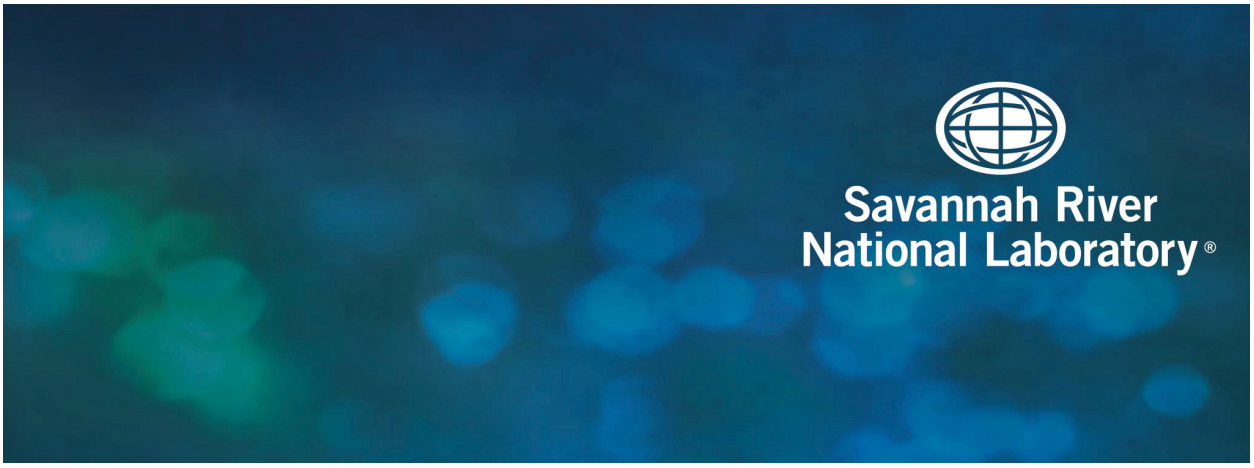
Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:



A U.S. DEPARTMENT OF ENERGY NATIONAL LAB • SAVANNAH RIVER SITE • AIKEN, SC • USA

Ion Chromatography (IC) Round Robin Analyses of Low Glycolate Concentrations in Recycle Collection Tank (RCT) Post Permanganate Treatment Simulant

T. L. White

M. J. Siegfried

W. T. Riley

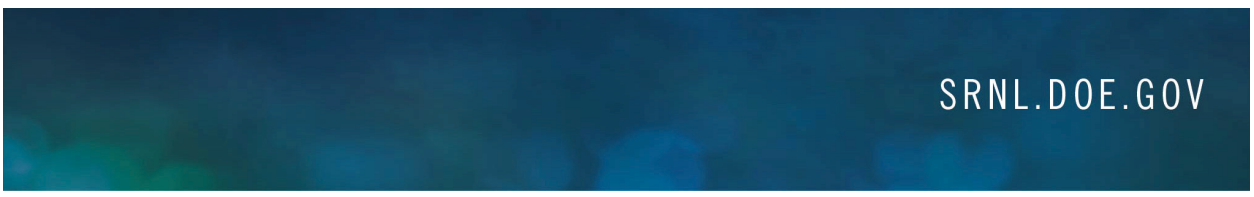
D. P. Lambert

R. N. Mahannah

S. P. Harris

November 18, 2021

SRNL-STI-2021-00476, Revision 0



DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2021-00476
Revision 0

Keywords: *Glycolate*
DWPF
RCT

Retention: *Varies*

Ion Chromatography (IC) Round Robin Analyses of Low Glycolate Concentrations in Recycle Collection Tank (RCT) Post Permanganate Treatment Simulant

T. L. White
M. J. Siegfried
W. T. Riley
D. P. Lambert
R. N. Mahannah
S. P. Harris

November 18, 2021

Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

Savannah River National Laboratory®

REVIEWS AND APPROVALS

AUTHORS:

T. L. White, Sensing & Metrology Date

M. J. Siegfried, Chemical Processing Date

W. T. Riley, Chemical Processing Date

D. P. Lambert, Chemical Processing Date

R. N. Mahannah, DWPF Laboratory Chemist Date

S. P. Harris, Computation and Modeling Date

TECHNICAL REVIEW:

B. B. Looney, Earth & Biological Systems, Reviewed per E7 2.60 Date

APPROVAL:

M. L. Whitehead, Manager Date
Sensing & Metrology

F. M. Pennebaker, Manager Date
Chemical Processing

T. H. Huff, Manager Date
DWPF and Saltstone Facility Engineering

PREFACE OR ACKNOWLEDGEMENTS

The authors wish to thank Holly Hall for adeptly coordinating both shipments of round robin samples to the respective laboratories. Additionally, we would like to thank Stephanie Craig, Kandice Miles, Kimberly Wyszynski, and Daniel Jones for their help in the process of preparing the round robin samples and analyzing them.

EXECUTIVE SUMMARY

This work is a demonstration of Ion Chromatography (IC) analysis of low concentrations of glycolate in chemical simulant designed to mimic the matrix in the Recycle Collection Tank (RCT) at the Defense Waste Processing Facility (DWPF) after sodium permanganate oxidation treatment. The IC method was previously developed [1] and this report covers the results of round robin testing with three analytical laboratories located at the Savannah River Site (SRS). The laboratories are termed the Sensing & Metrology (S&M) laboratory at the Savannah River National Laboratory (SRNL), the Processing Science Analytical Laboratory (PSAL) at SRNL, and the DWPF laboratory at SRS. Each laboratory received four samples: (1) 200 mL of 21.3 mg/L glycolate in RCT post permanganate strike sulfite quenched simulant, (2) 200 mL of 38.0 mg/L glycolate in RCT post permanganate strike sulfite quenched simulant, (3) 200 mL of 54.9 mg/L glycolate in RCT post permanganate strike sulfite quenched simulant, and (4) 600 mL of RCT post permanganate strike sulfite quenched simulant to use for matrix matched blanks.

