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Organics Characterization of DWPF Alternative Reductant Simulants, Glycolic Acid, and Antifoam 747

October 1, 2013

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October 1, 2013

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EXECUTIVE SUMMARY

The present study examines the fate of glycolic acid and other organics added in the Chemical Processing Cell (CPC) of the Defense Waste Processing Facility (DWPF) as part of the glycolic alternate flowsheet. Adoption of this flowsheet is expected to provide certain benefits in terms of a reduction in the processing time, a decrease in hydrogen generation, simplification of chemical storage and handling issues, and an improvement in the processing characteristics of the waste stream including an increase in the amount of nitrate allowed in the CPC process. Understanding the fate of organics in this flowsheet is imperative because tank farm waste processed in the CPC is eventually immobilized by vitrification; thus, the type and amount of organics present in the melter feed may affect optimal melt processing and the quality of the final glass product as well as alter flammability calculations on the DWPF melter off gas.

To evaluate the fate of the organic compounds added as the part of the glycolic flowsheet, mainly glycolic acid and antifoam 747, samples of simulated waste that was processed using the DWPF CPC protocol for tank farm sludge feed were generated and analyzed for organic compounds using a variety of analytical techniques at the Savannah River National Laboratory (SRNL). These techniques included Ion Chromatography (IC), Gas Chromatography-Mass Spectrometry (GC-MS), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), and Nuclear Magnetic Resonance (NMR) Spectroscopy. A set of samples were also sent to the Catholic University of America Vitreous State Laboratory (VSL) for analysis by NMR Spectroscopy at the University of Maryland, College Park.

Analytical methods developed and executed at SRNL collectively showed that glycolic acid was the most prevalent organic compound in the supernatants of Slurry Mix Evaporator (SME) products examined. Furthermore, the studies suggested that commercially available glycolic acid contained minor amounts of impurities such as formic and diglycolic acid that were then carried over in the SME products. Oxalic acid present in the simulated tank farm waste was also detected. Finally, numerous other compounds, at low concentrations, were observed present in etheric extracts of aqueous supernate solutions of the SME samples and are thought to be breakdown products of antifoam 747.

The data collectively suggest that although addition of glycolic acid and antifoam 747 will introduce a number of impurities and breakdown products into the melter feed, the concentrations of these organics is expected to remain low and may not significantly impact REDOX or off-gas flammability predictions. In the SME products examined presently, which contained variant amounts of glycolic acid and antifoam 747, no unexpected organic degradation product was found at concentrations above 500 mg/kg, a reasonable threshold concentration for an organic compound to be taken into account in the REDOX modeling. This statement does not include oxalic or formic acid that were sometimes observed above 500 mg/kg and acetic acid that has an analytical detection limit of 1250 mg/kg due to high glycolate concentration in the SME products tested. Once a finalized REDOX equation has been developed and implemented, REDOX properties of known organic species will be determined and their impact assessed. Although no immediate concerns arose during the study in terms of a negative impact of organics present in SME products of the glycolic flowsheet, evidence of antifoam degradation suggest that an alternative antifoam to antifoam 747 is worth considering. The determination and implementation of an antifoam that is more hydrolysis resistant would have benefits such as increasing its effectiveness over time and reducing the generation of degradation products.

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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
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

DWPF continues to produce canisters containing radioactive materials immobilized in glass for on-site storage as shown in Figure 1-1. Conditioned tank farm waste feed [Fact Sheet, 2012] is processed through the CPC, qualified by analysis and the Product Composition Control System (PCCS), stored in the Melter Feed Tank (MFT), and then transferred to the melter for vitrification [Jantzen, 2012]. The adjustments made to the tank farm waste feed in the CPC are critical to producing a quality glass product. DWPF uses a REDOX model based on the oxidation state of iron to predict glass quality [Jantzen, 2012]. Qualified feed from the MFT should have the correct balance of reductants and oxidants to form a melt without foaming or metal formation issues. Organic compounds present in the MFT that are not correctly accounted for in the REDOX model can result in an iron valence state that differs from the REDOX model predicted value leading to less than optimal melt processing and glass product. In addition, these compounds add carbon and hydrogen to the melter off gas flammability calculation and thus reliable measurements of these compounds are important for operation [Lambert, 2011].

