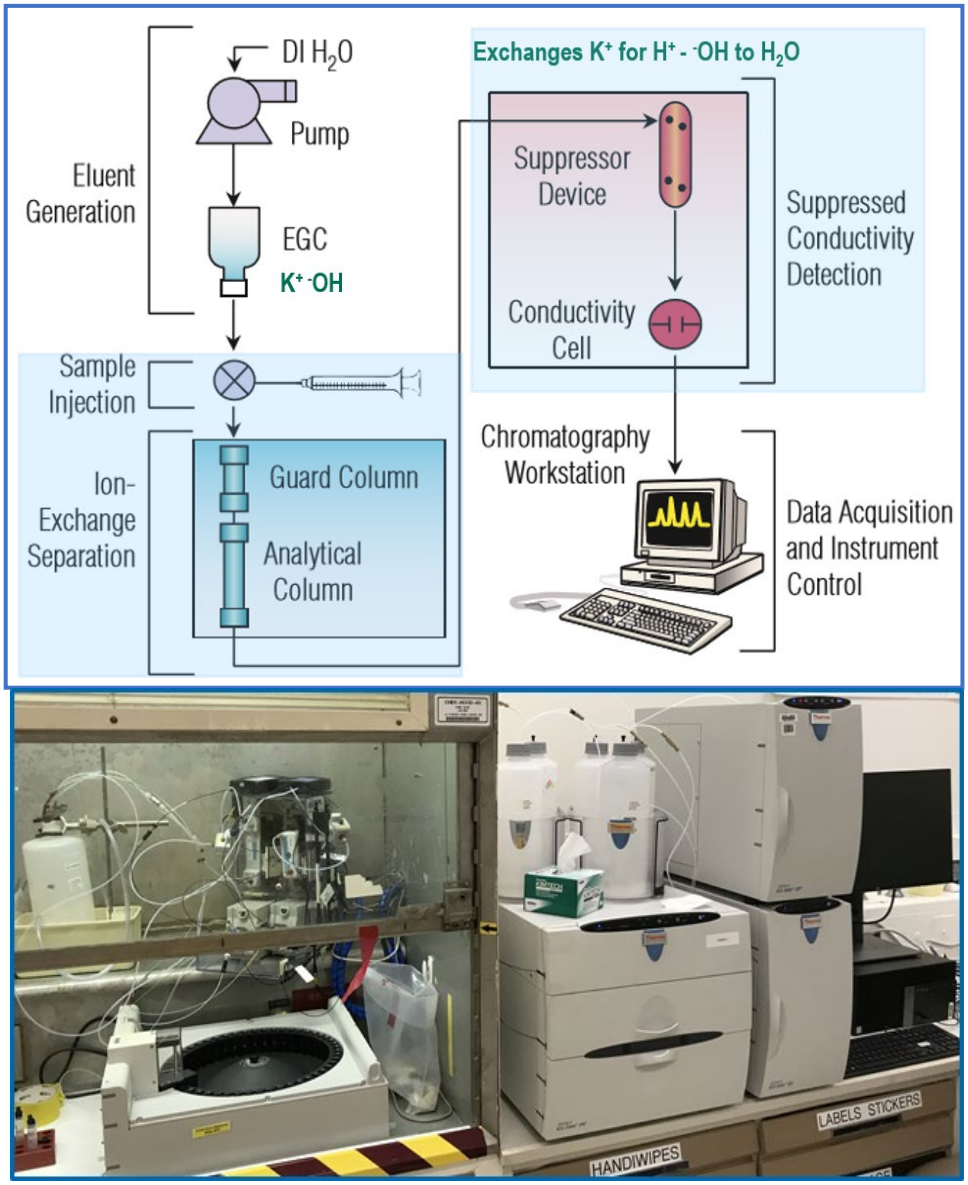


Fig. 1 Ion Chromatography System (ICS) [17] in a Containment Unit (CU) for radioactive sample analysis (note the blue areas housed in the CU)

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.

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

Each tank waste aliquot was diluted 1 to 10 using deionized water (18 MΩ cm) and 15 mL of solution was passed through a Dionex OnGuard II H^+ 2.5 cc cartridge followed by collecting the next 4 mL in a 5 mL autosampler vial for analysis.

Bruker 300 MHz Ultrashield AVANCE Spectrometer

A sample (1.5 mL) of filtered (0.45 micron) waste or simulant sample is pipetted into a Sigma-Aldrich Norell Select Series 5 mm NMR tube maintaining the outside of the tube contamination free. The tube is securely capped and then loaded into the top of the NMR magnet for analysis. For a SAM analysis, all four samples are analyzed in succession with the magnet either unlocked or locked if D_2O is added. Unlocked refers to shimming the NMR magnet to obtain a sharp Lorentzian peak shape of the protons on glycolate followed by an analysis of the batch of samples at 5 minutes a sample. Practically, all samples need to be analyzed within 1 hour to avoid losing peak resolution if the magnet is operated unlocked. To keep the magnet shim for an extended period, the samples need to be D_2O diluted, with loss of some sensitivity. 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 [10,11]. 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). 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).