- Based on results from the round robin that were statistically analyzed using JMP statistical software, a reporting limit of 20 mg/L for glycolate was determined for routine analyses.
- Potential interferences were analyzed and determined to be present at levels below 5 mg/L using this method of analysis.
- A special studies analysis that requires a concerted effort to avoid false positive or erroneous results was determined to have a reporting limit of 10.5 mg/L using JMP statistical software.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CPC	Chemical Processing Cell
CSTF	Concentration, Storage and Transfer Facilities
DWPF	Defense Waste Processing Facility
IC	Ion Chromatography
ICS	Ion Chromatography System
LOD	Limit of Detection
LOQ	Limit of Quantitation
LWS	Liquid Waste System
OGCT	Off-Gas Condensate Tank
P/G	Permanganate to Glycolate ratio
PSAL	Processing Science Analytical Laboratory
RCT	Recycle Collection Tank
S&M	Sensing & Metrology
SAM	Standard Addition Method
SB	Sludge Batch
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility

1.0 Introduction

The Recycle Collection Tank (RCT) at the Defense Waste Processing Facility (DWPF) receives condensate feed from the Chemical Processing Cell (CPC), the vitrification process, and other operations involved in producing borosilicate glass waste forms. The RCT delivers recycle effluent from DWPF processes to the Concentration, Storage and Transfer Facilities (CSTF) for waste storage. When operating the Nitric-Glycolic flowsheet at DWPF, glycolate may be present at low concentrations in the condensate stored in the RCT that could lead to potential flammability issues when transferred to the CSTF. A sodium permanganate treatment has been developed [2] to remove glycolate from the RCT effluent to ensure the CSTF can safely receive the feed. The destruction of glycolate will be demonstrated and monitored using ion chromatography (IC) analysis.

The feasibility and performance of glycolate analysis by IC [1] was demonstrated in a round robin study between the Sensing & Metrology (S&M) laboratory at Savannah River National Laboratory (SRNL), the Processing Science Analytical Laboratory (PSAL) at SRNL, and the DWPF laboratory at SRS on RCT samples. DWPF and PSAL laboratories do not currently have a contained IC system for use in analyzing radioactive RCT samples for glycolate. Thus, the round robin used an RCT simulant based on the DWPF permanganate process. The RCT simulant consisted of RCT permanganate strike heel blended with Slurry Mix Evaporator Condensate Tank (SMECT) product from Sludge Batch 10 (SB10) (pH 1 to 5) and corrosion control chemicals hydroxide and nitrite. This simulant covered a nominal entrainment of glycolate, was low in solids, and sulfite quenched.

One concern is the presence of radioactive cesium in the RCT, primarily from the Melter off gas and process foam over, may result in significant sample dilution to meet sample handling requirements. Additionally, as the Salt Waste Processing Facility (SWPF) processes higher concentration cesium streams, the cesium concentration in the RCT will increase requiring further dilution. As a reference point, Tank 22 H sampling (nearly equivalent to the RCT tank in contents) shows cesium at 1 x 10^8 dpm/mL which means ~10-20 mL of undiluted sample can be safely handled in a containment unit for sample analysis. This sample would be diluted 20 times (200 mL) prior to handling in the containment unit. To mitigate the cesium dose and lower the nitrate peak eluting after the glycolate peak, the simulant was diluted 1:20 prior to analysis.

A second concern is the permanganate strike will introduce impurities that will elute at the same retention time as glycolate on the IC chromatogram. This would lead to a glycolate value that is biased high or a false positive value if no glycolate is present.

The round robin was designed to address these two potential issues. RCT blanks, simulant without the glycolate spike, were included in the round robin to determine IC interferences. Additionally, low (nominal 20 mg/L), medium (nominal 35 mg/L), and high (nominal 50 mg/L) glycolate spikes were part of the round robin to account for varying cell dilutions and demonstrate linearity. Listed below is the round robin protocol where n is the number of times each sample is analyzed.

- RCT post permanganate blank (n = 7) – dilute 1:20 and use OnGuard II H^+ cartridges.
- RCT post permanganate 20 mg/L (n = 7) – dilute 1:20 and use OnGuard II H^+ cartridges.
- RCT post permanganate 35 mg/L (n = 7) – dilute 1:20 and use OnGuard II H^+ cartridges
- RCT post permanganate 50 mg/L (n = 7) – dilute 1:20 and use OnGuard II H^+ cartridges
- 200 mL diluted spike samples and 600 mL of simulant blank were sent to DWPF, SRNL, and PSAL for analysis. Each set of samples were analyzed within 2 weeks of the glycolate spike addition.

All raw data was sent to the Advanced Modeling, Simulation and Analysis group for statistical analysis. This group made the initial recommendation for the 5 to 10 replicates (n) based on Table 1 below where 2 sigma differences between laboratories will be observed. Using data generated from all three laboratories inputted into JMP statistical software, a reporting limit for glycolate above blank interferents was determined.

Table 1-1: Two samples analyzed at separate laboratories

Confidence	Power	Sigma Diff to Detect	Total Sample Size	Samples per Lab
95%	80%	1	34	17
95%	80%	1.25	23	11.5
95%	80%	1.5	17	8.5
95%	80%	2	11	5.5

2.0 Experimental Procedure

2.1 Ion Chromatography System

A complete description of the contained IC system at the S&M laboratory is described in technical report SRNL-STI-2019-00247. Likewise, both the PSAL laboratory and the DWPF laboratory used a Dionex Ion Chromatography System (ICS) with AS-11HC analytical columns. The SRNL IC method used by all laboratories is listed in Table 2-1. A second method was also used by the DWPF laboratory called the DWPF IC method listed in Table 2-2. The DWPF laboratory used both the SRNL IC method and the DWPF IC method for RCT round robin samples and the comparison is in Section 3.6.

Table 2-1: SRNL IC method

SRNL Glycolate Method	
Injection	25 µL
Flow rate	1.1 mL/min
Stop Time	20 min
Guard Column	IonPac AG11-HC 4x50 mm
Analytical Column	IonPac AS11-HC 4x250 mm
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	1.0 mg/L to 50 mg/L, r = >0.995
Retention Time of Glycolate	4.5 min

Table 2-2: DWPF IC method

DWPF Method	
Injection	25 uL
Flow Rate	1.0 mL/min
Stop Time	30.2 min
Guard Column	AG11-HC 4x50mm
Analytical column	AS11-HC 4x250mm
Suppressor	AERS 500
Mobile Phase	2.5-60 mM KOH gradient
KOH conc.at retention time	2.5 mM at 0 minutes
KOH conc.at retention time	2.5 mM at 4.5 minutes
KOH conc.at retention time	20 mM at 13 minutes
KOH conc.at retention time	20 mM at 18 minutes
KOH conc.at retention time	60 mM at 23 minutes
KOH conc.at retention time	60 mM at 27 minutes
KOH conc.at retention time	2.5 mM at 27.1 minutes
KOH conc.at retention time	2.5 mM at 30.2 minutes
Total time	30.2

2.2 RCT Simulant

The RCT simulant represents transfer from the SMECT or Off-Gas Condensate Tank (OGCT) onto the heel in the RCT and approximates the expected compositions of these tanks on a routine basis. The heel

simulants were made from reagent chemicals and from a characterized Sludge Receipt and Adjustment Tank (SRAT) product sample from an SB10 simulant run (Tank 51-3 in Reference [4]) and pre-adjusted with corrosion control chemicals hydroxide and nitrite. Condensate was represented using CPC simulant dewater from an SB10 simulant run (TK51-3 Dewater in Reference [4]). The mass and concentration of RCT simulant components are provided in Table 2-3.

