Development of Ion Chromatography Methods to Support Testing of the Glycolic Acid Reductant Flowsheet in the Defense Waste Processing Facility

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EXECUTIVE SUMMARY

Ion Chromatography (IC) is the principal analytical method used to support studies of Sludge Reciept and Adjustment Tank (SRAT) chemistry at DWPF. A series of prior analytical "Round Robin" (RR) studies included both supernate and sludge samples from SRAT simulant, previously reported as memos, are tabulated in this report.[2,3] From these studies it was determined to standardize IC column size to 4 mm diameter, eliminating the capillary column from use. As a follow on test, the DWPF laboratory, the PSAL laboratory, and the AD laboratory participated in the current analytical RR to determine a suite of anions in SRAT simulant by IC, results also are tabulated in this report. The particular goal was to confirm the laboratories ability to measure and quantitate glycolate ion. The target was + or – 20% inter-lab agreement of the analyte averages for the RR. Each of the three laboratories analyzed a batch of 12 samples. For each laboratory, the percent relative standard deviation (%RSD) of the averages on nitrate, glycolate, and oxalate, was 10% or less. The three laboratories all met the goal of 20% relative agreement for nitrate and glycolate. For oxalate, the PSAL laboratory reported an average value that was 20% higher than the average values reported by the DWPF laboratory and the AD laboratory. Because of this wider window of agreement, it was concluded to continue the practice of an additional acid digestion for total oxalate measurement. It should also be noted that large amounts of glycolate in the SRAT samples will have an impact on detection limits of near eluting peaks, namely Fluoride and Formate.

A suite of scoping experiments are presented in the report to identify and isolate other potential interlaboratory discepancies. Specific ion chromatography inter-laboratory method conditions and differences are tabulated. Most differences were minor but there are some temperature control equipment differences that are significant leading to a recommendation of a heated jacket for analytical columns that are remoted for use in radiohoods. A suggested method improvement would be to implement column temperture control at a temperature slightly above ambient to avoid peak shifting due to temperature fluctuations. Temperature control in this manner would improve short and longer term peak retention time stability.

An unknown peak was observed during the analysis of glycolic acid and SRAT simulant. The unknown peak was determined to best match diglycolic acid. The development of a method for acetate is summaraized, and no significant amount of acetate was observed in the SRAT products tested. In addition, an alternative Gas Chromatograph (GC) method for glycolate is summarized.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ARP	Actinide Removal Process
CPC	Chemical Process Cell
DOE	Department of Energy
EM	Environmental Management Division of DOE
FAVC	Formic Acid Vent Condenser
FTIR	Fourier Transformed InfraRed Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
MCU	Modular Caustic Side Solvent Extraction Unit
MWWT	Mercury Water Wash Tank
NI	New Information
NMR	Nuclear Magnetic Resonance Spectroscopy
PISA	Potential Inadequacy in the Safety Analysis
PSAL	Process Science Analytical Laboratory
RR	RR
REDOX	Reduction-Oxidation
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TOC	Total Organic Carbon Analysis
TT&QAP	Task Technical and Quality Assurance Plan
VOA	Volatile Organic Analysis
VSL	Catholic University of America Vitreous State Laboratory

1.0 Introduction

The Defense Waste Processing Facility (DWPF) and the Savannah River National Laboratory are currently studying the use of glycolic acid ($C_2H_4O_3$) to replace formic acid (CH_2O_2) as the mercury reducing agent in the Slurry Receipt and Adjustment Tank (SRAT). The numerous benefits of the glycolic acid flowsheet include a better safety margin due to reduced production of hydrogen gas, better rheology due to the SRAT staying acidic during the entire SRAT cycle, and less sludge foaming due to reduced catalytic activity of glycolic acid with SRAT metallic compounds. [1]

Ion Chromatography (IC) is the principal analytical method used to support studies of SRAT chemistry. IC measures anions such as nitrate, nitrite, formate, glycolate, oxalate, sulfate, fluoride, and chloride that indicate the REDuction/OXidation (REDOX) conditions and corrosive properties of the SRAT Feed and SRAT Product. Since the glycolic acid flowsheet is a new process, the analytical reliability of glycolate determinations by IC drew special scrutiny and therefore the following studies were conducted.

- A series of analytical RR studies involving IC analyses that included at least three laboratories, the DWPF laboratory, the Process Science Analytical Laboratory (PSAL) at 999-W and the Analytical Development (AD) laboratory at 773-A. Two of these RR studies also included the F/H area laboratory.[2,3]

In response to the results obtained from the RR studies:

- Multiple scoping experiments were performed to help define operating parameters around the IC analysis. Dilution protocols and the impact of filtration on anion determinations were investigated.

- Additional modeling was performed exploring the equipment and method differences between the testing laboratories. Most differences were minor but there are some temperature control equipment differences that are significant leading to a recommendation of a heated jacket for analytical columns that are remoted for use in radiohoods.

- A method for acetate detection was developed since it has a similar retention time as glycolate and would have an impact on the REDOX for the SRAT. No significant amount of acetate was observed in the SRAT products tested.

- An unknown peak was identified during the analysis of SRAT simulants and spike addition experiments into SRAT simulant resulted in a match for diglycolic acid. Testing of incoming 70% wt. glycolic acid for impurities, also showed the presence of this peak in the glycolic acid.

Alternative analytical methods for the measurement of carboxylic acids were also explored. Derivatization of carboxylic acids by esterification, then analysis method by

Gas Chromatography - Mass Spectrometry (GC-MS) was investigated. Testing shows erratic results for using this technique for the carboxylic acids of interest to DWPF. Multiple complications with this method limit its practicality in monitoring the carboxylic acids in SRAT cycle products. More work would need to be applied to this method to be viable for use.

2.0 Experimental Procedure

2.1 Sludge Sub-Sampling for Anion Determinations

For each RR study, samples were provided to the laboratories either as a bulk sample from which the laboratories took subsamples to create replicates or individual replicates were provided from which the laboratories took aliquots for analysis (previous RR studies). Details of the specific sampling is provided in relevant experimental sections of 3.1 – 3.3. For the current RR study, also called RR 4, to virtually eliminate sub-sampling as a source of analytical error, pre-weighed aliquots of SRAT simulant were provided to each IC laboratory. A 250 mL plastic bottle was filled to about half capacity with sludge simulant. A magnetic stir bar was added and the bottle was capped and shaken vigorously for about 30 seconds by hand with the stir bar left in the bottle to aid the sludge agitation process prior to removing each aliquot. A 2.0 mL slurry pipette with the tip cut off to increase the orifice was used to transfer approximately 1 gram of the sludge to a 15 mL plastic bottle that had been tared on 4 place analytical balance. The sample weight was recorded and provided to the IC laboratories.

2.2 AD Ion Chromotography Laboratory Experimental Conditions

The Analytical Development (AD) Ion Chromatography analysis uses Manual L16.1, Procedure ADS-2310 “Analysis of Ions in Solutions using a Dionex ICS3000 Ion Chromatography System”. Mobile phase or eluent hydroxide is diluted with DI water to desired concentration point-of-use at the instrument from a concentrate. Incoming samples are diluted with DI water to within the calibration curve range of 1 to 50 mg/L. The anion method is set up to quantify fluoride, glycolate, formate, chloride, nitrite, bromide, nitrate, sulfate, oxalate, and phosphate. The wetted components of the Dionex RFIC-3000 Ion Chromatography System have been remoted for radiological use and consisted of an AS-DV autosampler, a gradient pump, and a suppressed conductivity detector. Software control of the system and data acquisition was through Dionex Chromeleon v.6.8. Below is a summary of the AD anion method conditions in Table 2.2-1.

Table 2.2-1 Summary of AD's IC Anion Operating Conditions

AD Dionex ICS-3000 Operating Conditions

	Analytical (4mm)
Column	**AG-19/AS-19**
Suppressor	**Self-Regenerating Suppressor (ASRS) 300**
CRD	**None Used**
CR-ATC	**yes**
Flow Rate	**1.0 ml/min**
Injection Loop	**25ul**
Calibration Standards (ppm)	**1, 5, 10, 50**
Gradient Method	**0-30 min. (5-25 mM KOH gradient)**
	30-48 min. (25 mM KOH)
	48-50 min. (5 mM KOH)
Column Temperature	**Room Temperature**
CD Detector Temperature	**35 C**
Retention Time of Fluoride	8.5 min
Retention Time of Glycolate	9.1 min
Retention Time of Formate	10.2 min
Retention Time of Chloride	12.7 min
Retention Time of Nitrite	14.6 min
Retention Time of Bromide	17.0 min
Retention Time of Nitrate	18.2 min
Retention Time of Sulfate	26.2 min
Retention Time of Oxalate	29.0 min
Retention Time of Phosphate	40.3 min

For each round robin, the instrument was calibrated using 1, 5, 10 and 50 ppm standards made from NIST traceable standards. The samples from each round robin were diluted with 18 MΩ deionized water to a weight of approximately 100 gram. From the 100x dilution an additional 500x and 5000x dilution were made, by weight, to inject into the instrument. The samples were filtered through a 0.45 μm filter and through the secondary filter provided in the cap of the IC vials supplied by the manufacturer. This slurry weighing and dilution protocol was used to mirror the DWPF production method of slurry weighted dilutions.

2.3 PSAL Ion Chromatography Laboratory Experimental Conditions

The Process Science and Analytical Laboratory (PSAL) ion chromatograph used a dual system Dionex ICS-5000 for the analyses of the round robin tests. The capillary system was used for the previous round robins and the analytical system (4 mm diameter column) was used for the current round robin. See Table 2.3-1.

Table 2.3-1 Summary of PSAL's IC Anion Operating Conditons

PSAL Dionex ICS-5000
Operating Conditions

	Capillary (0.25mm)	Analytical (4mm)
Column	**Ion Swift MAX-100**	**AS-11HC**
Suppressor	**ACES-300**	**ASRS 4mm**
CRD	**CRD200**	**CRD200**
Flow Rate	**0.012 ml/min**	**1.0 ml/min**
Injection Loop	**0.4ul**	**25ul**
Calibration Standards (ppm)	**1, 5, 10, 20**	**1, 5, 10, 20**
Gradient Method	**0-0.1 min (0.20 mM KOH)**	**0-4 min. (0.5 mM KOH)**
	0.1-2.0 min. (2.0 mM KOH)	**4.1-25 min. (35 mM KOH)**
	2.0-8.0 min. (15 mM KOH)	**25.1-27 min. (60 mM KOH)**
	8.0-14.0 min. (35 mM KOH)	**27.1-32 min (0.5 mM KOH)**
	14.1-24.0 min. (0.2 mM KOH)	
Column Temperature	**35 C**	**35C**
CD Detector Temperature	**35 C**	**35C**

For each round robin, the instrument was calibrated using 1, 5, 10 and 20 ppm standards made from NIST traceable standards. Both methods used a gradient run to separate the peaks and decrease run time. The samples from each round robin were diluted with deionized water to a volume of 100 ml. From that dilution an additional 500x and 5000x dilution were made to inject into the instrument. Two different dilution methods were used. These are described in section 3.5. For the samples in the initial round robins, the additional 500x and 5000x dilutions were made from the filtered 100x dilution. For the current or round robin 4, the additional 500x and 5000x dilutions were made from the 100x dilution unfiltered and then additional dilutions filtered prior to injection into the instrument. Section 3.5 describes these methods and it was found that these differences did not make a significant difference in the results.