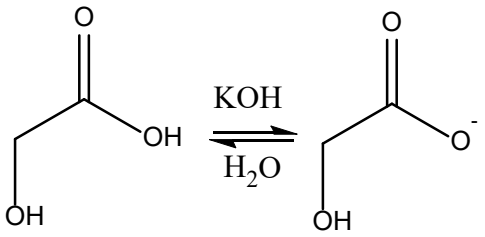
Typical glycolate sample preparation protocol using a mix of CST/MST and SAM

A tank 22 DWPF recycle sample was portioned into 6 mL aliquots. Both D_2O (1.2 mL) and glycolate spikes were added at 6.7, 13.3 and 26.6 mg/L. Each aliquot was treated twice with a mix of 3g CST/1 g MST for a contact time of 10 seconds. The solution containing the titanates was filtered through a PES filter to remove solids and the filtrate was analyzed H NMR.

Results and discussion

Ion Chromatography of Glycolate

Glycolic acid, shown in Figure 2, is a weak acid [13] (pKa = 3.87) that can chelate [14] 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 [15] these matrix effects by removing transition metals and alkali/alkaline earth metals resulting in sharp gaussian peaks [16]. 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

Fig. 2 Glycolic acid and the conjugate base

Each OnGuard II H^+ 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 3 is a pictorial description of the cartridges and resin.

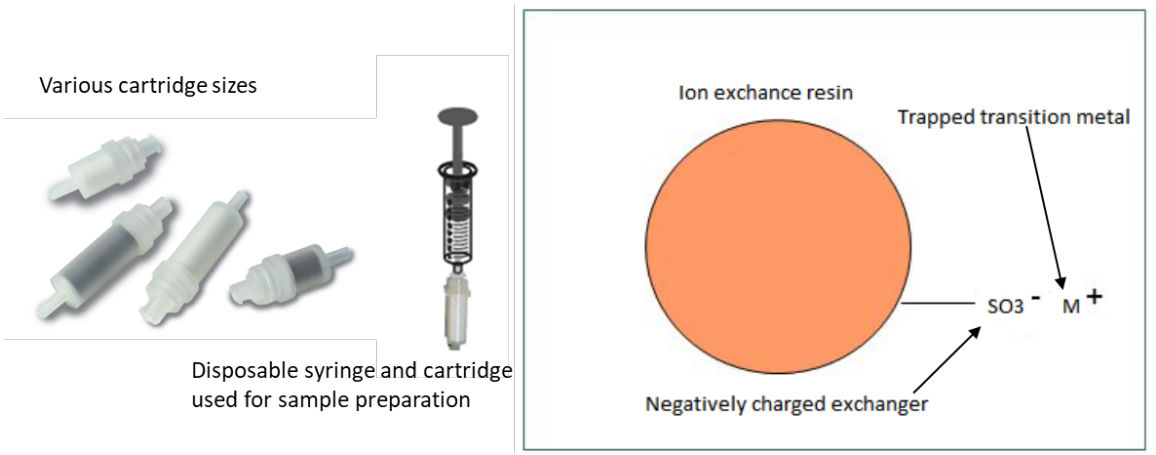


Fig. 3 Dionex OnGuard II H^+ cartridges [16] used to remove matrix effects for low concentration analysis of glycolate

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). The strong acids 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, quadradic calibration 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 4 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).