Table 2-3. Mass and Concentration of RCT Simulant Components

	Target	Scoping		Round Robin	
Chemical/Simulant	**Molarity**	**Added (g)**	**Molarity**	**Added (g)**	**Molarity**
50% Sodium Hydroxide	0.220	1.918	0.223	3.836	0.220
Sodium Nitrate	0.008	0.078	0.008	0.159	0.009
Sodium Nitrite	0.187	1.411	0.190	2.817	0.187
Di Water		20.070		43.103	
TK51-3 SRAT Product		0.048		0.086	
TK51-3 SRAT Dewater		80.584		161.171	
20% Sodium Permanganate	0.033	2.496	0.033	5.106	0.032
Sodium Sulfite	0.146	2.005	0.148	4.001	0.146

Residual glycolate concentrations in the RCT simulant were assumed to be 125 mg/kg. To decompose glycolate, sodium permanganate was added at a permanganate to glycolate molar ratio (P/G) of 20:1 and the solution was stirred for 72 hours. Based on prior work [3], Table 2-4 shows the glycolate concentration would be below 0.1 mg/L and thus the remaining glycolate concentration at the sulfite quench step would be negligible as a contributor to the glycolate spike or blank for the round robin study. Sulfite was added at three times the stoichiometric ratio to convert any unreacted permanganate to manganese dioxide solids and allowed to stir for two weeks changing the color from purple to clear with brown solids.

Table 2-4. Predicted Glycolate Concentrations (mg/L)

Initial Glycolate = 35 mg/L						
P/G Ratio	**T = 0**	**2 Hours**	**3 Hours**	**4 Hours**	**6 Hours**	**8 Hours**
10	3.50E+01	1.15E+01	8.06E+00	6.10E+00	4.08E+00	3.12E+00
20	3.50E+01	3.30E+00	1.43E+00	7.08E-01	2.39E-01	1.10E-01
30	3.50E+01	8.97E-01	2.30E-01	7.25E-02	1.19E-02	3.27E-03
50	3.50E+01	6.18E-02	5.48E-03	6.97E-04	2.77E-05	2.76E-06
Initial Glycolate = 65 mg/L						
P/G Ratio	**T = 0**	**2 Hours**	**3 Hours**	**4 Hours**	**6 Hours**	**8 Hours**
10	6.50E+01	9.66E+00	5.36E+00	3.33E+00	1.63E+00	9.45E-01
20	6.50E+01	9.34E-01	2.00E-01	5.33E-02	6.93E-03	1.59E-03
30	6.50E+01	7.94E-02	6.30E-03	7.34E-04	2.51E-05	2.24E-06
50	6.50E+01	5.34E-04	5.85E-06	1.26E-07	3.16E-10	4.27E-12

2.3 First Scoping Round Robin

RCT simulant was prepared that consisted of RCT permanganate strike heel blended with SMECT product from SB10 (pH 1 to 5) and corrosion control chemicals hydroxide and nitrite. This simulant covered a nominal entrainment of glycolate, was low in solids, and sulfite quenched. One purpose of this simulant was to capture all potential analytes that could elute at the same time as glycolate and interfere with the analysis [5]. Three different dilutions of the simulant (Table 2-5) were prepared to capture a dilution range of 20 to 200 and sent to the laboratories. This range of dilutions was set up to examine what dilutions give acceptable chromatography. The final concentration of each dilution was 1.5 mg/L and above the 1 mg/L level of quantification (LOQ) of the instrument. For each dilution, 200 mL of glycolate spiked sample and 200 mL of unspiked glycolate blank sample were sent to each laboratory for analysis.

Table 2-5. First round robin

	Glycolate				
#	Dilution	Nominal spike, mg/L	Spike before sample dilution, mg/L	Sample after dilution, mg/L	Blank, mg/L
A	1 to 20	50 (A)	30.4	1.52	0
B	1 to 100	250 (B)	152	1.52	0
C	1 to 200	500 (C)	304	1.52	0

2.4 Second Round Robin

RCT simulant was prepared that consisted of RCT permanganate strike heel blended with SMECT product from SB10 (pH 1 to 5) and corrosion control chemicals hydroxide and nitrite. This simulant covered a nominal entrainment of glycolate, was low in solids, and sulfite quenched. Three different glycolate concentrations of the simulant (Table 2-6) at the same 1:20 dilution were prepared and sent to the laboratories. The final concentration of each dilution ranged between 1-3 mg/L and above the 1 mg/L LOQ of the instrument. For each dilution, 200 mL of glycolate spiked sample and 200 mL of unspiked glycolate blank sample were sent to each laboratory for analysis.

Table 2-6. Second round robin

	Glycolate				
#	Dilution	Nominal spike, mg/L	Spike before sample dilution, mg/L	Sample after dilution, mg/L	Blank, mg/L
A	1 to 20	20 (A)	21.3	1.07	0
B	1 to 20	35 (B)	38.0	1.90	0
C	1 to 20	50 (C)	54.9	2.74	0

2.5 OnGuard II H^+ Cartridges

As described prior [1], OnGuard II H^+ cartridges improve the chromatography of glycolate at low concentrations in Liquid Waste System (LWS) samples. One caution is rinsing is required to flush sulfate, nitrate, and acetate impurities from the cartridge since they can interfere with the glycolate analysis. The S&M laboratory and the PSAL laboratory pretreated each received diluted round robin sample using Dionex OnGuard II H^+ 2.5 cc Cartridges. For each diluted sample and blank, 15 mL of solution was passed at 2 mL/min through the cartridge and discarded. The next 4 mL of solution was collected in an IC vial and analyzed.

The DWPF laboratory water rinsed each OnGuard II H^+ cartridge with 25-30 mL of water prior to passing 5-6 mL of sample through and collecting the next 4.5 mL for analysis. This difference in cartridge protocol stemmed from DWPF glovebox protocol and sample handling protocol at DWPF limiting the aliquot volume of radioactive RCT sample to approximately 10 mL.

2.6 Quality Assurance

Records for this work are contained in electronic notebook C8102-00273-04. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 RCT Sulfite Quenched Simulant

Destruction of permanganate prior to the addition of the glycolate spike was critical to avoid analyte loss. The purple color of permanganate fades to nearly clear when sulfite oxidizes to sulfate as shown in figure 3-1. Additionally, the samples were analyzed within 2 weeks after addition of the glycolate spike to avoid potential reaction chemistry of Mn^{2+} present in SRAT product [2] oxidizing to Mn^{3+} and aiding in the oxidation of glycolate.