2.4 DWPF Ion Chromatography Laboratory Experimental Conditions

The DWPF Ion Chromatograph System used a dual system Dionex ICS-3000 for the analyses of the round robin tests. DWPF used an AG11 and AS11 column set up for the initial round robin tests. For the current or round robin 4 tests DWPF used both an AG-11/ AS11 column setup and an AG-11HC and AS-11HC column set up. See Table 2.4-1.

Table 2.4-1 Summary of DWPF's IC Anion Operating Conditons

DWPF Dionex ICS-3000
Operating Conditions

	Analytical (4mm)	Analytical (4mm)
Column	**AG-11/AS-11**	**AG-11HC / AS-11HC**
Suppressor	**ASRS-300 4mm**	**ASRS-300 4mm**
CRD	**None Used**	**None Used**
CR-ATC		
Flow Rate	**1.5 ml/min**	**1.0 ml/min**
Injection Loop	**25ul**	**25ul**
Calibration Standards (ppm)	**1, 10, 20**	**1, 10, 20**
Gradient Method	**0-4 min. (0.5 mM KOH)**	**0-4 min. (0.5 mM KOH)**
	4.1-25 min. (35 mM KOH)	**4.1-25 min. (35 mM KOH)**
	25.1-27 min. (60 mM KOH)	**25.1-27 min. (60 mM KOH)**
	27.1-32 min (0.5 mM KOH)	**27.1-32 min (0.5 mM KOH)**
Column Temperature	**Room Temperature**	**Room Temperature**
CD Detector Temperature	**35 C**	**35C**

For each round robin, the instrument was calibrated using 1, 10 and 20 ppm standards made from NIST traceable standards. Both methods used a gradient run to separate the peaks and decrease run time. The samples from each round robin were diluted with 18.2-18.3 18 MΩ deionized water to a weight of approximately 100 gram. From the 100x dilution an additional 500x and 5000x dilution were made, by weight, to inject into the instrument. The DWPF samples were filtered through a 0.2 um filter and through the secondary filter provided in the cap of the IC vials supplied by the manufacturer.

The goal for the DWPF laboratory, which will operate in a "production mode", is to maximize peak resolution and minimize turnaround time. The current DWPF formic acid flow sheet allows the IC runs to be completed in a 17 min run, with the typical IC run for a sample taking approximately 4 hours. To resolve the fluoride, glycolate, and formate peaks the gradient method had to be extended to 32 min run, increasing the time for a typical IC sample run to approx. 7.5 hours. With the facility operating in a "sample and send" mode the increase in time should not be an issue. However, should the facility have to go to a "sample and hold" mode, the increased time will have to be evaluated.

2.5 Quality Assurance

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

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3.0 Results and Discussion

3.1 RR 1

The first RR involved a SRAT simulant and a supernate fraction made from the filtrate of the SRAT simulant as well as the analysis of a solution of 70 wt% glycolic acid and a 1000 ppm glycolate IC standard. Four labs participated in this RR study, AD, PSAL, DWPF and F/H.

- All labs were able to obtain acceptable results on the (±10%) on the IC standard.
- All labs, except PSAL, were able to obtain acceptable results (±10%) on analysis of the solution of 70wt% glycolic acid. The PSAL result was high.
- All labs, except PSAL, were able to obtain acceptable results (±20%) on analysis of glycolate in supernate obtained from filtration of simulant slurry. The PSAL result was high. The oxalate results were erratic but AD, DWPF and F/H labs were able to obtain acceptable results on nitrate, sulfate, and chloride anions.
- All labs except AD were able to obtain acceptable results on glycolate analysis of simulant slurry. ADs results was nearly 50% low. Acceptable results were obtained by all labs measuring nitrate and chloride anions though there were issues with the other anions.

Several issues and best practices were noted by personnel from each of the laboratories in this first RR study and although these have been documented elsewhere[2], they are repeated here. Many of these issues have been resolved during subsequent RR tests and some of the best practices are in place now.

- Degradation of standards (refrigeration and storage in dark place are recommended) – through the course of these RR studies, degradation of standards was determined not to be an issue during the shelf life of the IC standards used.
- Peaks shifting (not a problem for chemists but may be an issue for shift technicians) – column heaters have been installed in the AD laboratory and have been recommended for the other labs to improve peak stability. This is also discussed in Section 3.7
- "Ugly" peaks – this is a potential issue for F/H labs, the other labs did have an impact from this.
- Many blanks needed after analyzing low dilution samples – most labs reported a trace amount of sulfate in subsequent blanks after analysis of a sample.
- Acetate, glycolate, fluoride peaks close together – acetate is not present in the slurry samples, peak separations have been obtained by using different columns and methods. This is also discussed in Section 3.8
- Cut off tips of pipettes to get better sampling of slurries with pipettes -
- Valves plugging – none of the labs had this issue.

- Supernate has carryover but not slurry – PSAL noted some carryover during the analysis of the filtered supernate but the other labs did not note this issue.
- Calibrate and analyze glycolate by itself – this is ADs current protocol. The other labs spike glycolate into the current standards for analysis.
- Need matrix matched standard for validation of data – the analysis of a matrix matched supernate standard was studied during the 2nd RR which is discussed in Section 3.2. This study indicated matrix interactions between cations and anions on the column were only an issue for the capillary column used by PSAL.
- Need more frequent change out of columns (every month or two). Change guard columns every four months - Each lab continues to change analytical columns and guard columns at regular intervals.
- Higher concentrations lead to later peaks – no issue noted by any of the labs.
- The capillary column used by PSAL is easily plugged (60 nm pores, 450 nm filter), smaller filter may improve results – PSAL has stopped using the capillary columns and currently uses a 4mm analytical column, see Section 2 for method conditions.
- Metal guard columns (shorter in length version of the analytical column placed upstream of the analytical column to protect the analytical column) - did not improve results in F/H lab testing but all the labs are using guard columns as a standard practice.

3.2 RR 2

The 2nd RR study involved the submission of a matrix matched supernate standard to all four labs. This study was performed to determine if the interaction glycolate experienced with other cations or the column would affect the retention time of glycolate and the measured concentration. In addition, as a best practice, it was determined that a matrix matched supernate standard be submitted in subsequent RR testing to assess the accuracy of the results obtained from supernate analysis.[3] The matrix matched standard was prepared at the Aiken County Technology Laboratory and sub-samples were given to each lab. Table 3.2-1 gives the results of the IC analysis versus the amount added gravimetrically to the matrix matched standard at the time of preparation.

The results of the 2nd RR study are contained in Table 3.2-1.

Table 3.2-1Results from IC Measurements of a Matrix Matched Supernate Sample

Analyte	Plan mg/L	DWPF, mg/L	% Δ	PSAL, mg/L	% Δ	AD, mg/L	% Δ	F/H Lab, mg/L	% Δ
Total Nitrate	54,621	50,647	-7.3%	49,583	-9.2%	53,050	-2.9%	53,422	-2.2%
Total Chloride	821	825	0.5%	765	-6.8%	794	-3.3%	877	6.8%
Total Sulfate	2,635	2,636	0.0%	2,957	12.2%	2,638	0.1%	2,908	10.4%
Total Oxalate	3,800	3,992	5.1%	7,827	106.0%	3,420	-10.0%	3,744	-1.5%
Total Glycolate	48,600	45,934	-5.5%	48,050	-1.1%	47,750	-1.7%	47,855	-1.5%

Except for the oxalate results, all labs were within 15% of the known amount of each anion contained in the sample. At the time of analysis, the PSAL lab was still using the capillary column. The PSAL lab has since discontinued use of the capillary column.

3.3 RR 3

The results of RR 3 IC analyses of glycolate, oxalate, and nitrate are tabulated in Table 3.3-1 and Table 3.3-2.

RR 3 samples were subsampled from sludge simulant GF40 and GN34, and distributed to the three analytical laboratories. The results for nitrate ion for the first RR showed that the three laboratories were in agreement (for the purpose of this report, “agreement” is arbitrarily as no more than 20% difference). The results for glycolate and oxalate ion for of the first RR showed that the three laboratories were not in agreement. All laboratories use modern Dionex reagent-free IC systems. The meaning here is that the mobile phase hydroxide or eluent is made point-of-use from a concentrate by the analytical instrument. All three laboratories use hydroxide based analytical columns. However, there are potential significant instrumental differences between the three laboratories. The DWPF and AD laboratories used a larger analytical (4mm) column for the first RR, whereas the PSAL lab used a capillary system. The glycolate analyses by the PSAL Laboratory ran approximately 25%-40% lower than the DWPF and AD laboratories. The initial thought was that the difference in dilution methods may have caused the large difference. However, Section 3.5 shows that the difference in dilution did not cause the difference. It is thought that the organic anions (glycolate, oxalate) on the capillary system do not perform as well after extended use due to the buildup of transition metals on the columns. The metals may affect how much of the anion elutes off the column and also may produce unwanted carryover. For the second RR, it was determined the PSAL laboratory should change to a 4mm diameter analytical column system.

Table 3.3-1 Anion Determinations of Sludge Simulant Sample GF40 in RR 3

Glycolate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	46,000	34,000	42,000
Determination 2	43,000	33,000	11,000*
Determination 3	41,000	32,000	44,000
Determination 4	43,000	33,000	45,000
Mean	43,000	33,000	44,000
Std. deviation	2000	1000	2000
% Std. deviation	5%	3%	4%
			* Outlier excluded from stat. analysis
Oxalate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	9300	7800	12,000
Determination 2	9000	7600	3200*
Determination 3	8800	7500	12,000
Determination 4	9200	7600	12,000
Mean	9100	7600	12,000
Std. deviation	220	100	0
% Std. deviation	2%	2%	0%
			* Outlier excluded from stat. analysis
Nitrate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	55,000	53,000	47,000
Determination 2	51,000	51,000	14,000*
Determination 3	49,000	49,000	47,000
Determination 4	51,000	51,000	48,000
Mean	52,000	51,000	47,000
Std. deviation	3000	2,000	1000
% Std. deviation	5%	4%	1%
			* Outlier excluded from stat. analysis

Table 3.3-2 Anion Determinations of Sludge Simulant Sample GN34 in RR 3

Glycolate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/)**
Determination 1	43,000	26,000	43,000
Determination 2	42,000	26,000	43,000
Determination 3	42,000	26,000	44,000
Determination 4	41,000	26,000	43,000
Mean	42,000	26,000	43,000
Std. deviation	1000	0	1000
% Std. deviation	2%	0%	2%
Oxalate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	8100	1200	5900
Determination 2	8200	1000	5700
Determination 3	8200	1200	6000
Determination 4	8300	1000	6200
Mean	8200	1100	6000
Std. deviation	100	100	200
% Std. deviation	1%	9%	3%
Nitrate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	46,000	45,000	46,000
Determination 2	45,000	45,000	45,000
Determination 3	45,000	45,000	46,000
Determination 4	45,000	45,000	45,000
Mean	45,000	45,000	45,000
Std. deviation	1000	0	1000
% Std. deviation	2%	0%	2%

3.4 RR 4

The results of the current RR, also known as RR4, IC analyses of glycolate, oxalate, and nitrate are tabulated in Table 3.4-1.