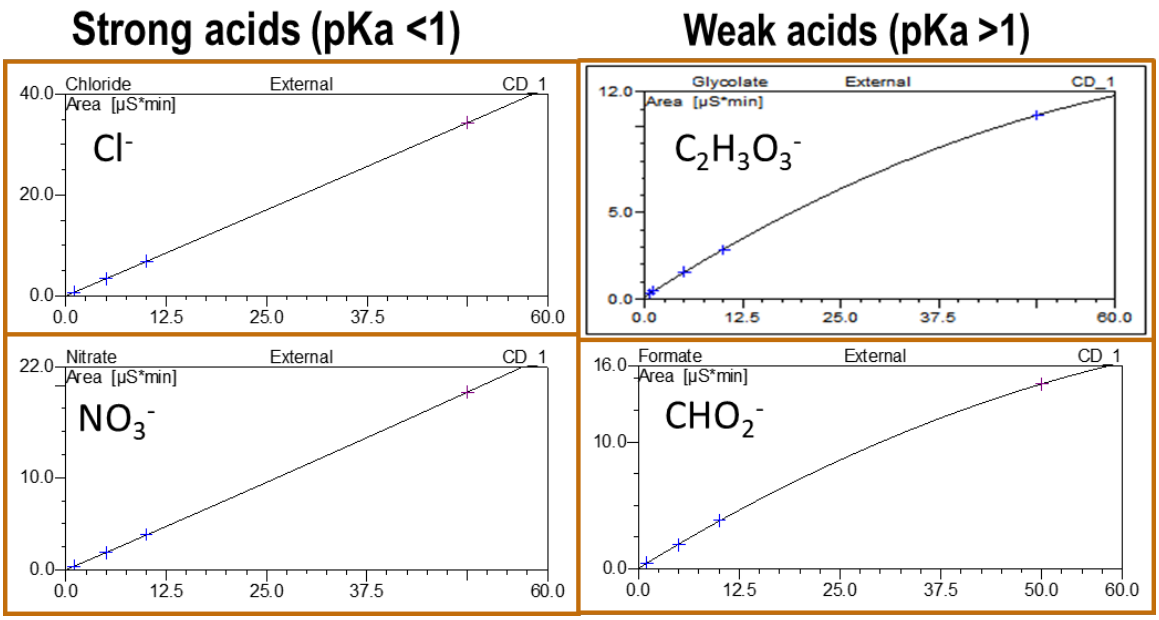


Fig. 4 Linear IC calibration curve for strong acids on the left and quadratic IC calibration curve for weak acids on the right

As shown in Figure 5, poor chromatography of glycolate spiked into a radioactive waste sample at 50 mg/L is observed when OnGuard II H^+ cartridges are not used. The use of OnGuard II H^+ cartridges greatly improved the peak resolution and reasonable data are 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 6).

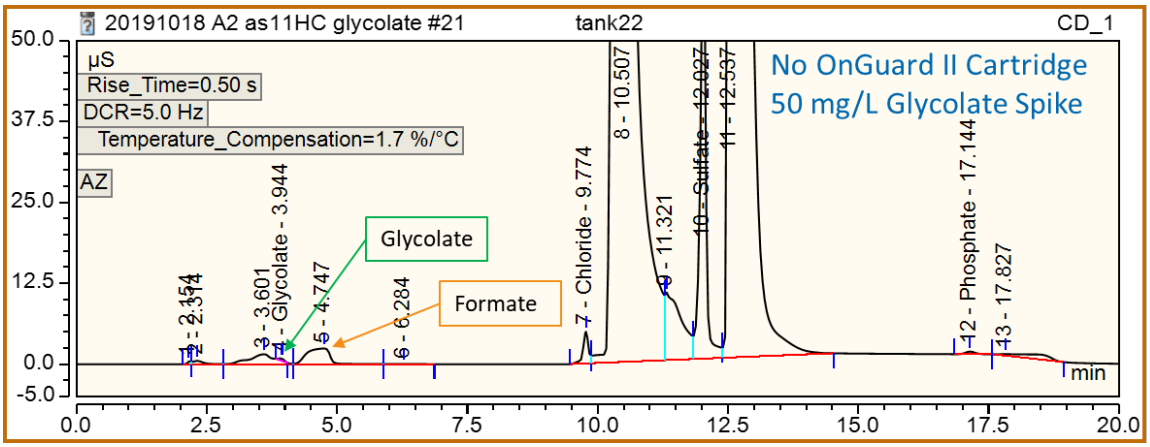


Fig. 5 A broad, flat-top glycolate peak at 4 minutes in a radioactive waste sample diluted 1:10 without the use of OnGuard II Cartridge

Figure 6 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.

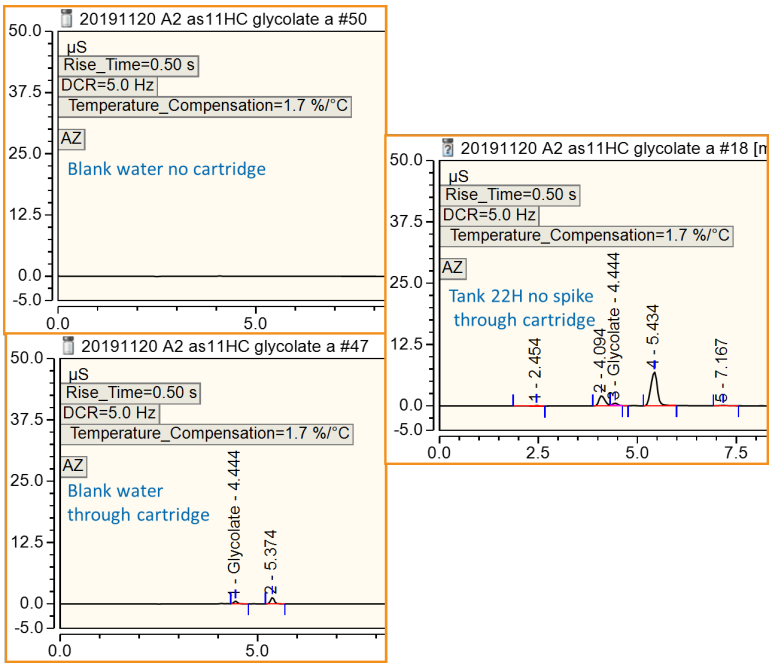


Fig. 6 Deionized or blank water used for IC analysis shows no interference where glycolate elutes (4.2 minutes) while blank water and Tank 22 material passed through the cartridge (5 mL) shows a low concentration interferent at 4.2 minutes

The interferent is minimized by rinsing the column with 10 mL of sample prior to sample collection as shown in Figure 7. Cartridge blanks should be analyzed with each set of samples.