Sulfite Quench Reaction

$$2\ NaMnO_4\ (aq) + 3\ Na_2SO_3\ (aq) + H_2O\ (l) \rightarrow 2\ MnO_2\ (s) + 3\ Na_2SO_4\ (aq) + 2\ NaOH\ (aq)$$

Oxidation-Reduction Reaction

$$2\ Mn^{7+} + 6\ e^- \rightarrow 2\ Mn^{4+}$$
$$3\ S^{4+} - 6\ e^- \rightarrow 3\ S^{6+}$$

Figure 3-1. Sulfite quench reaction

3.2 Testing Simulant with Standard Addition Method (SAM)

Initial testing of the RCT post permanganate strike quenched simulant was performed by spiking in 4 levels of glycolate at 0 mg/L, 1.0 mg/L (1 x 20 = 20 mg/L before dilution), 2.0 mg/L (2 x 20 = 40 mg/L before dilution), 4.0 mg/L (4 x 20 = 80 mg/L before dilution), and 6.0 mg/L (6 x 20 = 120 mg/L before dilution). These samples were analyzed within 24 hours. Linear regression of the data gave a straight line ($R^2 > 0.995$) with an R^2 value of 0.999 as shown in Figure 3-2. This result demonstrated glycolate could be measured in the RCT post permanganate strike quenched simulant down to at least 20 mg/L and in line with a prior [1] LOQ value of 12 mg/L ($2\sigma \pm 20\%$) on Tank 22 radiological samples. The RCT from DWPF feeds Tank 22 and thus this previous work [1] is one example of RCT material meeting the reporting limit of 20 mg/L prior the matrix increasing in complexity with a permanganate strike.

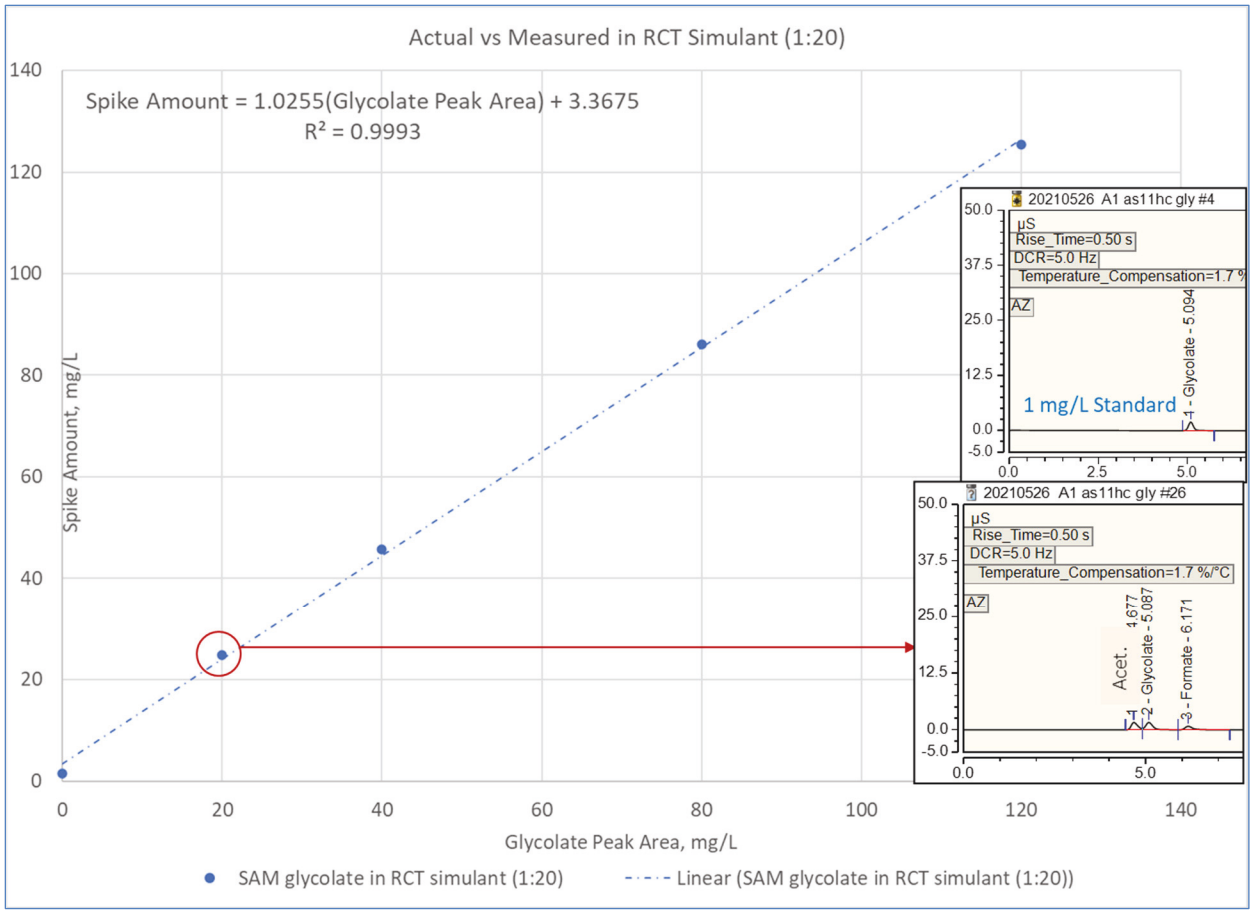


Figure 3-2: SAM on RCT post permanganate quenched simulant showing linearity and response of IC to glycolate in the range of 120 to 0 mg/L after 1:20 fold dilution with OnGuard II H^+ cartridges

The matrix matched blank showed interferences primarily from the use of OnGuard II H^+ cartridges as shown in Figure 3-3. Acetate, glycolate, and formate are added at trace concentrations to the samples. Note in Figure 3-2 the origin does not go through 0 due to impurities.