RR 4 samples were subsampled from a composite sludge simulant, and distributed to the three analytical laboratories. The results for nitrate, glycolate and ions for the RR4 showed that the three laboratories were in agreement (for the purpose of this report, "agreement" is arbitrarily as no more than 20% difference). The results for oxalate ion for this round as well as from the previous RRs showed that the three laboratories were not in agreement. Mechanisms for oxalate degradation have been observed before[4,5] which may complicate measurement. Due to the increased uncertainty associated with oxalate measurement it has been the practice to perform a separate oxalate measurement by acid digestion[6]. It should also be noted that the total oxalate in this RR is a small

amount (~ 0.1 – 0.3 wt. %), and approaches the bottom end of the calibration curve with the chosen dilutions.

Table 3.4-1 Anion Determinations of Sludge Simulant Sample in RR 4

Glycolate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	41,000	42,000	42,000
Determination 2	41,000	42,000	42,000
Determination 3	41,000	43,000	42,000
Determination 4	41,000	43,000	43,000
Determination 5	42,000	41,000	45,000
Determination 6	42,000	44,000	sample not provided
Determination 7	42,000	42,000	45,000
Determination 8	42,000	43,000	44,000
Determination 9	43,000	43,000	44,000
Determination 10	43,000	43,000	44,000
Determination 11	43,000	44,000	44,000
Determination 12	43,000	45,000	44,000
Mean	42,000	43,000	44,000
Std. deviation	1000	1000	1000
% Std. deviation	2%	2%	2%
Oxalate	**DWPF Lab (mg/L)**	**PSAL Lab (mg/L)**	**AD Lab (mg/L)**
Determination 1	1460	2480	1410
Determination 2	1480	2610	1420
Determination 3	1480	2670	1470
Determination 4	1490	2730	1450
Determination 5	1270	2830	1520
Determination 6	1230	2720	sample not provided
Determination 7	1220	2620	1490
Determination 8	1200	2710	1450
Determination 9	1130	2640	1460
Determination 10	1160	2330	1470
Determination 11	1260	2720	1480
Determination 12	1310	2720	1480
Mean	1310	2650	1460
Std. deviation	130	130	30
% Std. deviation	10%	5%	2%

Table 3.4-1 Anion Determinations of Sludge Simulant Sample in RR 4 (Continued)

Nitrate	DWPF Lab (mg/L)	PSAL Lab (mg/L)	AD Lab (mg/L)
Determination 1	68,000	65,000	66,000
Determination 2	68,000	64,000	66,000
Determination 3	68,000	63,000	66,000
Determination 4	68,000	63,000	67,000
Determination 5	67,000	62,000	66,000
Determination 6	67,000	64,000	sample not provided
Determination 7	67,000	64,000	66,000
Determination 8	68,000	65,000	66,000
Determination 9	68,000	64,000	66,000
Determination 10	68,000	63,000	66,000
Determination 11	68,000	64,000	67,000
Determination 12	68,000	64,000	67,000
Mean	68,000	64,000	66,000
Std. deviation	500	1000	500
% Std. deviation	1%	1%	1%

3.5 Results of Dilution Protocal Tests

Since much better inter-laboratory agreement was observed for the supernate sample versus the sludge samples, an investigation was performed by both the AD and the PSAL Laboratory to determine if the sample dilution protocol of sludge samples was a factor in the differences.

3.5.1 *AD Laboratory Dilution Testing*

Dilution protocol testing was performed on the AD IC system and method. Samples were subsampled from sludge simulant ID 12-GN49-7485a for the testing. Three randomized replicates of various dilution and filter protocols were tested. The goal was to determine if the order of the filtration step had an impact on the glycolate quantification. All samples are subjected to a final filter on the Dionex autosampler vial caps prior to injection onto the column for analysis. Only a slight difference was noted between dilution protocols measurements. With the exception of oxalate measurements, all protocols were comparable inside the 10% uncertainty window. In the case of formate the quantified value would record as a less than reporting limit. Therefore, the differences were considered only a minor contribution to uncertainty. The results are summarized in Chart 3.5.1-1. For the purposes of the RR 4 analysis, described in section 3.4, protocol A was followed. Protocol D & E, dilution with 60 mMol or 1 mMol sodium hydroxide, will be discussed in section 3.5.3

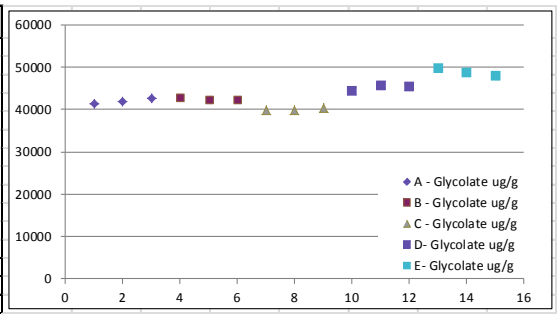
A = prep 100x, prep 500x, prep 5000x, **0.45 um FILTER,** Dionex vials
B = prep 100x, prep 500x, prep 5000x, Dionex vials
C = prep 100x, **0.45 um FILTER,** prep 500x, prep 5000x, Dionex vials

D = in 60 mMol OH^-, prep 100x, prep 500x, prep 5000x, **0.45 um FILTER,** Dionex vials
E = in 1 mMol OH^-, prep 100x, prep 500x, prep 5000x, **0.45 um FILTER,** Dionex vials

Chart 3.5.1-1 AD Dilution Testing Anion Determinations

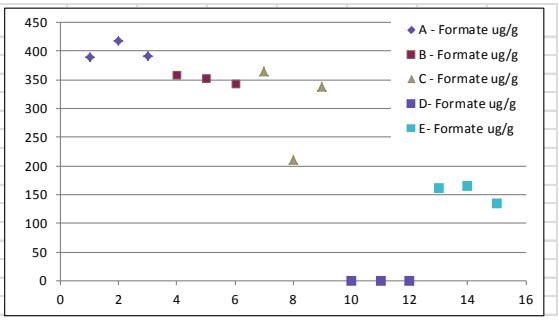
(Glycolate)

Name	A - Glycolate ug/g	B - Glycolate ug/g	C - Glycolate ug/g	D- Glycolate ug/g	E- Glycolate ug/g
prep A1	41439				
prep A2	41940				
prep A3	42585				
prep B1		42783			
prep B2		42450			
prep B3		42302			
prep C1			39911		
prep C2			39933		
prep C3			40376		
prep D1				44487	
prep D2				45752	
prep D3				45425	
prep E1					49774
prep E2					48762
prep E3					48072



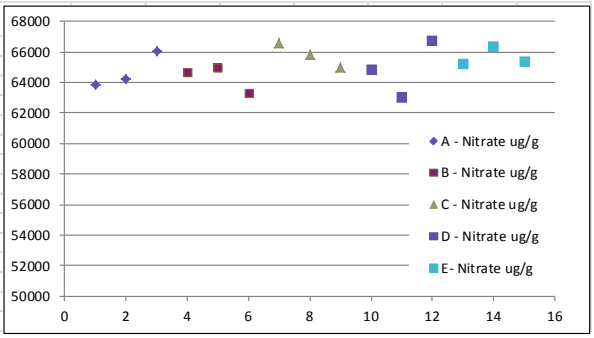
(Formate)

Name	A - Formate ug/g	B - Formate ug/g	C - Formate ug/g	D- Formate ug/g	E- Formate ug/g
prep A1	390				
prep A2	418				
prep A3	392				
prep B1		359			
prep B2		354			
prep B3		344			
prep C1			364		
prep C2			210		
prep C3			337		
prep D1				0	
prep D2				0	
prep D3				0	
prep E1					161
prep E2					166
prep E3					134



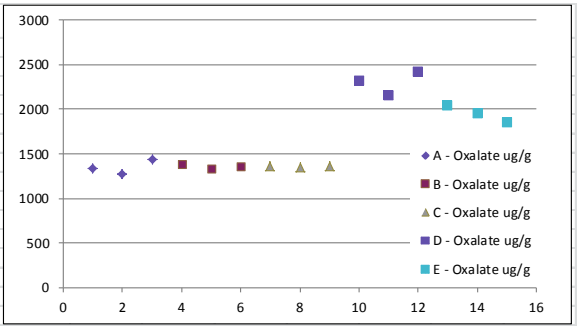
(Nitrate)

Name	A - Nitrate ug/g	B - Nitrate ug/g	C - Nitrate ug/g	D - Nitrate ug/g	E- Nitrate ug/g
prep A1	63816				
prep A2	64209				
prep A3	66076				
prep B1		64684			
prep B2		64962			
prep B3		63310			
prep C1			66570		
prep C2			65815		
prep C3			64957		
prep D1				64858	
prep D2				63022	
prep D3				66722	
prep E1					65230
prep E2					66334
prep E3					65364



(Oxalate)

Name	A - Oxalate ug/g	B - Oxalate ug/g	C - Oxalate ug/g	D - Oxalate ug/g	E - Oxalate ug/g
prep A1	1339				
prep A2	1275				
prep A3	1443				
prep B1		1384			
prep B2		1341			
prep B3		1360			
prep C1			1362		
prep C2			1347		
prep C3			1362		
prep D1				2322	
prep D2				2160	
prep D3				2427	
prep E1					2044
prep E2					1959
prep E3					1858



3.5.2 *PSAL Laboratory Dilution Testing*

Dilution protocol testing was performed on the PSAL Laboratory IC system and method. No significant difference in glycolate measurements were obtained as a function of the sludge dilution protocol. Two different dilution protocols were tested. The results are summarized in Table 3.5.2-1.

For the purposes of the RR 4 analysis, described in section 3.4, protocol 2 was followed.

Protocol 1
1. 100x dilution- 1 g of sludge diluted to 100 mL with de-ionized water
2. Filtered 10 mL of the 100x dilution
3. 50x dilution of the filtrate-0.2 mL of the filtrate to diluted to 10 mL
4. Analyzed this 5000x total dilution of the original sludge

Protocol 2
1. 100x dilution- 1 g of sludge diluted to 100 mL with de-ionized water
2. 50x dilution -0.2 mL of the unfiltered 100x dilution to 10 mL
3. Filtered the 5000x total dilution
4. Analyzed this 5000x dilution

Table 3.5.2-1Anion Determinations of Sludge Simulant Sample in RR 4

Sample I.D.	Sample Type	Glycolate Results in mg/L (Protocol 1)	Glycolate Results in mg/L (Protocol 2)
12-GN49-7485A	SRAT	45,400	45,000
12-GN49-7491A	SME	35,900	37,800
12-GN50-7513A	SRAT	40,100	40,200
12-GN50-7519A	SME	32,000	35,000

3.5.3 *Effect of Caustic Dilution on Anion Determinations*

Tests were performed to determine if the use of dilute caustic solution that matched the IC column eluent solution would have any effect versus simply diluting the sludge samples with de-ionized water. The caustic dilution was selected as 60 mMol KOH. This was selected to match the final gradient concentration in the DWPF IC method. The results show that caustic dilution had no impact on the nitrate value. The tests also show this diluent had a slight positive effect on the determinations of glycolate, yet still comparable inside the 10% uncertainty window. The exception was the formate peak was not resolved and the oxalate ion quantification results increased by about 50 % (see

protocol D & E in the charts in Chart 3.5.1-1). Testing using caustic dilution more closely matching the initial DWPF IC method gradient concentration (1 mMol KOH), did not show broadened peaks, yet showed the positive impact on the oxalate ion quantification (see protocol E in the charts in Chart 3.5.1-1). In general, tests with stronger solutions of caustic were not successful as the IC retention peaks were deleteriously broadened, leading to poor IC performance.