Fig. 7 Interferent from column in radioactive waste sample that levels out at 10 mL of cartridge volume

Figure 8 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 radioactive waste sample. Seven 5 mL radioactive waste samples were spiked at an amount under ten times the estimated LOD (~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 radioactive waste 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.

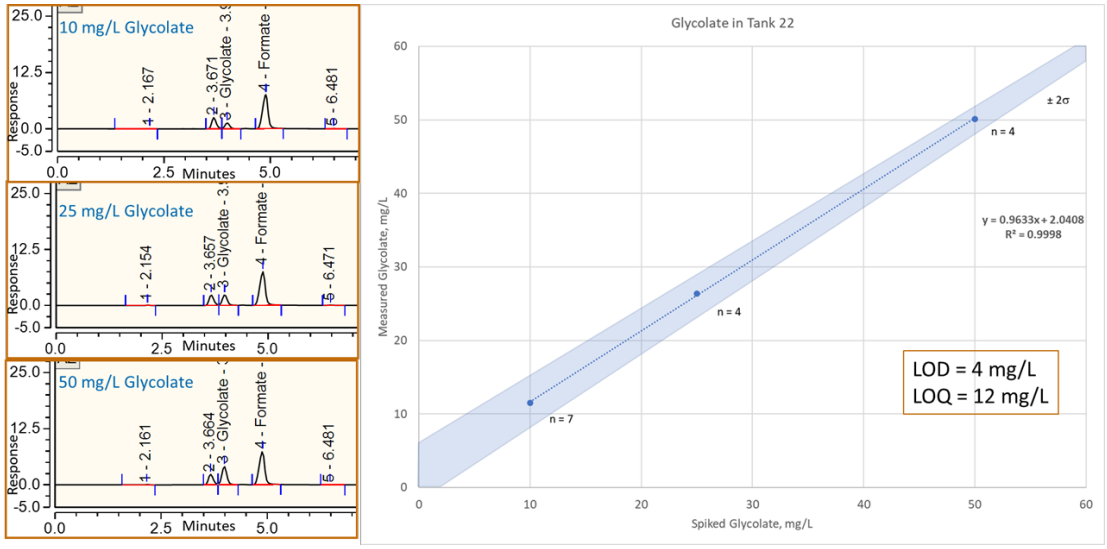


Fig. 8: Chromatograms showing Tank 22 with 50, 25, and 10 mg/L of glycolate used to determine the LOD and LOQ[4]

A recent [21] round robin between three laboratories analyzed glycolate at three concentration levels and the results are shown in Figure 9. Both SRNL and PSAL laboratories flushed the OnGuard II H^+ cartridges with 15 mL of sample followed by collecting the next 5 mL for analysis. These laboratories found similar results near the expected values. The DWPF laboratory flushed the cartridges with approximately 15 mL of deionized water prior to passing 5 mL of sample through the cartridge and collecting the next 4 mL for analysis. This methodology may have slightly diluted the samples leading to decreased glycolate values. The average of the blanks across all laboratories was 2 mg/L indicating a reporting limit (20 mg/L) well above the blank.

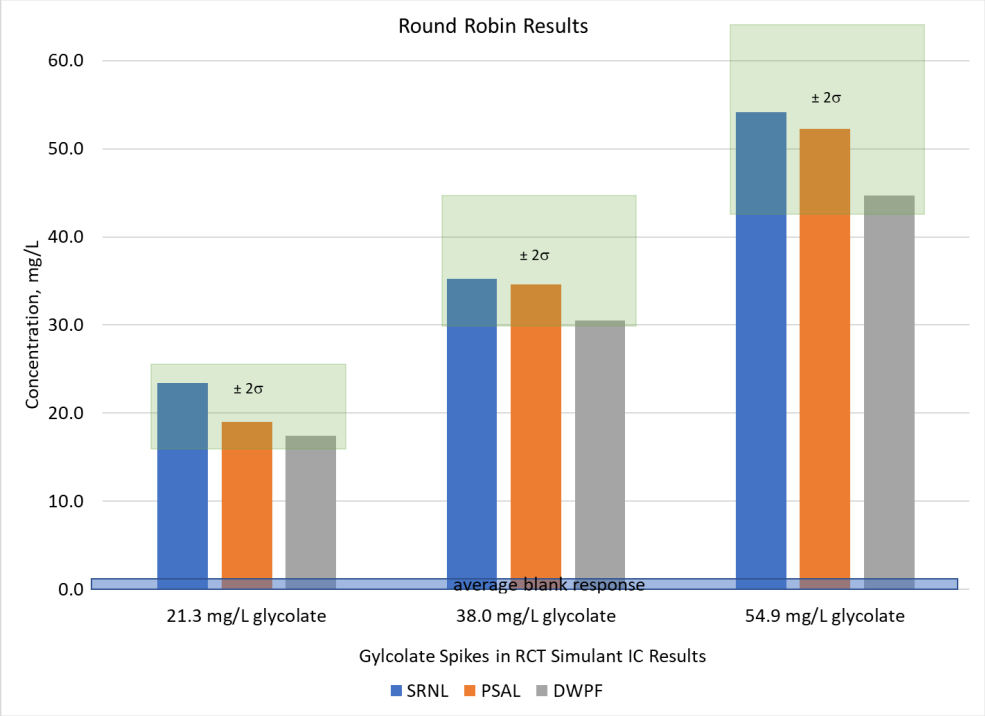


Fig. 9: Results of round robin testing by laboratory using Tank 22 simulanted waste with 50, 25, and 10 mg/L of glycolate [21]