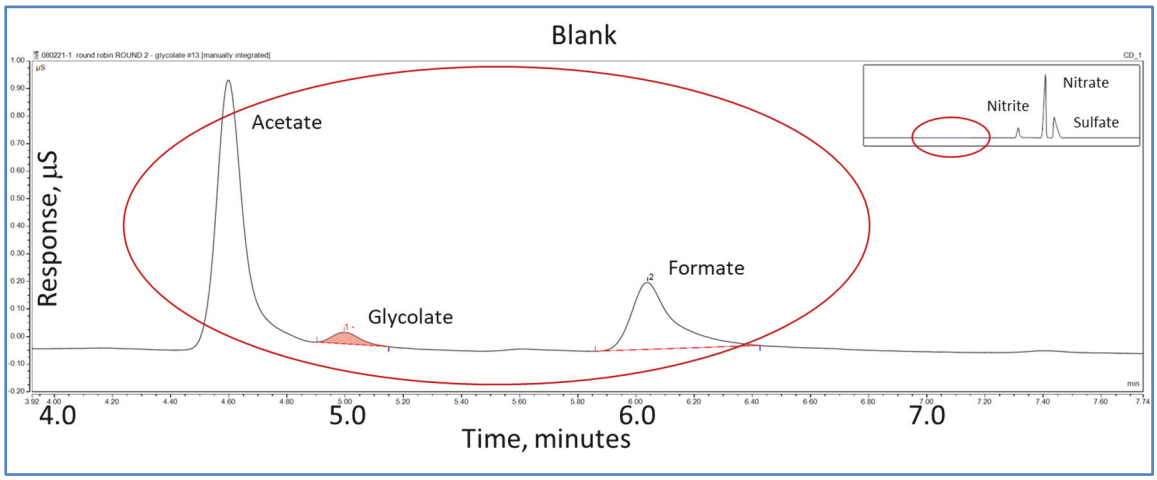


Figure 3-3. Matrix matched blanks showing impurities

These impurities (Figure 3-3) are not problematic in samples where glycolate is > 20 mg/L as shown in Figure 3-4.

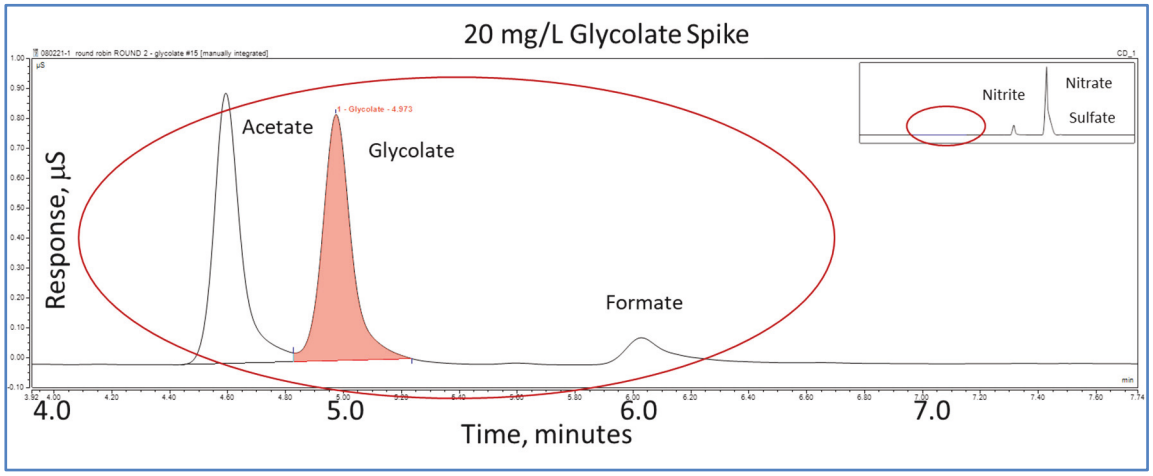


Figure 3-4. Glycolate spike in RCT simulant showing plenty of signal for spilt peak or peak-to-peak integration

3.3 First Scoping Round Robin

Sulfite was used to quench the first-round robin prior to the addition of glycolate on the same day. The samples were analyzed 2 months after makeup where it was determined some glycolate had degraded. This outcome highlights the difficulty of completely halting the reaction between permanganate and glycolate. Table 3-1 shows the results where the 30.4 mg/L Glycolate A samples diluted 1:20 had complete degradation of glycolate. Both the samples and the matrix blank gave similar values of 1 mg/L. The more dilute Glycolate B [152 mg/L] showed 50% degradation and the most dilute Glycolate C [304 mg/L] showed 25% degradation. During the second-round robin section 3.4, steps were taken to avoid degradation and are described there. Regardless, all three laboratories showed similar results. For all laboratories, Glycolate A samples were like the blanks, Glycolate B sample data showed a rsd (%) of + or – 15, and Glycolate C sample data yielded a rsd (%) of + or – 10. Note samples were analyzed using both the SRNL IC method and the DWPF IC method at the S&M laboratory and the DWPF laboratory. In this round robin, the DWPF IC method gave slightly higher values (Table 3-1) than the SRNL IC method.

Table 3-1: Round robin 1 results of degraded samples

Lab (method)	Glycolate A [30.4]	Glycolate A blank [0]	Glycolate B [152]	Glycolate B blank [0]	Glycolate C [304]	Glycolate C [0]
S&M (SRNL)	1.91	1.81	73.5	0.781	223	0.673
PSAL (SRNL)	2.73	3.16	60	6.64	199	10.56
DWPF (SRNL)	2.57	2.40	83.9	9.89	230	18.2
S&M (DWPF)	2.00	1.37	82.1	4.53	230	8.56
DWPF (DWPF)	4.69	4.50	93.4	18.9	259	35.7
Average	2.78	2.65	78.6	8.15	228	14.7
Std. Dev.	1.01	1.10	11.2	6.14	19.2	11.9
rsd(%)	36.2	41.7	14.3	75.3	8.39	80.6

Notes
(Ion chromatography method used; SRNL or DWPF)
[Calculated Concentration Corrected for Diluion, mg/L]
Nominal Concentration: A = 50 mg/L diluted 1 to 20, B = 250 mg/L diluted 1 to 100, C = 500 mg/L diluted 1 to 200