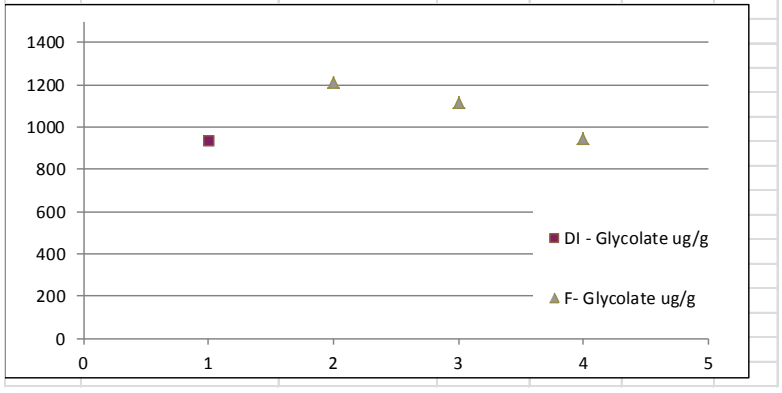
3.6 Effect of Acid Leach of Filtetred Solids on Anion Determinations

Acid leach tests of the filtered slurry were performed to determine if a significant concentration of anions were insoluble in DI water, yet soluble in the HNO_3 acid. The test method comprised of: First 0.45 micron filters (aerodisc non-sterile 25mm) were loaded with 5 ml of a 500x dilution of sludge slurry simulant ID 12-GN49-7485a. The filter was then air dried with 5 ml of air passed through the filter, then 1 ml of 0.1% HNO_3 acid was charged onto the filter, then held for 5 min, then the remaining 4 ml of 0.1% HNO_3 was passed through the filter, collecting the total of 5 ml of acid and analyzed on the AD IC method. Results are shown as triplicate measurements of the 500x, labeled "F1, F2, F3" vs. a DI blank sample loaded on a 0.45 micron filter and subjected to the same treatments, in Chart 3.6-1 acid leach of filtered solids. The results indicated that the acid leach did not result in a significant increase in the measurements of anions of interest, and therefore the amount of anions retained on the filter that are not soluble in DI water are considered an insignificant contribution.

Chart 3.6-1 Acid Leach of Filtered Solids. Chart shows IC results of glycolate, formate, and oxalate analysis of filter residue with no apparent difference from the blank for all analytes.

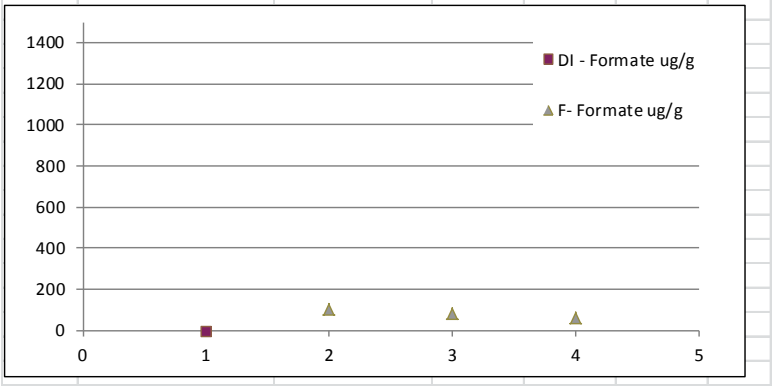
(Glycolate)

Name	DI - Glycolate ug/g	F- Glycolate ug/g
DI - 500	937	
F1 - 500		1210
F2 - 500		1115
F3 - 500		947



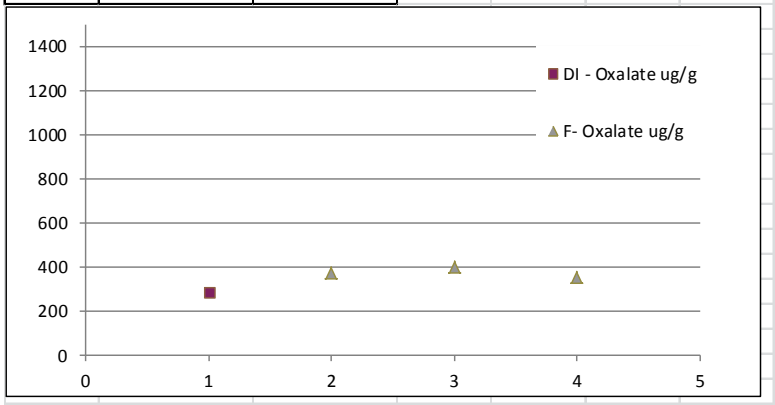
(Formate)

Name	DI - Formate ug/g	F- Formate ug/g
DI - 500	0	
F1 - 500		100
F2 - 500		80
F3 - 500		58



(Oxalate)

Name	DI - Oxalate ug/g	F- Oxalate ug/g
DI - 500	289	
F1 - 500		371
F2 - 500		398
F3 - 500		351



3.7 Column Modeling Leading to Recommendation of Heated Jacket for Columns

One aspect of the RR testing between the analytical laboratories was the opportunity to explore the differences between the IC methods designed to measure the same analytes. The similarities and differences are outlined in sections 2.2 -2.4 in this report. Globally the differences between the methods are minor proven by the ability to reach commonality in the RR measurements. However, there are some equipment differences that are significant. One aspect that is significant is that the PSAL IC system has not been modified from the manufacturer, while the DWPF and AD instruments have been modified for use in a radiohood. Specifically, the wetted components (column, suppressor, detector, etc…) are remoted into the radiohood. This has an impact on temperature control at the column, which in turn impacts operating pressure of the column. In the case of PSAL, the columns are enclosed inside of a temperature

controlled oven set to 35 °C. While the DWPF and AD instruments are in environments that can swing as much as +/- 8 °C. This has a large impact in retention time and in some cases order of elution of target ions.

Dionex has modeling software (Virtual Column) that can be used as a tool to estimate practical method profiles for a given column set and target analytes. Using this tool it can be observed that for the AS-11 column carbonate ion can either be before, after, or overlaid on top of the nitrate peak, depending upon temperature in the range of interest. Also, for the AS-11HC it can be observed that nitrate ion can either be before, after, or overlaid on top of the sulfate peak, depending upon temperature in the range of interest. Shown below are screenshot images of the modeling software Chart 3.7-1 and Chart 3.7-2 Virtual Column. The minimum displayed in the gradient slope profile represents an overlap of anions, a condition to be avoided. A recommendation resulting from this modeling work is that IC columns in radiohoods should be fitted with constant temperature jackets. These columns should be set to a constant temperature at least 5 °C above ambient, and the gradient profiles then adjusted for the desired peak separation.

Chart 3.7-1 Virtual column (AS11) conditions. Minimum in the gradient slope profile is a peak overlap condition to be avoided.

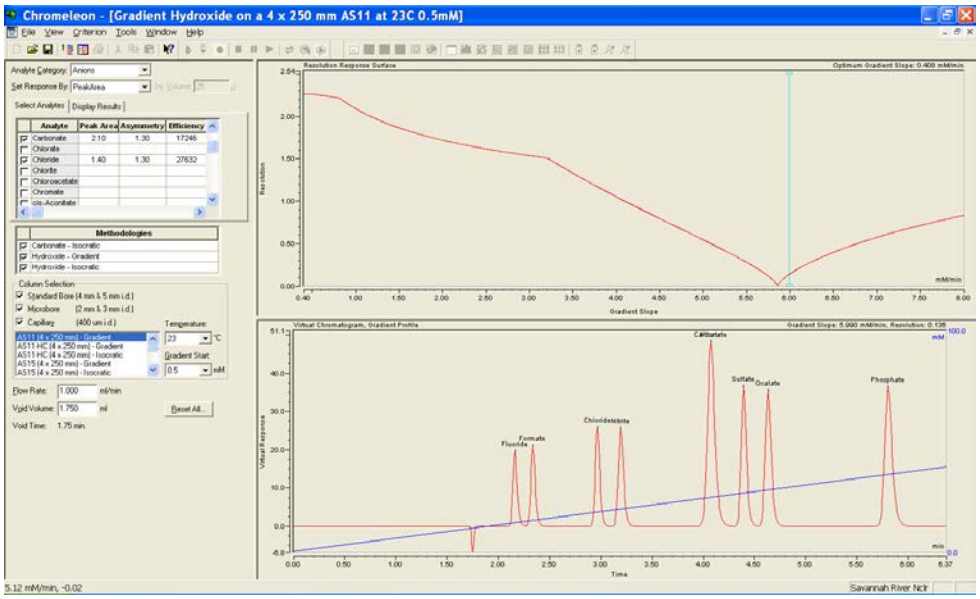
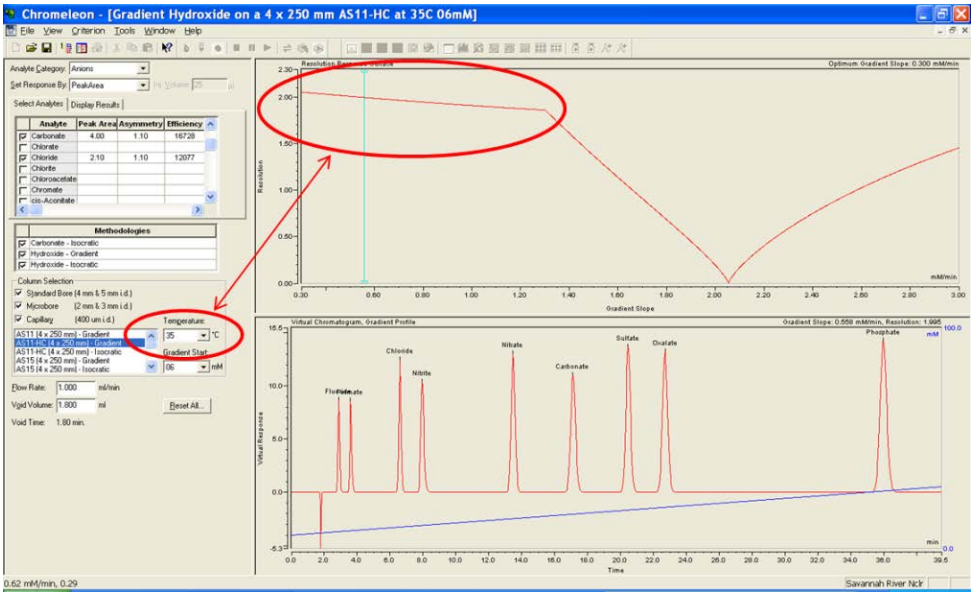


Chart 3.7-2 Virtual Column screenshots (AS-11HC) of AS-11HC column conditions. Flat profile in the gradient slope profile is optimum operating condition, representing here the 35 °C column temperature of the PSAL AS-11HC method.