H NMR of Glycolate Quantify by Standard Addition Method

To quantify glycolate, four samples for H NMR analysis are generated from the one tank sample using the standard addition method [9] (SAM). Glycolate is spiked into three of the samples in increasing concentration, the four samples are analyzed for glycolate, and the peak heights are graphed (peak height vs spike amount). The output of a hypothetical SAM quantification is shown in Figure 10 where linear regression is used to determine the glycolate concentration at the x-axis. The sample/spike table describes the concentrations of the spikes. Peak heights corresponding to the nuclear spin relaxation resonance of hydrogen atoms (Figure 10) on the glycolate molecule are plotted versus the concentration of the spike (mg/L) added. The value at the x-axis is negative and reported as an absolute value in mg/L. The 2-sigma error is where the green error line intersects the x-axis above and below the x-axis concentration estimate.

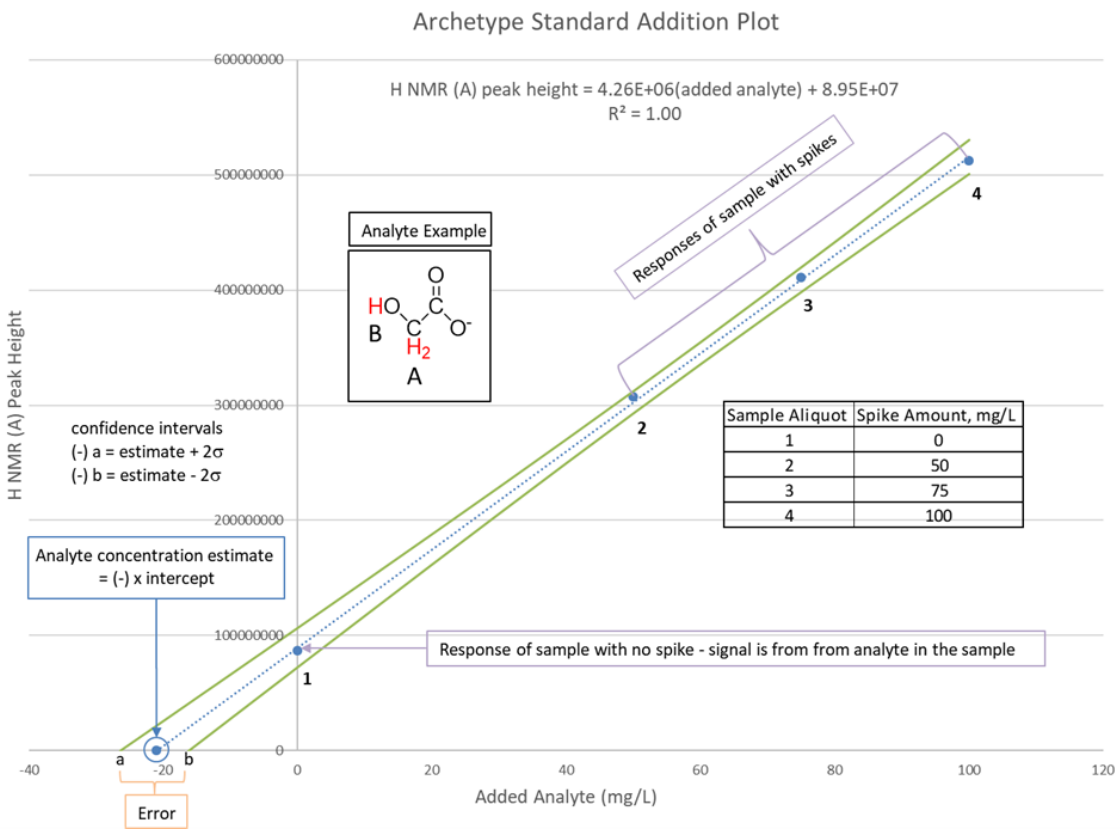


Fig. 10 Archetype standard addition method (SAM) plot

Real waste testing of this method [4, 5] was done on five aliquots (2 mL) of Tank 22 radioactive waste (nominally 1.00E+08 dpm/mL). Figure 11 shows the shows the resulting plot of spike addition vs peak height showing glycolate was not present. Linear regression was used to determine a limit of quantitation (LOQ) of 6 mg/L and a limit of detection (LOD) of 2 mg/L with a linearity of R^2=0.9988. The signal from the methylene group on glycolate is shown on the plot. This methodology was repeated for Tank 22 samples after treatment with ion-exchange titanates (Figure 13).