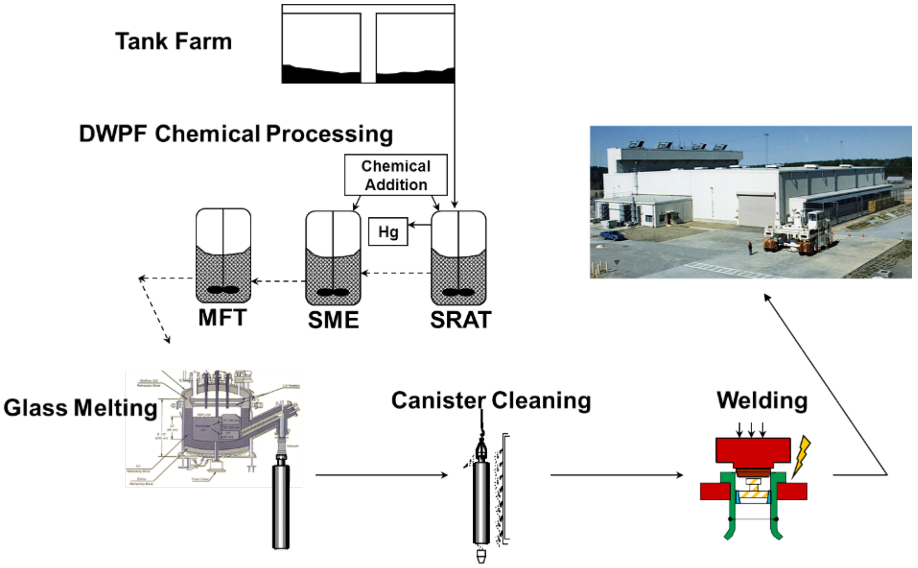


Figure 1-1: DWPF Vitrification Overview – Tank Farm Feed is processed in the CPC by 1) adding nitric and formic acid with heating in the Slurry Receipt and Adjustment Tanks (SRAT), 2) qualify, 3) transfer product to the Slurry Mix Evaporator SME, 4) add Borosilicate (frit) and concentrate, 5) qualify, and 6) transfer to MFT.

Two major sources of organic compounds in the CPC are antifoam 747 and formic acid, as well as oxalic acid from the tank and filter cleaning process at 512-S. Antifoam 747 is a non-ionic super spreader surfactant that is added to the CPC during sludge processing to reduce foaming. Formic acid is an organic acid (pKa 3.75) used in the CPC to reduce mercury oxide to elemental mercury for steam striping and removal, to adjust the pH of the waste for desired rheology properties, and to achieve the correct REDOX potential for the melter. Despite having processing and storage issues, formic acid has worked well in the process as an organic reductant [Pickenheim, 2009]. Ten sludge batches have successfully been vitrified and poured into canisters for long term storage. However, during operation of the CPC process hydrogen generation from the reaction of formic acid with noble metals requires constant purging of the vessel, analysis for hydrogen to prevent a flammable offgas, and safety interlocks.

The purge requirement can be lowered, and the safety significane of the offgas analyzers can be lowered if glycolic acid is used.

Scoping evaluations have been performed to determine the feasibility and advantages of using glycolic acid instead of formic acid in the CPC of DWPF [Pickenheim, 2009]. Glycolic acid may have the advantages of generating less hydrogen, improving the rheology of the material to be processed, simplifying chemical storage issues, and increasing CPC throughput [Pickenheim, 2009]. Bench-scale scoping studies with simulated waste used both glycolic acid and antifoam 747. The SME product was examined by a variety of analytical methods to determine what starting organic compounds remained and what organic compounds were formed.

1.1 Work Authorization

This work was requested by SRR (HLW-DWPF-TTR-2013-0003).

1.2 Organic Compounds Formed in the CPC

This report covers (1) a chemical overview of glycolic acid and antifoam 747, (2) the analysis of DuPont glycolic acid 70 wt.% technical solution, (3) the determination of antifoam 747 degradation products in the SME product, and (4) the determination of acetic acid and malonic acid as potential decomposition products from glycolic acid in the SME product.

1.2.1 *VSL Analyses*

Researchers at VSL developed an extraction protocol followed by NMR analysis at the University of Maryland of waste simulants GN56, GN57, and 70 wt.% glycolic acid technical solution.

1.2.2 *SRNL Analyses*

Researchers at SRNL analyzed SME products of waste simulant and DuPont glycolic acid 70 wt.% technical solution by a variety of analytical techniques such as Ion Chromatography (IC), Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES), Inductively Couple Plasma Mass Spectrometry (ICP-MS), Gas Chromatography (GC), and Nuclear Magnetic Resonance (NMR) Spectroscopy. In addition, the VSL extraction protocol, described in Appendix A, was followed and the residues were characterized.

2.0 Experimental Procedure

Testing was completed by researchers at VSL and SRNL on SME products GN56 and GN57 described in Appendix A and on DuPont glycolic acid 70 wt.% technical solution. Samples of SME product were generated from bench scale CPC testing [Lambert, 2013].