3.4 Second Round Robin

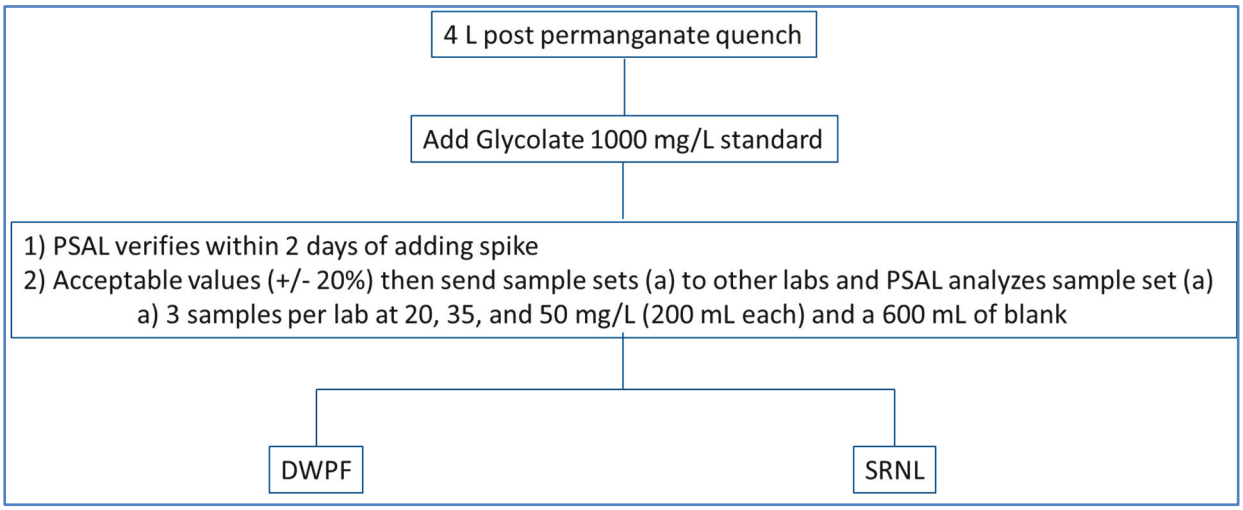


Figure 3-5: Round robin 2 verification and shipping schematic

Several good practices were undertaken to avoid glycolate degradation. Figure 3-5 is a schematic of the process of adding the glycolate spike at PSAL, verifying at PSAL (Table 3-2), and shipping the approved samples to the S&M laboratory and the DWPF laboratory for analyses within 2 weeks to avoid glycolate degradation. Additionally, the quenched simulant was "aged" for 1 week prior to spiking and verifying the concentration at PSAL as shown in Table 3-2. Thus, each laboratory received a calculated value of 21.3 mg/L, 38.0 mg/L, and 54.9 mg/L for glycolate, and which was confirmed at PSAL within 24 hrs. of the spike addition. All samples were analyzed within 2 weeks of shipping and Appendix A has a summary.

Table 3-2: Round robin 2 samples prior to shipping

Sample	Gly20	Gly35	Gly50
Calculated concentration, mg/L	21.3	38.0	54.9
PSAL check, mg/L ($2\sigma \pm 20\%$)	19.3	37.3	54.8

3.5 Second-Round Robin Results Using the SRNL IC Method

Table 3-3 summarizes the round robin results for each laboratory. All laboratories demonstrated a narrow range for precision on analysis of 21 spiked samples (rsd(%) < 4). DWPF had a low bias of about 20%. This laboratory analyzed samples a few day later than PSAL and S&M due to shipping time and some degradation may have occurred. Additionally, some sample dilution may have occurred during the sample preparation step using the OnGuard II H^+ cartridges. Personnel at the DWPF laboratory water rinsed their cartridges to remove impurities prior to passing 5 to 6 mL sample through and then collected about 4 mL for analysis. The Dionex OnGuard II Cartridge product manual recommends a minimum of 6 mL [7]. Both SRNL and PSAL passed 15 mL of sample through prior to analysis. The additional 10 mL of sample rinse would be sufficient to remove all water and avoid potentially slight dilution of the sample. The difference in protocol is a result of limited sample volume DWPF personnel can handle in a glove box and represents how radioactive RCT material will be handled at DWPF.

It is important to note that the average of the blanks across all laboratories was 2 mg/L indicating a reporting limit well above that value should be set to avoid false positive results. This data suggests a reporting limit of 20 mg/L (10 x higher) is established. The SRNL IC method with split peak or valley-to-valley integration produced the most accurate glycolate values.

Table 3-3. Second round robin results

SRNL IC method						
SRNL laboratory	Day1	Day1	Day2	Day2	Day3	Day3
#	Gly20	Gly20blank	Gly35	Gly35blank	Gly50	Gly50blank
1	23.5	2.39	35.1	1.168	54.1	1.18
2	23.6	2.26	35.0	1.113	54.5	1.29
3	23.5	2.49	35.3	1.231	54.6	1.21
4	23.9	2.34	35.3	1.046	54.1	1.21
5	23.5	2.43	35.2	1.048	54.2	1.08
6	23.2	2.39	35.3	1.052	54.1	1.42
7	23.2	2.53	35.1	1.071	54.2	1.23
Average	23.5	2.40	35.2	1.10	54.2	1.23
sd	0.194	0.084	0.112	0.066	0.176	0.098
rsd(%)	0.83	3.47	0.319	5.98	0.3236	7.93

SRNL IC method				
PSAL laboratory	Day1	Day1	Day1	Day1
#	Glyblank	Gly20	Gly35	Gly50
1	0.924	19.3	37.3	54.8
2	1.87	20.5	35.4	53.3
3	1.76	19.0	34.4	51.9
4	1.75	18.7	34.3	50.7
5	1.49	18.5	33.4	52.4
6	1.62	19.0	33.4	50.4
7	1.55	17.9	33.9	52.0
Average	1.57	19.0	34.6	52.2
sd	0.288	0.731	1.29	1.40
rsd(%)	18.4	3.85	3.72	2.67

SRNL IC method						
DWPF laboratory	Day1	Day1	Day2	Day2	Day3	Day3
#	Gly20	Gly20blank	Gly35	Gly35blank	Gly50	Gly50blank
1	17.0	3.21	31.0	3.18	43.9	3.37
2	17.1	3.39	30.9	3.48	44.2	3.21
3	17.3	3.34	30.7	3.37	44.4	3.33
4	17.5	3.24	30.3	3.38	44.8	3.45
5	17.4	3.35	30.8	3.43	44.9	3.40
6	18.1	3.43	30.2	3.28	45.1	3.43
7	17.7	3.31	29.9	3.25	45.3	3.77
Average	17.4	3.33	30.5	3.34	44.7	3.42
sd	0.334	0.0709	0.364	0.0992	0.459	0.161
rsd(%)	1.92	2.13	1.19	2.97	1.03	4.70

Figure 3-6 compares the laboratory results at each glycolate spike level. Overlap was observed for the error ($2\sigma \pm 20\%$) bars of all three laboratories at each spike level. Additionally, the average blank response was about 10 times lower than the 21.3 mg/L analyte response. This means at a glycolate concentration of 20 mg/L there is plenty of response to observe and interferences will not significantly affect the results.