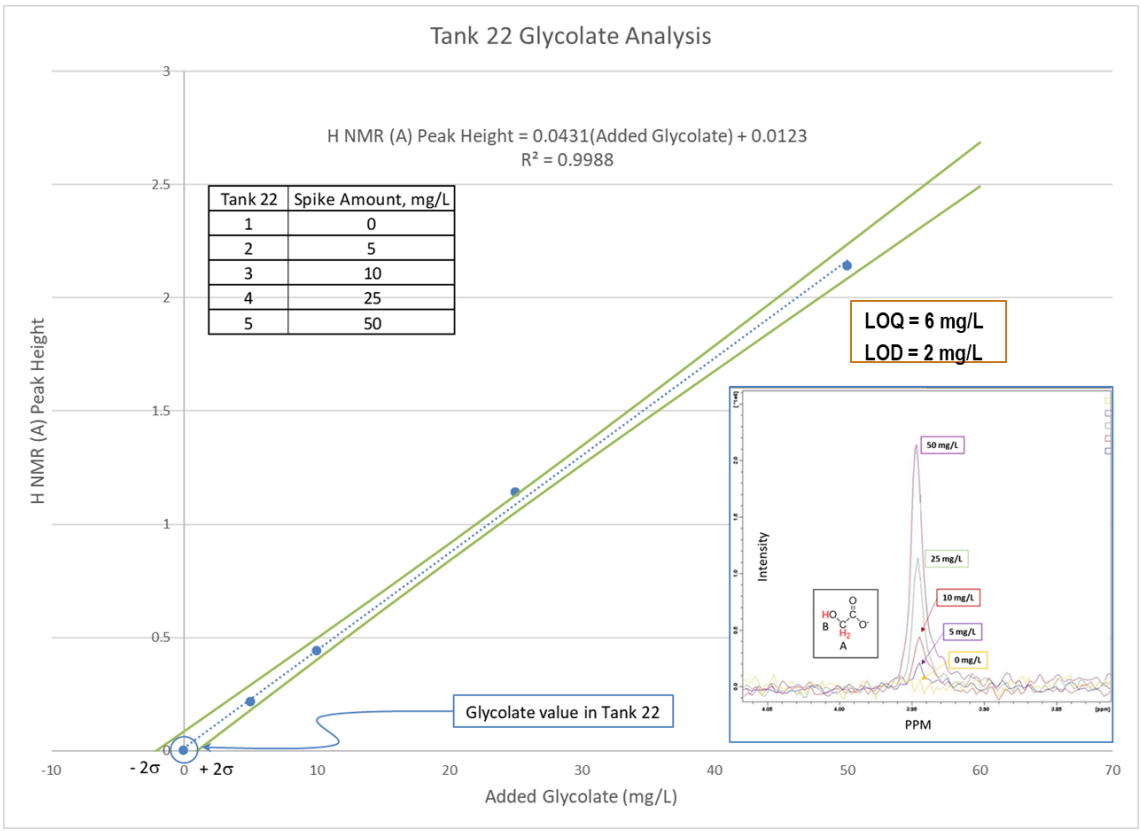
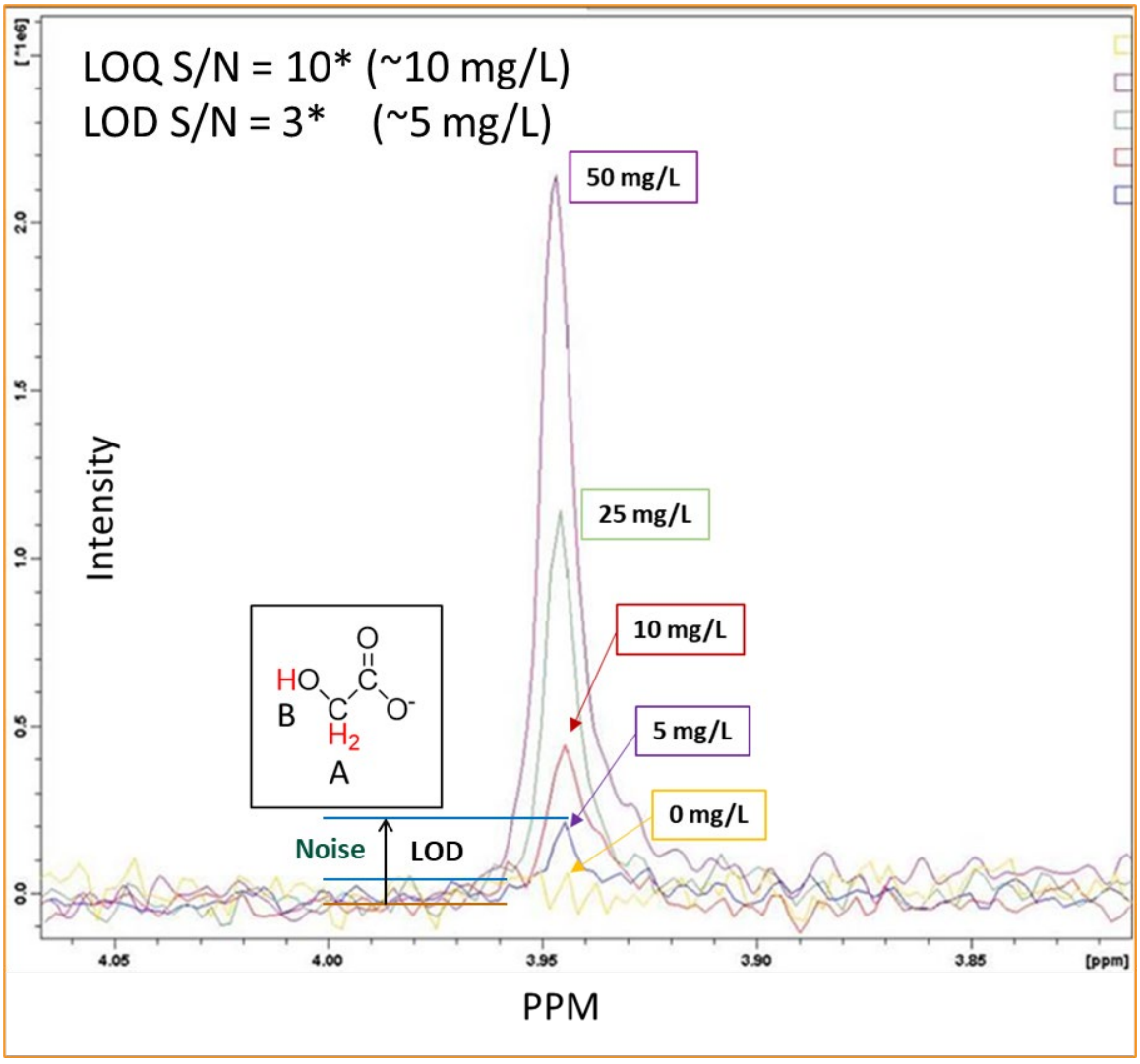