2.1 VSL Testing

VSL was tasked with the analysis using NMR spectroscopy of SME product samples that were clarified by centrifugation. Due to the presence of iron and/or other paramagnetic species that shorten the relaxation time of the excited nuclei, direct NMR analysis of the supernate solutions did not provide any useful information in terms of structure elucidation. Attempts were then made to remove iron prior to NMR analysis through addition of hydroxide but were proven unsuccessful. Subsequently, extraction of organics present in the aqueous solutions was studied using various polar and non-polar solvents. The most successful extraction protocol involved the use of diethyl ether. Briefly, ~10 g of the supernate solution of a SME product sample was extracted twice with diethyl ether. The extracts were combined, dried with $MgSO_4$ overnight, the solvent was removed, and the residue was weighed. The residue and DuPont glycolic acid 70 wt.% technical solution were analyzed by NMR at University of Maryland [Appendix, VSL E-mail dated 6/03/2013.]

2.2 SRNL Testing

SRNL examined SME product samples by IC for water soluble small carboxylic organic acids (chain length approximately 5 carbons or less). Methods were developed in-house to quantify acetic, glycolic, malonic, and diglycolic acid. An established IC method currently determines formic and oxalic acids.

Chromatograms of other acids such as tartaric, succinic, maleate, and glutarate were simulated as possible impurities using modeling Dionex Virtual Column software and compared to actual analyses of SME product to determine their potential presence. Some additional inorganic compounds (iodide, selenate) were also modeled as potential impurities. Other methods of analysis used to characterize SME product were GC-MS, ICP-AES, and NMR.

3.0 Results and Discussion

Sample preparation and analysis were performed at SRNL and VSL / University of Maryland. Table 3-1 describes the samples examined by each laboratory. The makeup of each sample is listed in Appendix B.

Table 3-1: SME Simulated Waste Samples

Sample	*Contains*		*Laboratory*
	Noble Metals-Hg	*Antifoam*	
70 wt.% Glycolic Acid	No	No	VSL and SRNL
GN56	No	Yes	VSL and SRNL
GN57	Yes	Yes	VSL and SRNL
GF40	Yes	Yes	SRNL
SB6i	No	No	SRNL

3.1 Chemistry of Glycolic acid and Antifoam 747

3.1.1 *DuPont 70 wt.% Technical Grade Glycolic Acid*

Glycolic acid is manufactured by DuPont (Figure 3-1) by treating formaldehyde with carbon monoxide and water in the presence of a sulfuric acid catalyst and pressure [Loder, 1936]. Acid-catalyzed formaldehyde carbonylation occurs by the Koch mechanism where oxygen protonated formaldehyde contains a carbocation and carbon monoxide forms a carbon-carbon bond in an addition step [Bell, 2008]. A water addition then occurs followed by a deprotonation step. Some of the potential byproducts and impurities from this process are formaldehyde (50-00-0), formic acid (64-18-6), diglycolic acid (110-99-6), methoxy acetic acid (625-45-6), and sulfate [Glycolic acid, 2000].

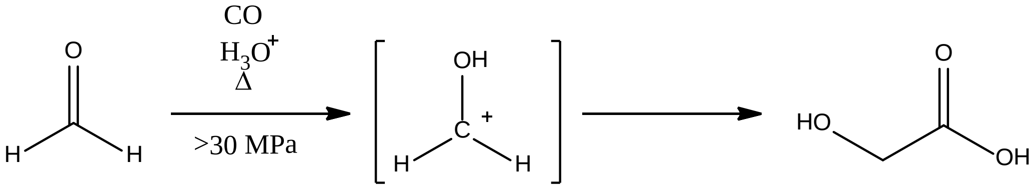


Figure 3-1: Glycolic acid manufacturing by acid-catalyzed carbonylation in the presence of water.

The resulting product can readily form cyclic (glycolide) and linear dimers in addition to longer chain polymers by dehydration and thus is sold as a 70 wt.% solution to ensure the monomer is the dominate species. Polymerization is a condensation reaction where the alcohol functional group of one glycolic acid monomer reacts with the carboxylic acid group of another monomer in a “head to tail” fashion [Hendricksen]. Note all condensation reactions of glycolic acid are reversible and catalyzed by acid or base. In the CPC, the concentration of acidic water is high relative to glycolic acid making oligomer formation unfavorable and favoring the left side of the equations in Figure 3-2.