3.8 AS18 Column Method Development for Acetate

One concern regarding glycolate analysis, or more generally for any IC analysis, is the risk of co-elution of other analytes. It is known through process knowledge, and confirmed with modeling software, that there are near eluting ions under the current IC methods. One analyte of specific interest is the acetate ion. This analyte should be confirmed as not present in the RR samples or SRAT products.

A method was developed to address this analyte using the current Dionex IC hardware with an AS18 analytical column and a column heater set to 50 °C. The column heater was purchased as an aftermarket product from Thermo Scientific, "Hot Pocket" 300mm. It was found that initial low concentrations of hydroxide mobile phase were required to separate glycolate from acetate. Also, it was determined that a ramp of the gradient was required to flush out from the column other ions present including nitrate, sulfate, oxalate, phosphate, for example, prior to the next injection. In addition, it was found that increasing temperature improved baseline resolution / selectivity (or alpha) between glycolate and acetate. Selectivity as related to temperature is outlined in Chart 3.8-1, Chart 3.8-2, and Chart 3.8-3.

Chart 3.8-1 AS18 Column Temperature Method Development

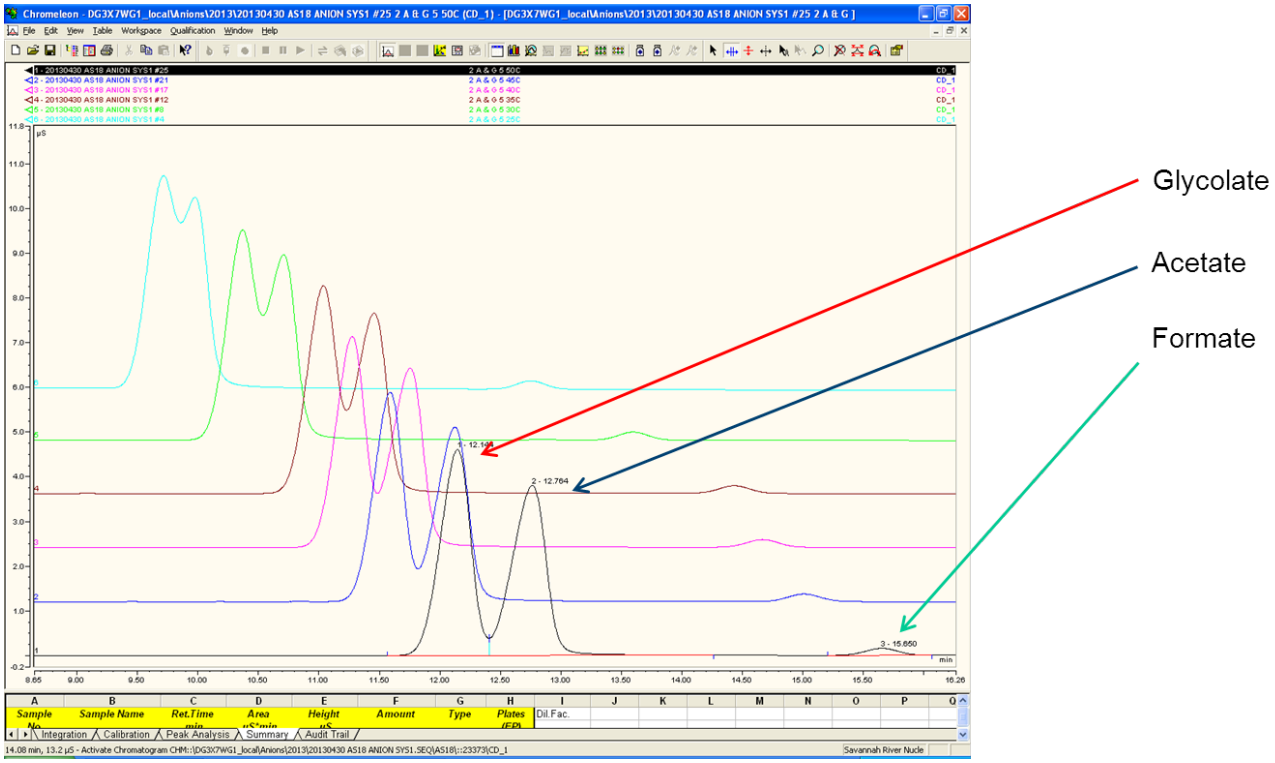


Chart 3.8-1 AS18 column temperature method development. Increasing temperature improves baseline resolution /selectivity, 2 mMol isocratic mobile phase concentration is charted.

Chart 3.8-2 AS18 Column Temperature Method Development Selectivity (α) Theory

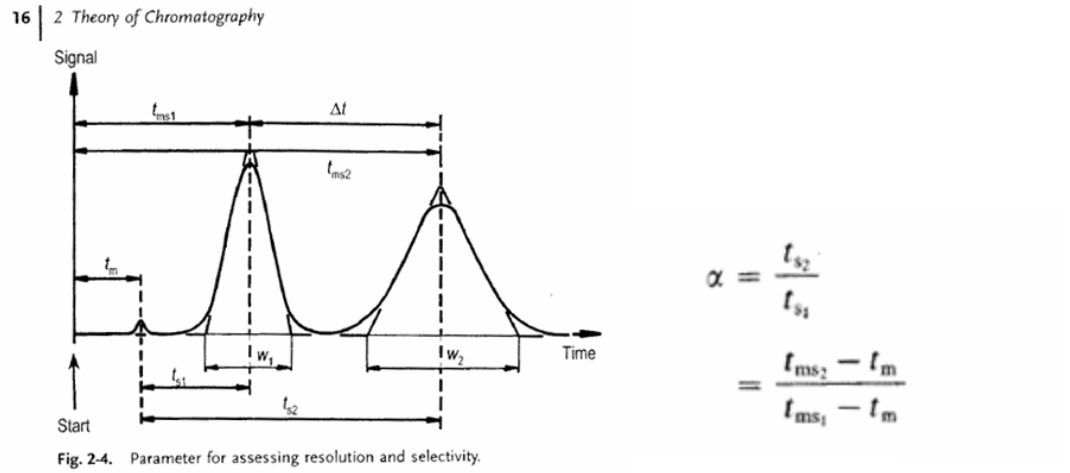


Chart 3.8-2 - Selectivity (α) is defined as the ratio of the solute retention times of two different signals, as shown in the above equation[7].

Chart 3.8-3 AS18 Column Temperature Method Development Selectivity (α) Results

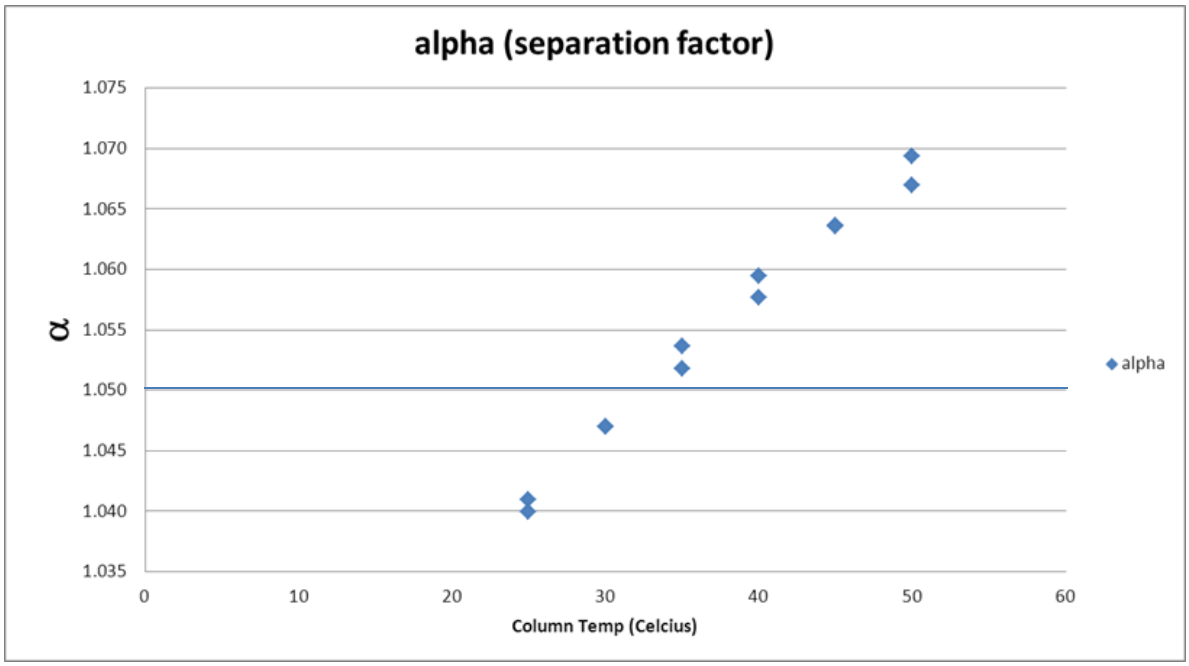


Chart 3.8-3 Column temperature (°C) test for peak selectivity / separation factor between glycolate and acetate with AS-18. α above 1.05 is considered minimum for liquid chromatography. Both isocratic 1 mMol (slightly higher points on graph per temperature) and 2 mMol hydroxide eluent concentrations are charted. The 2 mMol concentration was selected for further method development and 50 °C was selected as operating temperature for this method.

Table 3.8-1 AS18 Method Conditions for Acetate Analysis

Acetate method - AD Dionex ICS-3000 Operating Conditions

	Analytical (4mm)
Column	**AG-18/AS-18**
Suppressor	Self-Regenerating Suppressor (ASRS) 300
CRD	**None Used**
CR-ATC	**yes**
Flow Rate	**1.0 ml/min**
Injection Loop	**25ul**
Calibration Standards (ppm)	**1, 5, 10, 50**
Gradient Method	**0-20 min. (2 mM KOH) [10mA ASRS setting]**
	20-40 min. (2-35 mM KOH gradient) [80 mA ASRS setting @ 30 min]
	40-50 min. (35 mM KOH)
	50-55 min. (2 mM KOH) [10mA ASRS setting]
Column heater	**Thermo Scientific "Hot Pocket" 300mm**
Column Temperature	**50 C**
CD Detector Temperature	**35 C**
Retention Time of Glycolate	12.1 min
Retention Time of Acetate	12.7 min
Retention Time of Formate	15.5 min

Using the above method conditions, acetate analysis was conducted on incoming 70 wt.% glycolic acid feed, and a selection of SRAT simulants that were currently on hand. In all cases, no acetate was found in the samples. A reporting limit (RL) was determine to be <1250 μg/g acetate. This value is fairly high due to the dilution required for reasonable chromatography of glycolic acid. Chromatograms are shown in Chart 3.8-4 RR Sample (RR 4) Acetate Analysis, and Chart 3.8-5 SRAT Simulant Acetate Analysis.