Fig. 11 Unlocked H NMR analysis of glycolate in radioactive tank waste (32 Scans, 9 s)

Figure 12 shows the overlapping spectrum of the CH_2 response (A). The signal-to-noise (S/N) can be used to visually determine the LOD at S/N=3 (~5 mg/L) and the LOQ at S/N=10 (~10 mg/L) [27]. Each response was scanned 32 times at 9 seconds a scan with a total analysis time including sample changeover of about an hour. The S/N increases as the square root of the number of scans $\sqrt{n}$; thus, many scans will be required to improve sensitivity.



32 scans @ 9 seconds a scan

5 mg/L changing scan #

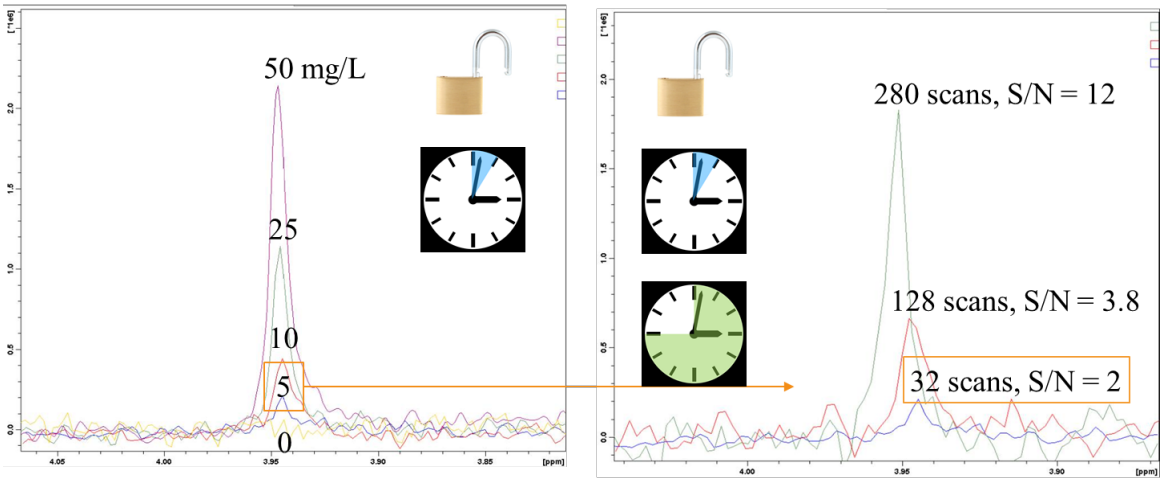


Fig. 12 5 mg/L glycolate in radioactive tank waste analyzed unlocked for different # of scans demonstrating increased sensitivity