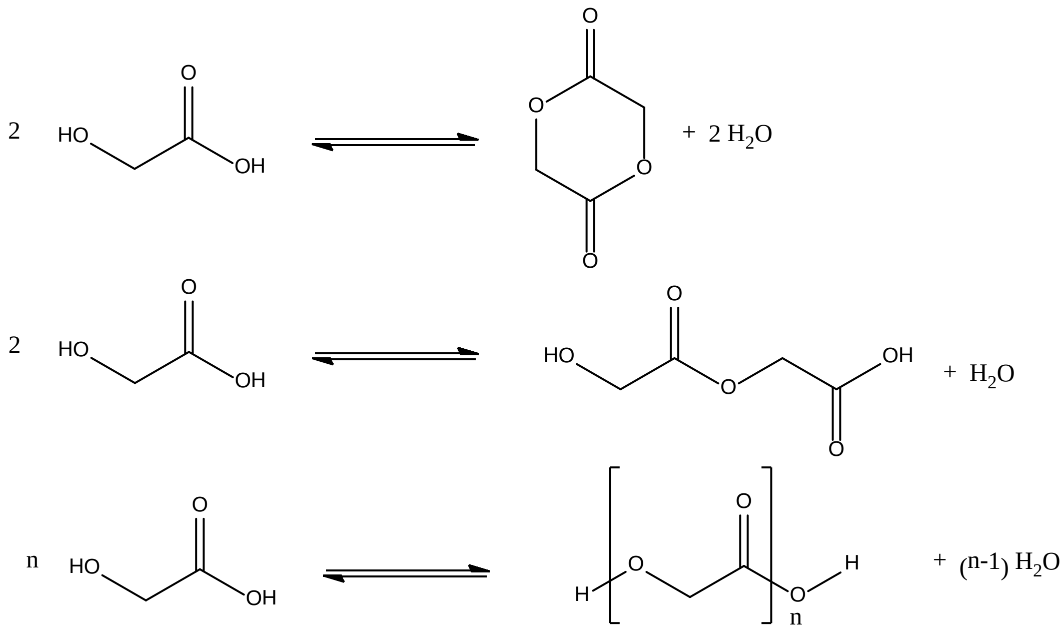


Figure 3-2: Glycolic acid dimer and oligomer formation from condensation reaction

3.1.2 *Antifoam 747*

Antifoam 747 is composed of low molecular weight trisiloxane polyether copolymers, as shown in Figure 3-3. The polymers can be denoted as MD'M where M is the trimethylsiloxy group $(CH_3)_3SiO_{1/2}$– and D' represents $–O_{1/2}Si(CH_3)(R)O_{1/2}–$ containing a relatively long side group (R = $–(CH_2)_3O(CH_2CH_3O)_nCH_3$) that is a methoxy terminated polyethylene oxide (PEO) chain of varying length. A propyl spacer bridges the silicon moiety to the PEO polymer [Peng, 2009]. The formulation contains 90 wt.% of the polymer where n = 7-9 and 10 wt.% where n = 11-13. The common route of synthesis for these polymers is by hydrosilylation of an olefinic-terminated PEO chain with a bis(trimethylsiloxy)methylsilane (1873-88-7), as shown in Figure 3-3.

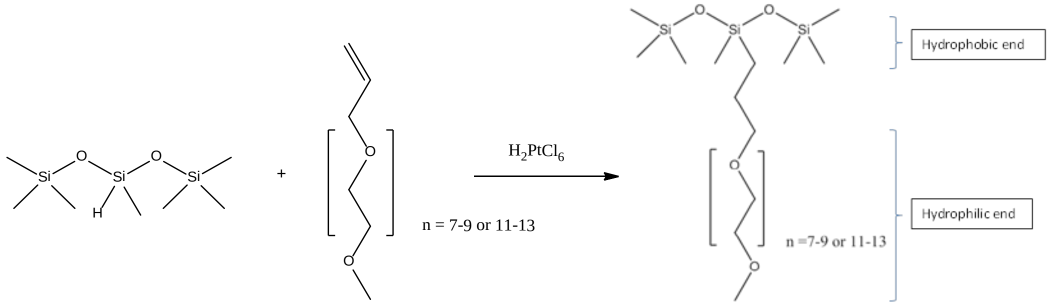


Figure 3-3: Antifoam 747 Nonionic Surfactant

When added to an aqueous solution, the silicon-based, nonionic surfactant initially resides on the surface of the water with a hydrophobic end that favors the air interface and a hydrophilic end that favors the water interface. The silicone-oxygen backbone is believed to orient itself on the surface of the water with the oxygen atoms in the water and methyl groups away from the water. These trisiloxane surfactants have been termed superspreaders due to their ability to reduce the surface tension of water promoting the wetting of a surface [Snow, 1995]. The surfactant has widespread use as an agriculture adjuvant and is commercially available as Momentive's Silwet L-77.