Chart 3.8-4 RR Sample (RR 4) Acetate Analysis

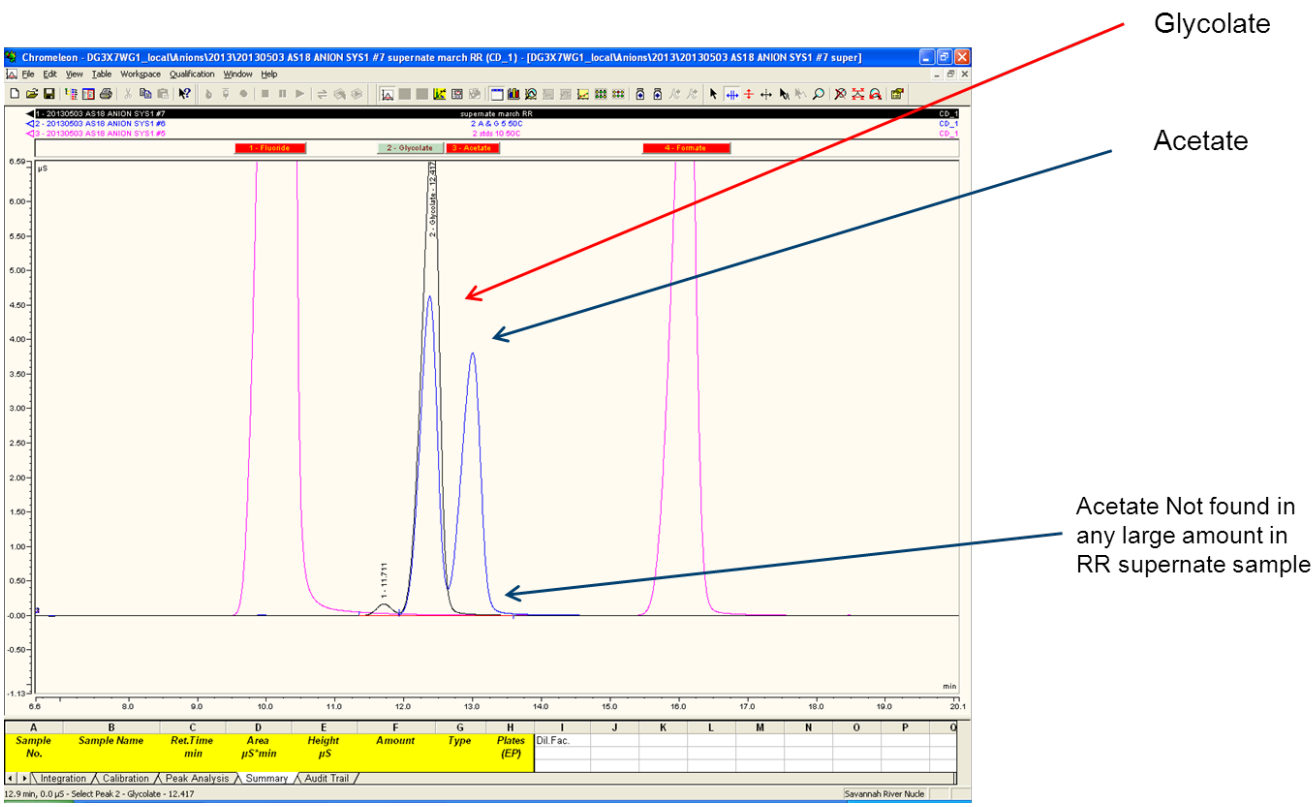


Chart 3.8-4 RR sample (RR 4) acetate analysis. In the measurement of the diluted 5000x RR supernate, there was not acetate detected. Limits were estimates at <1250 µg/g acetate.

Chart 3.8-5 SRAT Simulant Acetate Analysis

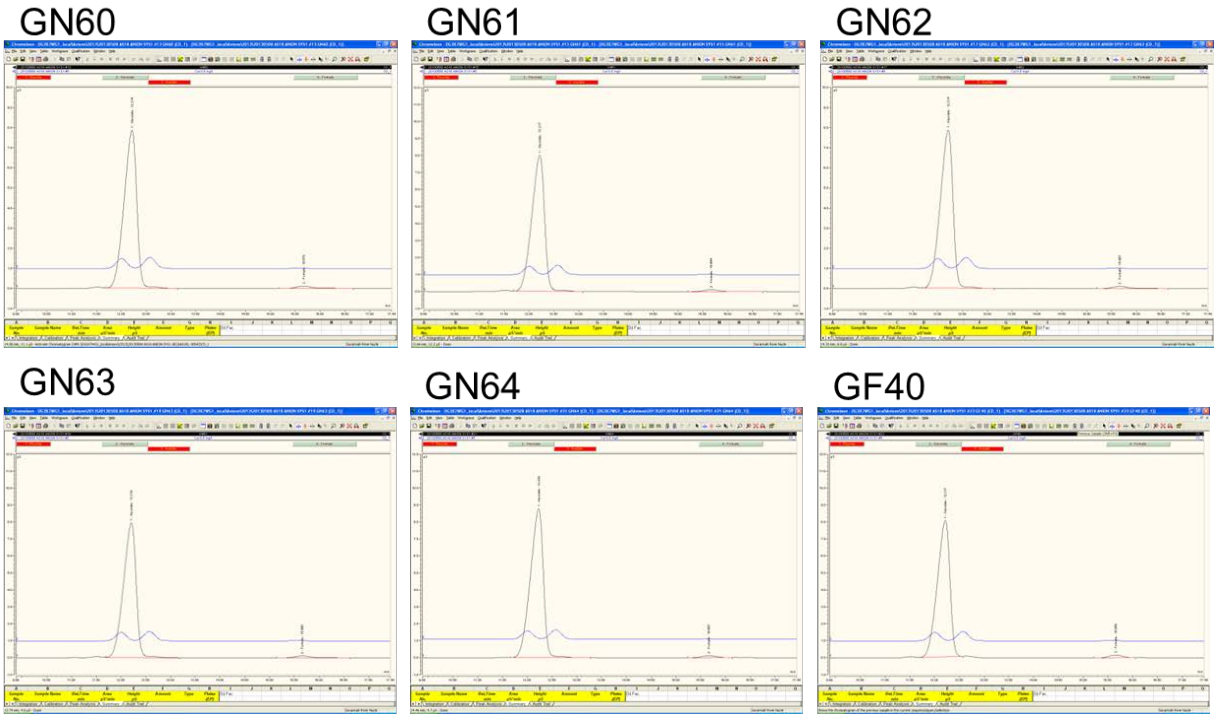


Chart 3.8-5 SRAT simulant acetate analysis. In all measurements of the diluted 5000x SRAT slurries, there was not acetate detected. The large peak at ~ 12 minute is glycolate. Reporting limits were estimates at <1250 μg/g for acetate.

3.9 AS19 Column SRAT Simulnat Unknown Peak Identification; Malonic Acid (Malonate), Glyoxylic Acid, Diglycolic Acid

Simulant SRAT slurry and supernate analysis identifies an unknown peak with retention time ~ 30 minutes using the AD IC method with the Dionex AS-19 column set. Chart 3.9-1 Unknown peak in SRAT simulant shows a small peak in the 500x dilution of the SRAT simulant 12-GN49-7485a. The peak has a retention time between that of sulfate and oxalate. The unknown peak can be estimated at 200-400 μg/g based upon near eluting peak response. A brief effort was made to identify the unknown peak. Virtual Column modeling software again was used to identify possible components near the retention time under the method conditions. A short list included; glutarate, iodide, maleate, selenate, succinate, tartrate. Possible other components were postulated based upon hypothetical reaction pathways in the SRAT including; malonate, glyoxylic acid, formaldehyde, and diglycolic acid. Of the compounds tested several can be discarded as unlikely reaction pathways. Iodide and selenate can be discarded as ICP-MS data did not show corresponding amounts of the iodine or selenium mass. Analytes tested as spike additions into SRAT simulants include; malonic acid (malonate), glyoxylic acid and diglycolic acid (diglycolate). Of the analytes tested only diglycolic acid has a reasonable

overlay with the unknown peak and also a likely impurity in 70 wt.% tech grade glycolic acid[8,9].

Chart 3.9-1 Unknown peak in SRAT Simulant

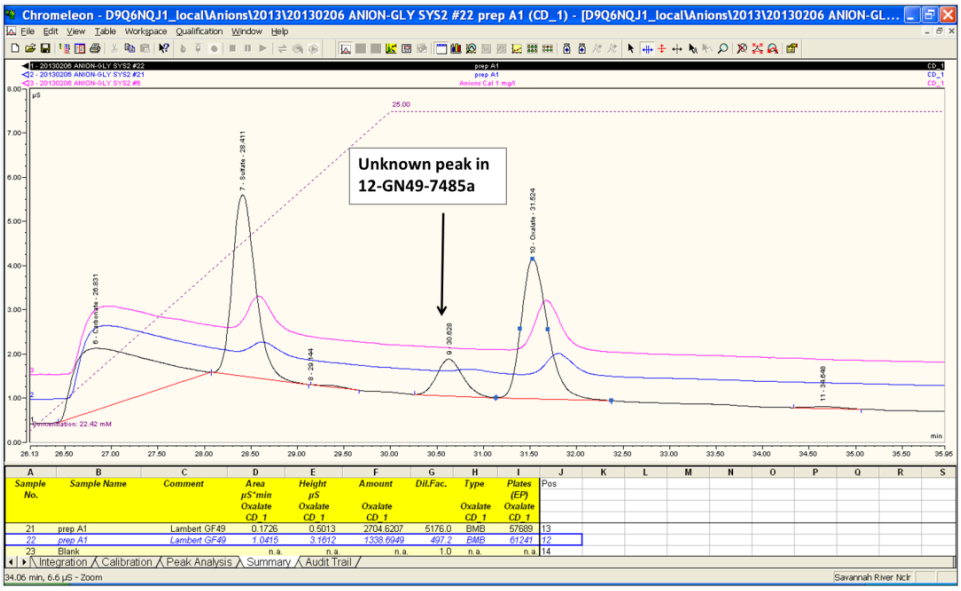


Chart 3.9-1 Unknown peak in SRAT simulant 12-GN49-7485a, peak at~ 30 minute has response ~ 200-400 ug/g (using response of near eluting peaks).