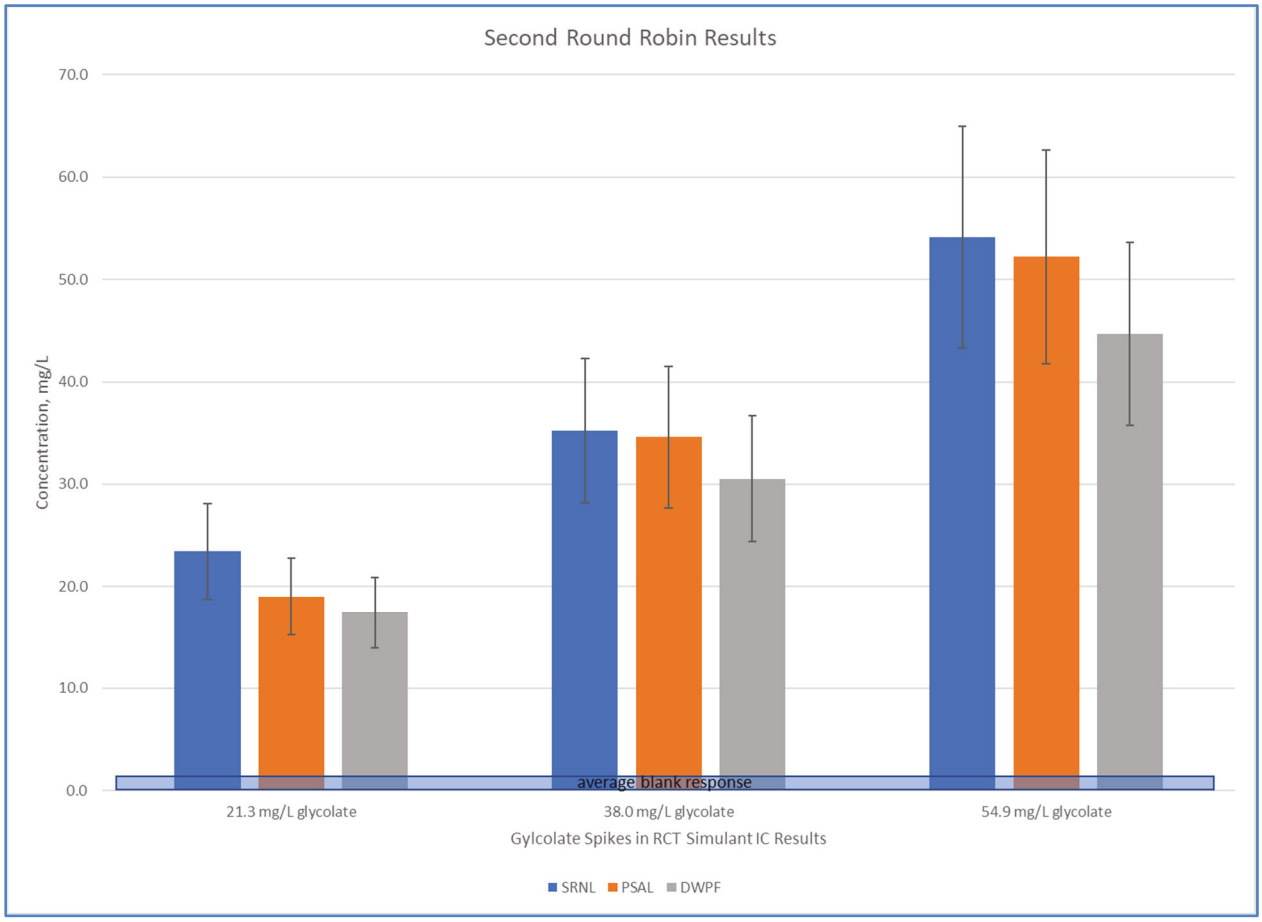


Figure 3-6. Second round robin results by laboratory including the average blank response (blue bar on baseline) using the SRNL IC method

3.6 Second Round Robin using DWPF IC Method

Slightly lower values (about 4%) for glycolate were observed using the DWPF IC method versus the SRNL IC method but within the error of the two methods ($2\sigma \pm 20\%$). Additionally, Table 3-4 shows integrating using valley-to-valley (SRNL processing method) instead of tangential integration (DWPF processing method) yielded glycolate values closer to the spiked amount. Similar results were observed at S&M were using valley-to-valley integration yielded results closer to the spiked glycolate value. If used, we recommend the DWPF IC method process data using valley-to-valley integration.

Table 3-4. DWPF IC method using 2 different processing methods

Valley to Valley integration						
DWPF IC method						
DWPF Laboratory	Day1	Day1	Day2	Day2	Day3	Day3
#	Gly20	Gly20blank	Gly35	Gly35blank	Gly50	Gly50blank
1	17.1	3.85	28.5	6.97	43.2	3.86
2	17.0	3.94	28.8	3.94	43.7	4.04
3	16.8	4.00	28.8	3.97	43.7	4.00
4	16.9	3.99	28.7	3.85	43.5	3.98
5	17.0	4.01	28.7	3.96	43.6	4.06
6	16.9	3.97	28.8	3.75	43.6	4.10
7	17.1	4.09	29.0	4.09	43.4	4.02
Average	16.9	4.02	28.8	3.913	43.5	4.04
sd	0.074	0.0446	0.1088	0.1281	0.0948	0.046
rsd(%)	0.43	1.11	0.378	3.27	0.2180	1.15
Tangential intergration						
DWPF IC method						
DWPF Laboratory	Day1	Day1	Day2	Day2	Day3	Day3
#	Gly20	Gly20blank	Gly35	Gly35blank	Gly50	Gly50blank
1	15.3	3.32	27.7	6.28	42.5	3.54
2	15.9	3.44	27.8	3.58	42.5	3.63
3	15.7	3.43	27.8	3.54	42.2	3.64
4	15.9	3.47	27.7	3.52	42.4	3.61
5	16.0	3.50	27.7	3.50	42.6	3.64
6	15.9	3.62	27.8	3.44	42.6	3.75
7	16.1	3.62	28.0	3.72	42.2	3.66
Average	16.0	3.55	27.8	3.546	42.5	3.66
sd	0.057	0.0693	0.1145	0.1043	0.1475	0.052
rsd(%)	0.36	1.95	0.412	2.94	0.3474	1.42

3.7 Statistical Analysis of SRNL IC Method with Valley-to-Valley Integration

All three laboratories sent data generated using the SRNL IC method with valley-to-valley integration to the Computation and Modeling group for JMP statistical analysis including an LOQ and Limit of Detection (LOD) analysis [6]. Data from all laboratories was included in the calculation to capture the error of multiple technicians, multiple instruments, and different laboratory locations. The results are summarized in Table 3-5. For production monitoring and analysis of glycolate, we recommend using the reporting limit of 20 mg/L to ensure an accurate ($2\sigma \pm 20\%$) glycolate measurement. Special studies would require more effort to prepare for analysis, including additional instrument preparation, study specific checks for blanks, extra precautions to assure operational stability, additional checks of reagents, running sufficient samples to

determine study specific LODs and LOQs, and/or running supplemental standard additions. Note that the tabulated LOD and LOQ values could be adjusted over time based on in-practice experience and the performance of the method on actual LWS samples.