For optimal performance, these trisiloxane surfactants should be used at a pH between 6.5 to 7.5 [Silwet L-77, 2013]. Acid and base catalyzed hydrolytic cleavage of the silicone-oxygen bonds has been investigated [Stevens, 1993; Knoche, 1994; Sun, 1996; Nikolov, 2011] and occurs readily below a pH of 5 and above pH 9. In addition, the surfactant has been reported to degrade in neutral aqueous environment after forty days [Peng, 2009]. Researchers in our laboratory made similar observations based on water drop spreading tests [Lambert, 2011]. Stevens proposed a hydrolytic pathway shown in Figure 3-4 where the two products formed are hexamethyldisilioxane (107-46-0), an oil, and a tetrasiloxane co-polymer with reduced surface activity due to increased water solubility [Sun, 1996]. Another low boiling potential by-product would be trimethylsilanol (1066-40-6). Researchers are examining ways to improve hydrolysis resistance of superspreaders and new surfactants show promise [Peng, 2009].

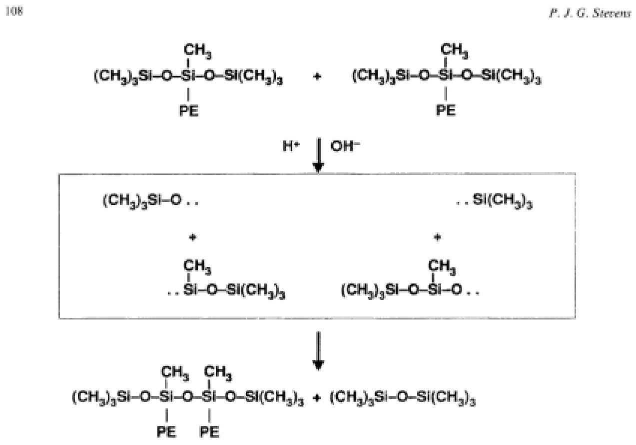


Figure 3-4: Hydrolytic Degradation of Antifoam 747

Other reactions can occur in the CPC in the presence of heating, time, acids, and noble metals. Table 3-1 highlights these potential degradation products for the purpose of identifying analytes that could be observed by analytical methods. These compounds can arise from the relatively slower cleavage of the carbon-oxygen bond of the PEO chain to form alcohols and diols such as glycol. Alcohols could then be oxidized to aldehydes and carboxylic acids.

Table 3-2: A Partial List of Potential Antifoam 747 Degradation Analytes.

Component	*CAS #*	*Formula*
Hexamethyldisiloxane	107-46-0	$C_6H_{18}OSi_2$
Trimethylsilanol	1066-40-6	$C_3H_{10}OSi$
Ethylene glycol	107-21-1	$C_2H_6O_2$
Ditheylene glycol	111-46-6	$C_4H_{10}O_3$
Triethylene glycol	112-27-6	$C_6H_{14}O_4$
Methanol	67-56-1	CH_4O
Allylic alcohol	107-18-6	C_3H_6O
Formic acid	64-18-6	CH_2O_2
Oxalic acid	144-62-7	$C_2H_2O_4$
Methoxy acetic acid	625-45-6	$C_3H_6O_3$

3.2 SRNL Results

DuPont glycolic acid 70 wt.% technical solution was analyzed by ion chromatography (IC), ICP-MS, GC and GC-MS. Particular attention was given to determining the presence of acetic acid or malonic acid as potential impurities. Analysis of SME products from bench scale testing was also analyzed and malonic acid or acetate was not observed. The major peak in all IC analysis samples was glycolate.

3.2.1 *DuPont Glycolic Acid 70 wt.% Technical Solution*

The received glycolic acid was analyzed by IC, GC-MS volatile organics analysis (VOA) and semi-volatile organics analysis (SVOA), and ICP-MS. Table 3-3 shows the results while Figure 3-5 is the IC chromatogram. Low levels of formic acid and sulfate were observed in addition to an unknown peak. This peak was in a region where diacidics tend to elute and also observed in some SME product runs. Modeling discussed in Section 3.2.2 was used to suggest possible candidates and malonate was predicted to appear to the left or sooner than the unknown peak. Standards were used to identify the peak and the best match was diglycolic acid (110-99-6) at <500 mg/L shown as peak 3 in Figure 3-6. Diglycolic acid was not spiked into the sample or analyzed by a secondary IC method.

Table 3-3: DuPont Glycolic Acid 70% Technical Solution.

Method	*Result*
GCMS VOA	No low boiling organics were detected above 1 mg/L
GCMS SVOA	No organics were detected above 1 mg/L
ICPMS	Al (5 ppm), Na (42 ppm), Mg (12 ppm), Ca (2.6 ppm), Fe (2.6 ppm) all other analytes were below 1 ppm including iodine
IC	Confirmed 70% concentration and low levels of formic acid and sulfate were observed. An unknown peak matched best diglycolic acid. No malonic or acetic acid was observed.