Chart 3.9-2 Unknown peak in SRAT Simulant (RR 4 sample), Malonate Spike

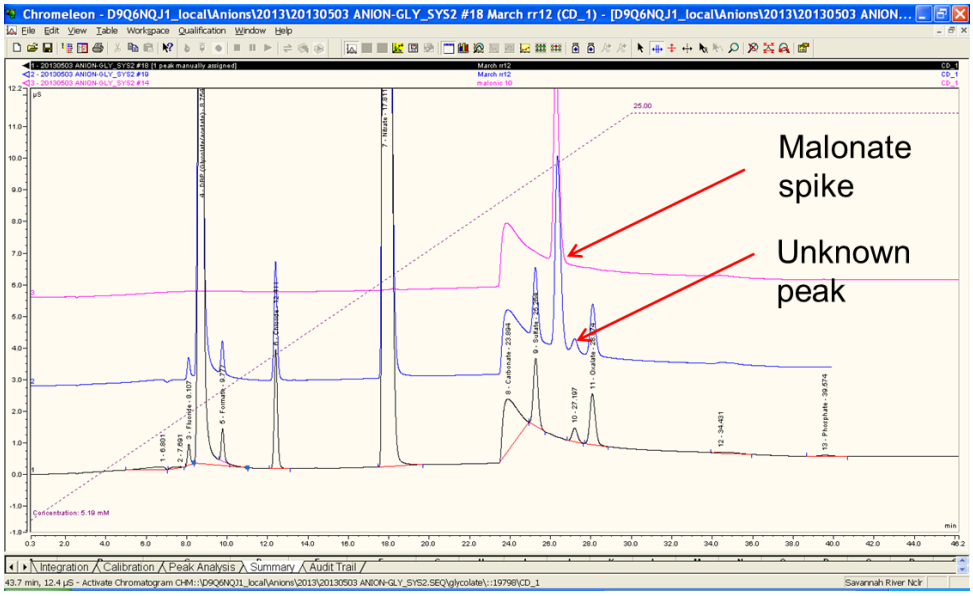


Chart 3.9-2 Unknown peak in SRAT simulant (RR 4 sample) overlay with malonic acid (malonate). The unknown peak and malonate spike to not overlay.

Chart 3.9-3 Unknown peak in SRAT Simulant (RR 4 sample), Glyoxylic Acid Spike

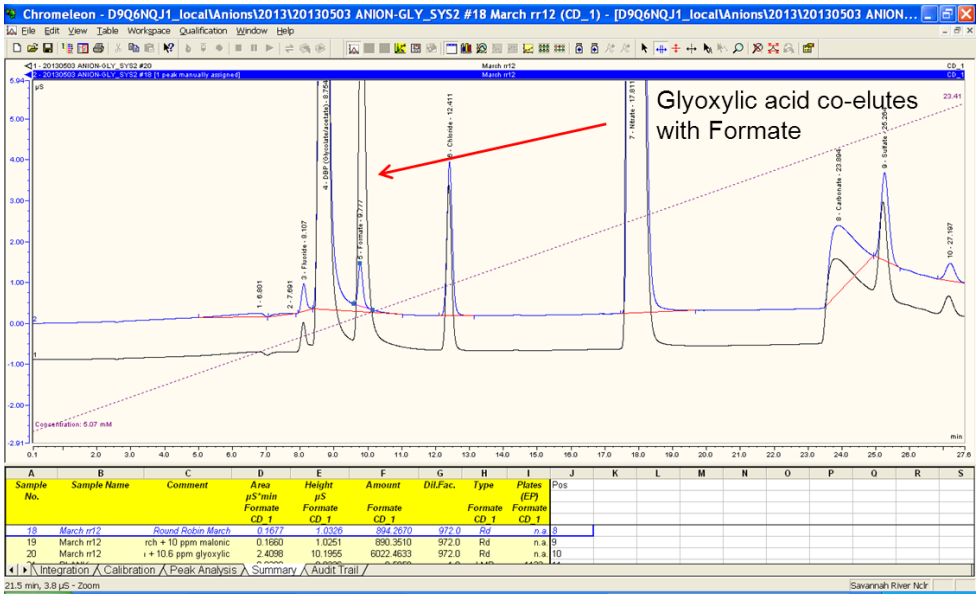


Chart 3.9-3 Unknown peak in SRAT simulant (RR4 sample) overlay with glyoxylic acid. The unknown peak and glyoxylic acid spike to not overlay, and would have similar retention time as formate.

Chart 3.9-4 Unknown Peak in SRAT Simulant (GN56 & GN57), Diglycolic Acid Spike

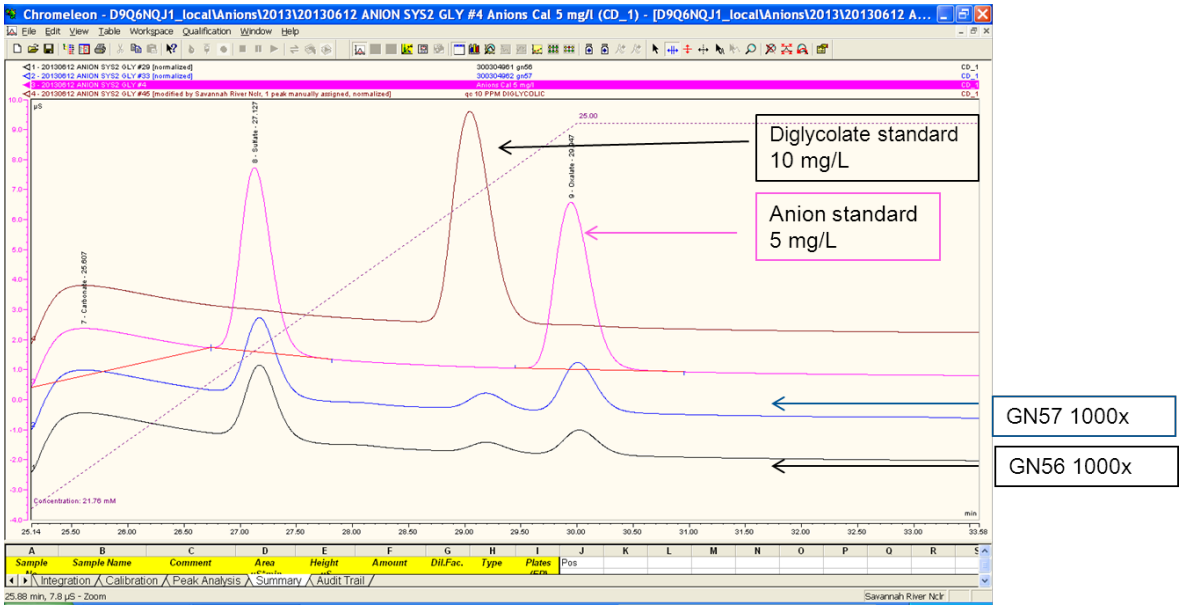


Chart 3.9-4 Unknown peak in SRAT simulant dilutions (GN56 & GN57) overlay with diglycolic acid. The unknown peak and diglycolic acid (diglycolate) spike do overlay, and does have similar retention time as the unknown peak. This compound is also a likely impurity in glycolic acid 70% technical solution.

3.10 Tests of Incoming 70 Weight Percent (Wt%) Glycolic Acid for Impurities by IC/ICP-MS

Tests on the incoming 70 wt.% tech grade glycolic acid were performed. The glycolic acid was analyzed by IC for confirm concentration, and also to search for impurities. IC analysis was run on 5/17/2012 and again on 5/8/2013. Both cases had the glycolic acid at the advertised 70 wt.% (within method uncertainty). In addition, a minor peak with the retention time of formate was observed, and a minor peak with the retention time of diglycolic acid was observed. See Chart Chart 3.10-1 IC chromatogram of 70 wt.% glycolic acid tech grade, and expanded view of the unknown peak assumed to be diglycolate. A later Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) scan of the glycolic acid was performed to record impurities. Chart 3.10-2 ICP-MS of 70 wt.% Glycolic Acid tech grade. ICP-MS analysis found, and trace ppb amounts of metals, ppm levels of common cations, also <20 ppb iodine from 5/16/13 analysis.

Chart 3.10-1 IC Chromatogram of 70 wt.% Glycolic Acid Tech Grade

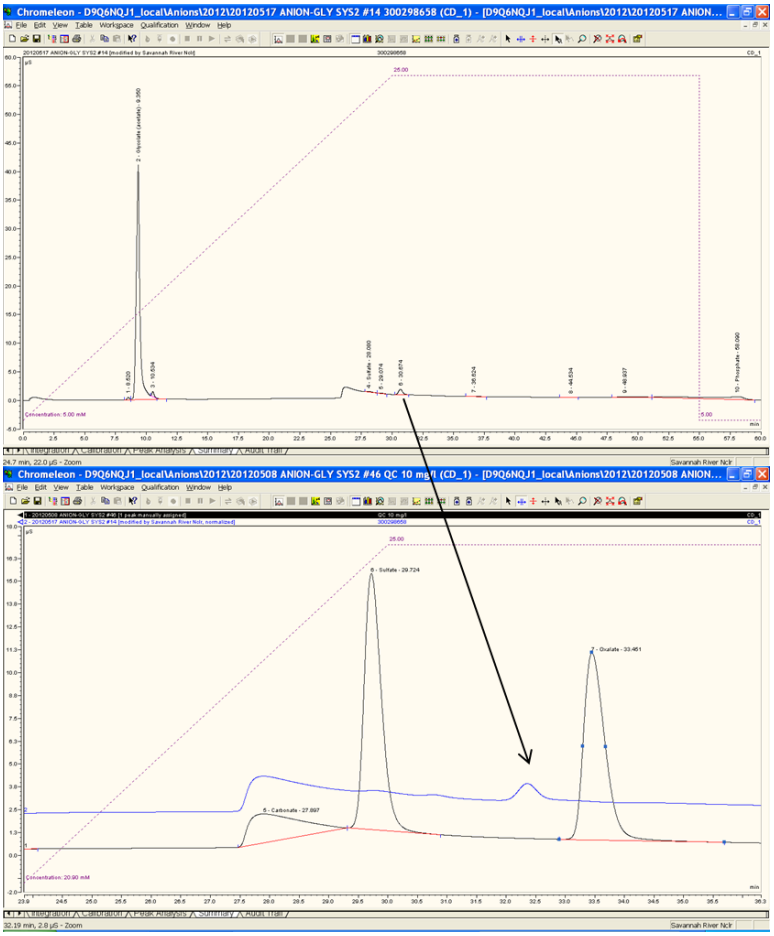


Chart 3.10-1 IC Chromatogram of 70 wt.% glycolic acid tech grade and expanded view of the unknown peak assumed to be diglycolate, overlaid with sulfate and oxalate standards.

Chart 3.10-2 ICP-MS of 70 wt.% Glycolic Acid Tech Grade

Quantitative Analysis - Summary Report SRNL					
5/23/2013					
Sample ID:	White 70 GA				
DF	1000x 100x				
Results (Mean Data)					
	Analyte	Mass	Conc.	RSD	Units
	Li	7	7.69	23.3	ppb
	Be	9	< 5	N/A	ppb
	B	11	946	5	ppb
	Na	23	41800	3.8	ppb
	Mg	24	12200	4.1	ppb
	Al	27	4930	2.4	ppb
	Ca	44	2600	18.3	ppb
	Cr	52	236	2.7	ppb
	Cr	53	234	19.4	ppb
	Fe	56	2520	2.3	ppb
	Fe	57	2670	3.4	ppb
	Ge	72	< 10	N/A	ppb
	As	75	< 5	N/A	ppb
	Se	78	< 5	N/A	ppb

Chart 3.10-2 ICP-MS analysis 70 wt.% glycolic acid tech grade, results show trace ppb amounts of metals, ppm levels of common cations, also <20 ppb iodine from 5/16/13 analysis (μg/L).