Radioactive samples from SRS tank waste often require their dose rate and activity lowered for safe handling when analyzing by H NMR. The removal of Cs-137 and Sr-90 significantly lowers the dose rate and radioactivity for safe sample handling at the NMR instrument. Both MST for Sr-90 and other metals, and CST for Cs-137/Sr-90 have successfully been used to remove these radionuclides [22-24] from strongly alkaline salt solutions [25]. Using CST and MST in tandem is very effective [22-24] and became the final protocol used to decontaminate radioactive samples after initial scoping testing. Other decontamination methodologies including the use of Caustic Side Solvent Extraction (CSSX) solvent, resorcinol/formaldehyde resin, zeolite, and ammonium molybdophosphate-polyacrylonitrile (AMP) were less viable options. These alternative methodologies had the potential to introduce organic impurities and/or would not effectively decontaminate cesium under alkaline conditions. For the effective use of CST and MST in removing Cs and Sr, the concentration of hydroxide should be below 0.5 M. Tank 22 waste samples meet this requirement. Highly caustic radioactive tanks waste (> 0.5 M $^{-}$OH) need pH adjustment with nitric acid to lower the hydroxide below 0.5 M. Additionally, these ion exchange titanates will remove actinides, lanthanides, and paramagnetic elements like iron III. Technetium-99 is not affected by the treatment.

To lower the dose prior to NMR analysis, Tank 22 samples (6 mL, initial 1.08E+08 dpm/mL) were batch treated for ten seconds twice with four grams of titanate ion-exchangers [23, 5] (3 grams CST and 1 gram MST) and filtered each time to remove the main contributors to dose rate, cesium and strontium (final 1.28E+02 dpm/mL). Additionally, paramagnetic elements, actinides, and lanthanides, were removed. The final solution was particle free and low in activity. Ion chromatography was used to show glycolate is not lost to CST, MST, or the PES filter [5] using simulated waste (recovery = 101%). Additionally, any loses would are captured in the error of the standard addition method

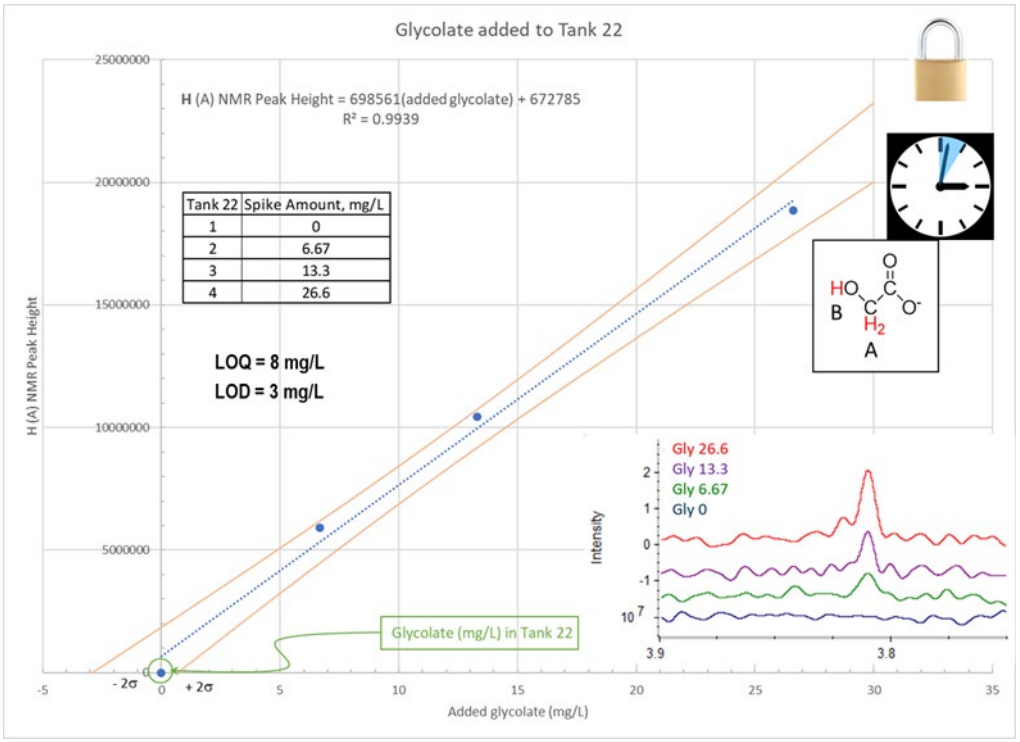


Fig. 13 Locked standard addition method of glycolate in Tank 22 radioactive waste with D_2O and treated with titanate ion-exchangers (32 scans, 9 s) [5]

Similar to Figure 11, glycolate analysis showed linearity ($R^2 = 0.9939$) with an LOQ of 8 mg/L and an LOD of 3 mg/L in a slightly diluted sample. The two experiments give similar LOQs and LODs since the number of scans are the same.

Conclusions

This work extended the analytical capabilities for glycolate analysis in radioactive waste samples by developing and demonstrating an innovative H NMR technique and a novel sample preparation protocol using ion-exchange titanates to lower dose rate. The method allows the user to directly view glycolate in radioactive waste samples with minimal dilution. When compared to IC, this method achieved lower LOQ and LOD values for radioactive waste 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 time consuming and manually labor intensive when compared to IC. Thus, the most appropriate application of the H NMR method should

target determining glycolate at concentration levels below 10 mg/L in DWPF Tank 22 radioactive waste.

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Conflict of Interest Statement (COI)

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