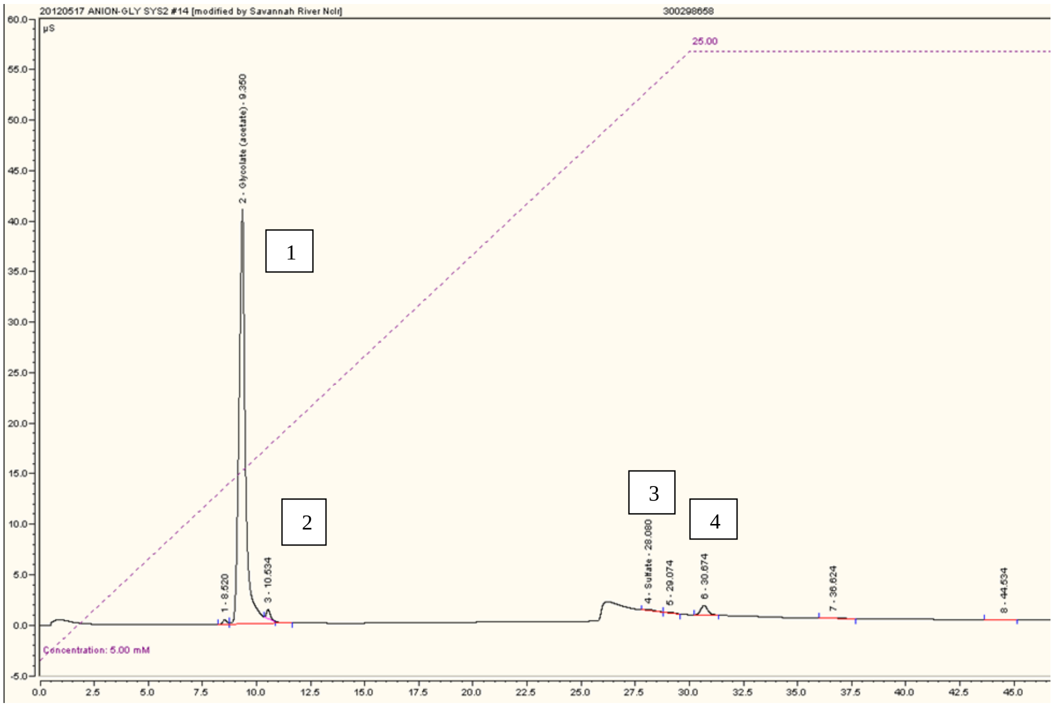


Figure 3-5: Ion Chromatography of Glycolic Acid 70% Technical Solution showing Glycolic acid (1), Formic acid (2), Sulfate (3), and Unknown Peak (4). On AS-19 column, acetic acid co-elutes with glycolic acid.

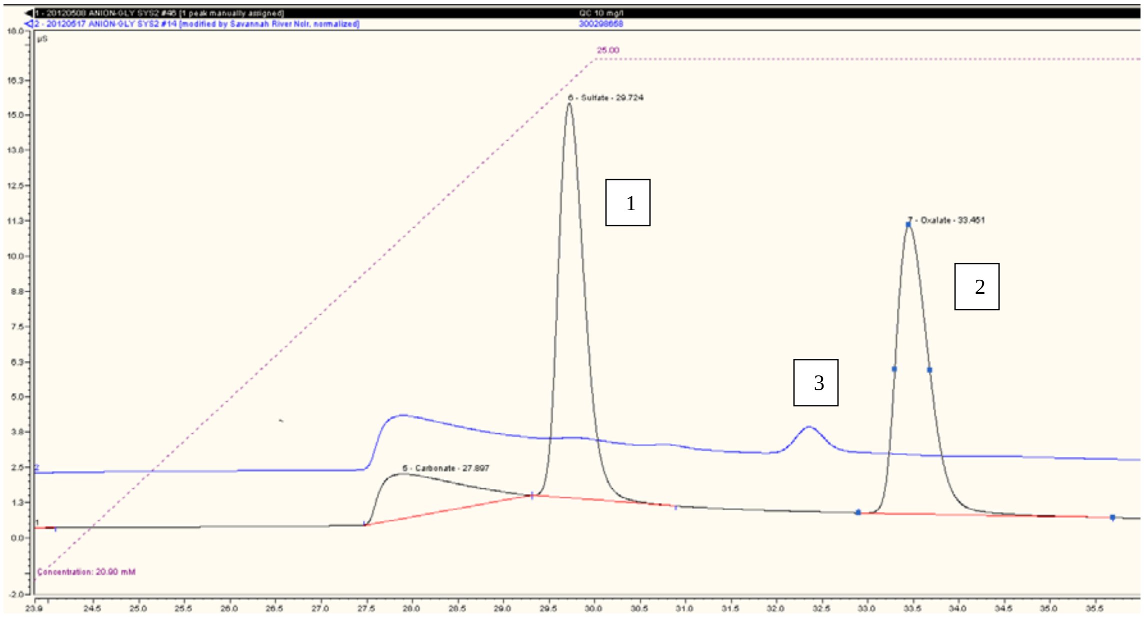


Figure 3-6: Ion Chromatography of Glycolic Acid 70% Technical Solution Enlarged Section from Figure 3-5 showing Sulfate (1) and Oxalate (2) in a 10 mg/L Standard (bottom), and the Unknown Peak (3) (Top).