3.11 Derivitization of DWPF alternatives for Analysis by GC-MS

One of the strategies explored to measure glycolic acid in SRAT cycle samples was an alternative or confirmatory method by Gas Chromatography - Mass Spectrometry (GC-MS). The GC-MS method for analysis involved a derivatization and extraction preparatory step. This preparatory step employed BF_3-butanol for preparing n-butyl esters from the mono and dicarboxylic acids in the SRAT cycle samples. The esterfication is intended to improve volatility and peak shape of the analytes for GC analysis. Also, due to the lack of discrimination between carboxylic acids in the esterification reaction, it was thought the butyl esters of formic acid, acetic acid, and oxalic acid would also be measureable by the method. Malonic acid was used as an internal standard to track reaction recoveries. See Chart 3.11.1: BF_3-butanol esterification reaction products for various carboxylic acids, for examples of reaction products.

Tests produced erratic results for using this technique for the carboxylic acids. Multiple complications with this method limit its practicality in monitoring the carboxylic acids in SRAT cycle products. First is the difficulty in using derivation reactions in producing reproducible analytical results in production environments. This would limit its use to simply a complimentary or confirmatory method. In addition, the choice of BF_3-butanol as derivatization reactant was problematic. Many of the reaction products of interest have boiling points below that of butanol, which is the solvent of the extracted products. Standard GC-MS semi-volatile analysis methods do not measure analytes of boiling points below that of the injected solvent. See Chart 3.11.2: Boiling points of reaction products and solvents associated with the BF_3-butanol derivatization. Glycolic acid was observed to be derivatizing into the product n-butyl glycolate. However, peak shape was very poorly defined due to the polar OH^- group of the molecule not eluting through the

GC column efficiently. In addition, note the large tri-buytl borate reaction byproduct eluting near the n-butyl glycolate masking quantification. See Chart 3.11-2 GC-MS chromatogram and MS fragments of BF_3-butanol esterification reaction products for various carboxylic acids. Dibutyl oxalate and the internal standard dibutyl malonate did perform well on the column and would be suitable for method development for these analytes. Further development for this technique using an alternative derivatization agent may produce an acceptable confirmatory method, however testing would be required.

Chart 3.11-1 BF_3-butanol Esterification Reaction Products for Various Carboxylic Acids.

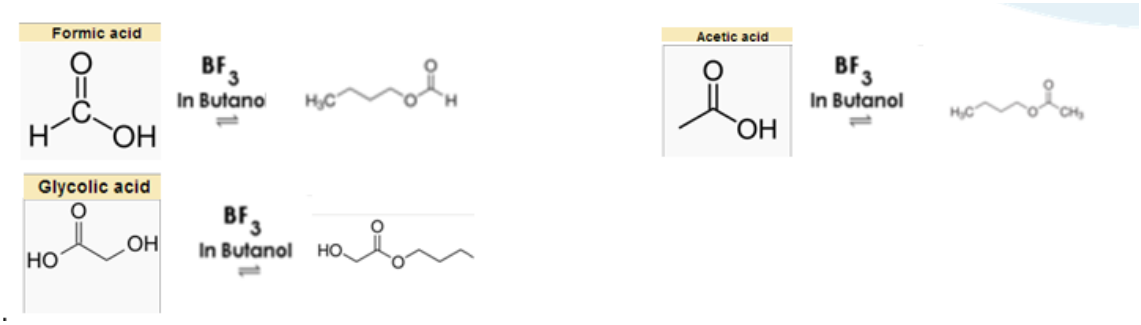


Table 3.11-1 Boiling points of Reaction Products and Solvents Associated with the BF_3-butanol Derivatization.

	Boiling Point (C)	Molecular Weight (g/mol)
Hexanes	69	86
n-butyl formate	107	102
n-butyl acetate	116	126
Butanol	117	74
n-Butyl glycolate	190	132
Dibutyl oxalate	239	202
Dibutyl malonate	251	216

Table 3.11-1 Boiling points of reaction products and solvents associated with the BF_3-butanol derivatization. Many of the reaction products of interest have boiling points below that of butanol, which is the solvent of the extracted products.

Chart 3.11-2 GC-MS Chromatogram and MS Fragments of BF_3-butanol Esterification Reaction Products for Various Carboxylic Acids.

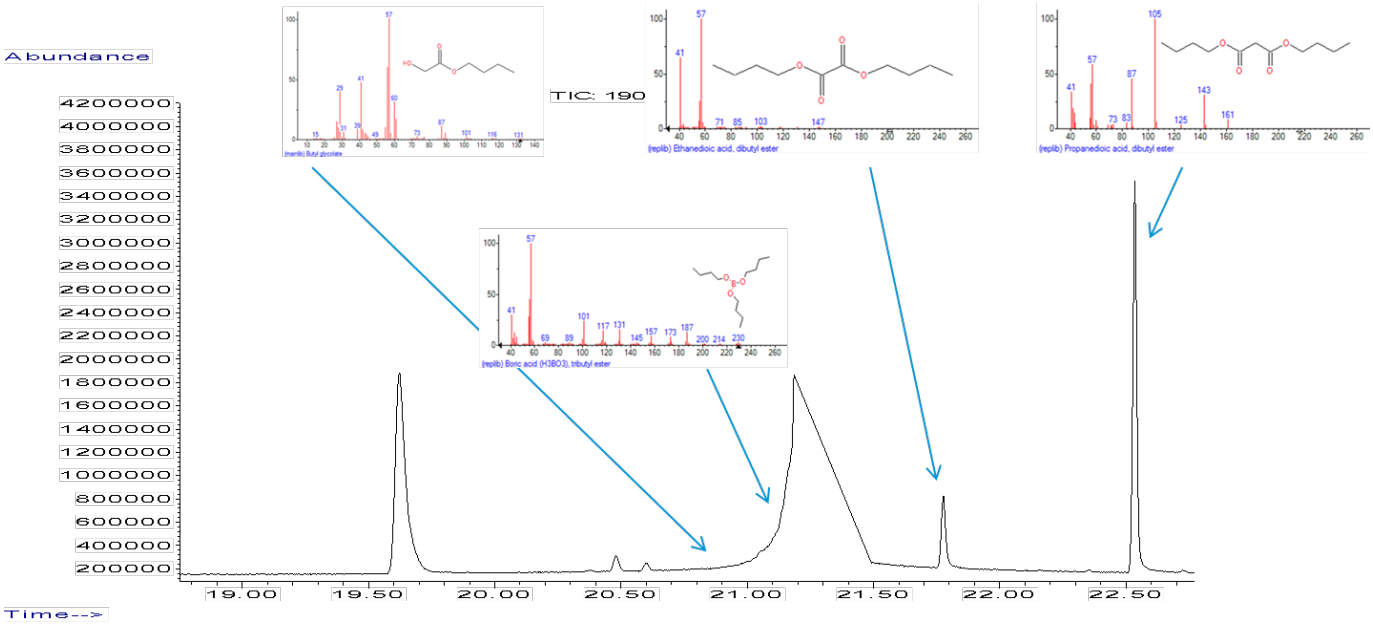


Chart 3.11-2 GC-MS chromatogram and MS fragments of BF_3-butanol esterification reaction products for various carboxylic acids. Note the large tri-buytl borate reaction byproduct eluting near the n-butyl glycolate masking quantification.

4.0 Conclusions

Ion Chromatography (IC) is the principal analytical method used to support studies of SRAT chemistry. IC measures anions such as nitrate, nitrite, formate, glycolate, oxalate, sulfate, fluoride, and chloride that indicate the redox conditions and corrosive properties of the SRAT Feed and SRAT Product. The analytical reliability of glycolate determinations by IC was challenged by multiple analytical round robins involving the DWPF laboratory, the PSAL laboratory at 999-W, and the AD laboratory at 773-A. The initial round robins involved a SRAT simulant and a supernate fraction made from the filtrate of the SRAT simulant.

The results of initial round robins showed that the three laboratories were in agreement (for the purpose of this report, "agreement" is arbitrarily as no more than 20% difference) on the supernate determinations. However, for the sludge samples, the laboratories were not in agreement on the important organic anions glycolate and oxalate.

The results of current of round robin 4 consisted of the three laboratories analyzing another SRAT simulant (no supernate this time). The laboratories all applied the same slurry dilution protocol to improve comparisons. The inter-laboratory agreement of the sludge analyses was better than initial round robins with only oxalate measurements differing more than 20%. Oxalate measurements continue to show higher variation. This larger uncertainty is currently addressed by an additional IC measurement using acid leach on the slurry for total oxalate. It should also be noted that large amounts of glycolate in the SRAT samples will have an impact on detection limits of near eluting peaks, namely fluoride and formate ions.

Multiple scoping experiments were also performed to help define operating parameters around the IC analysis. Dilution protocol testing and testing on an acid leach of filtered solids was performed to determine the impact of filtration on anion determinations. It was observed that for the protocols tested, the order of when the filtration step occurs has no significant alteration to the glycolate measurement. The slurry dilution protocol as used by the round robin was part of this analysis. The acid leach of filtered solids did not result in a significant increase in the measurements of anions of interest, and therefore the amount of anions retained on the filter that are not soluble in DI water are considered an insignificant contribution.

Additional modeling was performed exploring the equipment and method differences between the testing laboratories. Most differences between the methods are minor, proven by the ability to reach commonality in the round robin measurements. However, there are some temperature control equipment differences that are significant leading to a recommendation of heated jacket for analytical columns that are remoted for use in radiohoods.

Acetate is a possible analyte that can have a similar retention time as glycolate on the IC methods tested. This anion also would have an impact on the REDOX of the SRAT, if it was present. Therefore, a method was developed with a Dionex AS18 column for acetate

analysis. All SRAT simulants tested with this method did not find the presence of acetate.

During the analysis of SRAT simulants the presence of an unknown peak was identified by IC. This unknown peak is a minor peak in the chromatogram, estimated at 200-500 μg/g in the SRAT slurry. Spike addition into SRAT simulant of potential analytes resulted in a match for diglycolic acid. Testing of incoming 70 wt.% glycolic acid for impurities, also showed the presence of this peak in the glycolic acid, and is the likely source of the impurity.

Alternative analysis methods for the measurement of carboxylic acids were also explored. Derivatization of DWPF carboxylic acids by esterification, then analysis method by Gas Chromatography - Mass Spectrometry (GC-MS) was explored. Multiple complications with this method limit its practicality in monitoring the carboxylic acids in SRAT cycle products. More work would need to be applied to this method to be viable for use.

5.0 Recommendations, Path Forward or Future Work

Recommendations summary:

- IC systems that have remoted components for use in a radiohoods benefit from the use of temperature control, set slightly above ambient, as supplied by a heated jacket for the analytical columns.

- In general IC dilution best practices involve dilution of the sample with the mobile phase (eluent). This concentration is recommended to be at the concentration of the initial gradinet profile. Diluent concentrations higher than the initial gradient concentration may cause peak shifts for the first eluting peaks.

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