Table 3-5. Glycolate analysis reporting limit

	Routine Operation	Special Study*
Reporting Limit (LOQ)	20.0 mg/L	10.5 mg/L
LOD	6.30 mg/L	3.15 mg/L
*SRNL-TR-2021-00660		

4.0 Conclusions

The goal of this work was to determine a reliable reporting limit for determining low concentrations of glycolate in the RCT. A complex RCT simulant was prepared to capture analysis interferants and other potential issues. Using JMP statistical analysis and empirical observations of peak response, peak shape, and interferents assessment, data from a round robin between three laboratories using the SRNL IC method with valley to valley integration was used to determine a routine operational reporting limit (LOQ) of 20 mg/L and a special study reporting limit of 10.5 mg/L. Below these concentrations, provisional (estimated) concentrations can be provided to LOD levels of 6.3 mg/L (routine) and 3.15 mg/L (special study).

The operational LOQ of 20 mg/L would also suffice for the DWPF IC method with valley-to-valley integration. This method yielded values near (about 4% lower) the SRNL IC method with valley-to-valley integration in the second-round robin and higher values in the first scoping round robin where some degradation of glycolate occurred. To avoid sample dilution during sample preparation using 2.5 cc OnGuard II H^+ cartridges, DWPF personnel should pass through the cartridge a minimum of 10 mL of sample prior to sample collection to ensure complete removal of deionized water from the water rinse step.

5.0 Recommendations, Path Forward or Future Work

A demonstration of glycolate analysis on radioactive RCT samples with some solids for routine operations (e.g., down to 20 mg/L) using the SRNL IC method with valley to valley integration would provide additional confidence and document method robustness/performance for real LWS samples. A demonstration of glycolate analysis on radioactive RCT samples with some solids for lower levels (e.g., down to 5 mg/L) would provide additional insights into what protocols would be needed to reliably achieve the lowest possible detection levels and accuracy for special study needs.

6.0 References

[1] T. L. White, D. P. DiPrete, F. F. Fondeur, "Glycolate Analysis of Tank 22: Developing and Testing Analytical Methods for the Savannah River Site Liquid Waste System," SRNL-STI-2019-00712, Rev. 0, 2020.

[2] J. R. Zamecnik, D. P. Lambert, W. T. Riley, W. G. Ramsey, "Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants – Protocol Runs for Nominal and Chemical Process Cell (CPC) Foam over Conditions," SRNL-STI-2019-00292, Rev. 0, 2019.

[3] M. J. Siegfried, S. P. Harris, C. A. Nash, W. H. Woodham, T. L. White, "Modeling the Destruction Glycolate in the Defense Waste Processing Facility (DWPF) Recycle Stream and Concentration Factors for Glycolate in the 2H Evaporator," SRNL-STI-2020-00247, Rev. 0, 2020.

[4] W. H. Woodham, A. M. Howe, M. J. Siegfried, "Sludge Batch 10 Flowsheet Testing with Non-radioactive Simulants," SRNL-STI-2021-00349, Rev. 0, 2021.

[5] T. L. White, D. P. Lambert, M. J. Siegfried, "Run Plan for Glycolate Analysis in Recycle Collection Tank (RCT) Round Robin," SRNL-L4130-2020-00011, 2020.

[6] S. P. Harris, "Statistical Analysis of Laboratory Round Robin Glycolate Test Data," SRNL-TR-2021-00660, Rev. 0, 2021.

[7] Thermo Scientific 'Dionex OnGuard II Cartridges Product Manual," P/N: 03688-08, February 2015.

Appendix A. Summary of Second Round Robin Results

Summary of Second Round Robin					
Calculated from run sheet, mg/L	21.3	38.0	54.9	method	processing
S&M Analysis results, mg/L (Average n=7)	23.5	35.2	54.2	a	c
PSAL Analysis results, mg/L (Average n=7)	19.0	34.6	52.2	a	c
DWPF Analysis results, mg/L (Average n=7)	17.4	30.5	44.7	a	c
DWPF method Analysis results, mg/L (Average n=7)	16.9	28.8	43.5	b	c
Intergration by DWPF workup					
DWPF Analysis results, mg/L (Average n=7)	14.5	27.0	40.8	a	d
DWPF method Analysis results, mg/L (Average n=7)	15.8	27.8	42.4	b	d
Laboratories					
S&M	Sensing and Metrology				
PSAL	Process Science Analytical Laboratory				
DWPF	Defense Waste Processing Facility				
Ion chromatography methods					
SRNL IC method					
DWPF IC method					
Processing					
SRNL workup of split peak or valley to valley integration					
DWPF workup of tangential integration					

[This Page Left Intentionally Blank]

Distribution:

cj.bannochie@srnl.doe.gov
William.bates@srnl.doe.gov
marion.cofer@srnl.doe.gov
alex.cozzi@srnl.doe.gov
connie.herman@srnl.doe.gov
brady.lee@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
Marissa.Reigel@srnl.doe.gov
eric.skidmore@srnl.doe.gov
michael.stone@srnl.doe.gov
william.swift@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
Records Administration (EDWS)
bill.clark@srs.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
Curtis.Gardner@srs.gov
Anna.Murphy@srs.gov
tony.polk@srs.gov
Anthony.Robinson@srs.gov mark-a.smith@srs.gov
patricia.suggs@srs.gov
thomas.temple@srs.gov
Kevin.Brotherton@srs.gov
Richard.Edwards@srs.gov
terri.fellinger@srs.gov
Joseph.fields@srs.gov
jeffrey.gillam@srs.gov
barbara.hamm@srs.gov
robert.hoeppel@srs.gov
Thomas.Huff@srs.gov
bill.holtzscheiter@srs.gov
Vijay.Jain@srs.gov
Fabienne.Johnson@srnl.doe.gov
Jeremiah.Ledbetter@srs.gov
chris.martino@srnl.doe.gov
jeff.ray@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
hasmukh.shah@srs.gov
aaron.staub@srs.gov
thomas.colleran@srs.gov
Spencer.Isom@srs.gov
MARIA.RIOS-ARMSTRONG@SRS.GOV
roger.mahannah@srs.gov
ben.dean@srs.gov
helen.boyd@srs.gov
thomas02.white@srnl.doe.gov
whitney.riley@srnl.doe.gov
stephen.harris@srnl.doe.gov
Anthony.Howe@srnl.doe.gov
dan.lambert@srnl.doe.gov
brian02.looney@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
edward.sadowski@srnl.doe.gov
Matthew.Siegfried@srnl.doe.gov
stephanie.taylor@srnl.doe.gov
Mary.Whitehead@srnl.doe.gov
Wesley.Woodham@srnl.doe.gov
andrew.marvel@srs.gov