3.2.2 *Ion Chromatography Analysis of SME Products*

A number of SME products, processed with varied amounts of glycolic acid and antifoam, were analyzed by IC. The chromatogram of one such product, GF40, is shown in Figure 3-7 along with chromatograms of the glycolate technical solution, malonic acid and SB6i; the latter is a sludge simulant without any organics. It is apparent that, in addition to a number of inorganic anions and glycolate, GF40 contains formate, oxalate, and an unidentified peak at ~27.3 min, which is identical to the one present in the glycolate technical solution. Subsequently, further analysis of SME products was predominantly aimed at:

a) determining the presence of acetate and malonate in the aqueous supernatants of SME product samples, and

b) identifying the unknown peak, carried over from the commercially available glycolic acid solution.

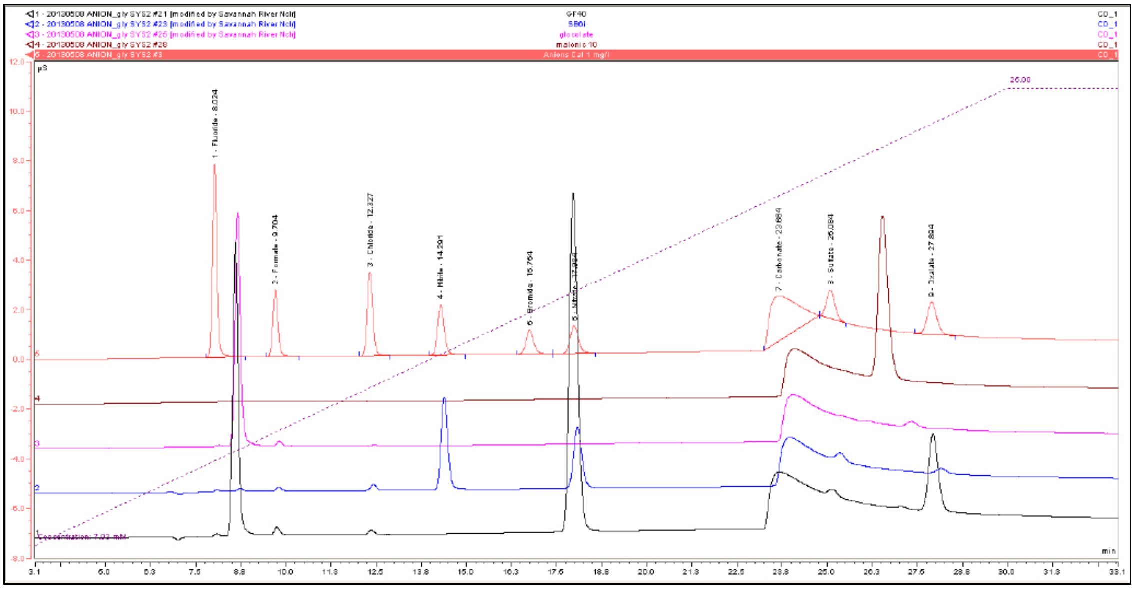


Figure 3-7. IC analysis on a Dionex AS-19 column of SME product GF40 (black line). The image also includes chromatograms of glycolic technical solution (pink line), sludge simulant SB6i (blue line), malonic acid (brown line), and various standards (red line).

Presence of acetate. Although presence of formate and oxalate is clearly evident in supernatants of SEM product samples, the presence of acetate is less clear in part due to similar retention times of glycolate and acetate under the eluting conditions employed. Subsequently, a method was developed that utilized a column heater and higher temperatures for the separation of the glycolate and acetate peaks. The results are shown in Figure 3-8. In general, switching from a Doinex AS-19 column to a Doinex AS-18 column with heating increased the retention times of the acids (Wiedenman, 2013). Optimal separation of glycolate and acetate peaks was achieved at 50ºC. Under the new eluting conditions, the retention times of the acids of interest were 12.1 min for glycolate, ~12.7 min for acetate, and 15.7 min for formate.

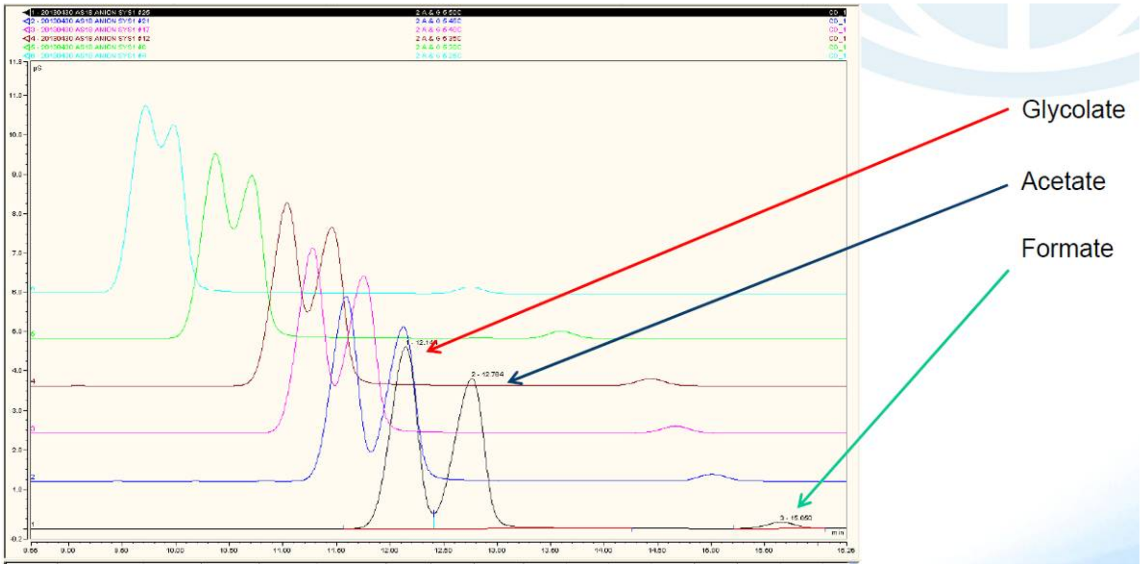


Figure 3-8. Development of a method for separating acetate and glycolate peaks using elevated temperatures on a Dionex AS-18 column. Optimal results were obtained at 50ºC (black line). Column temperatures are indicated.

A typical chromatogram SME product, obtained using the new elution method of Figure 3-8, is shown in Figure 3-9. In Figure 3-9, the large peak is glycolate and to the right is acetate followed by formate. A 0.5 ppm standard of glycolate and acetate is also shown as the above line in the chromatogram. Additional SME products were examined using this methodology and confirmed the absence of acetate above 1,250 mg/kg, which is near the estimated limit of the method. Figure 3-10 shows the analysis of a series on SME products using the Dionix AS-18 method. Dupont glycolic acid 70 wt.% technical solution was also examine and no acetate was observed.

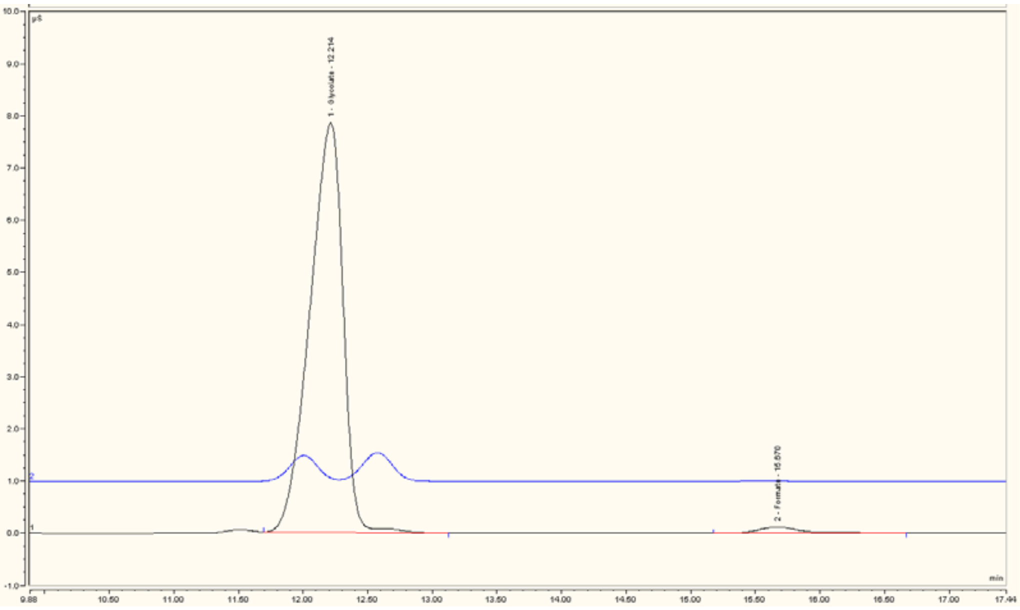


Figure 3-9: Typical Ion Chromatography of SME product (bottom) and a 500 ppb standard (top) of glycolate and acetate.

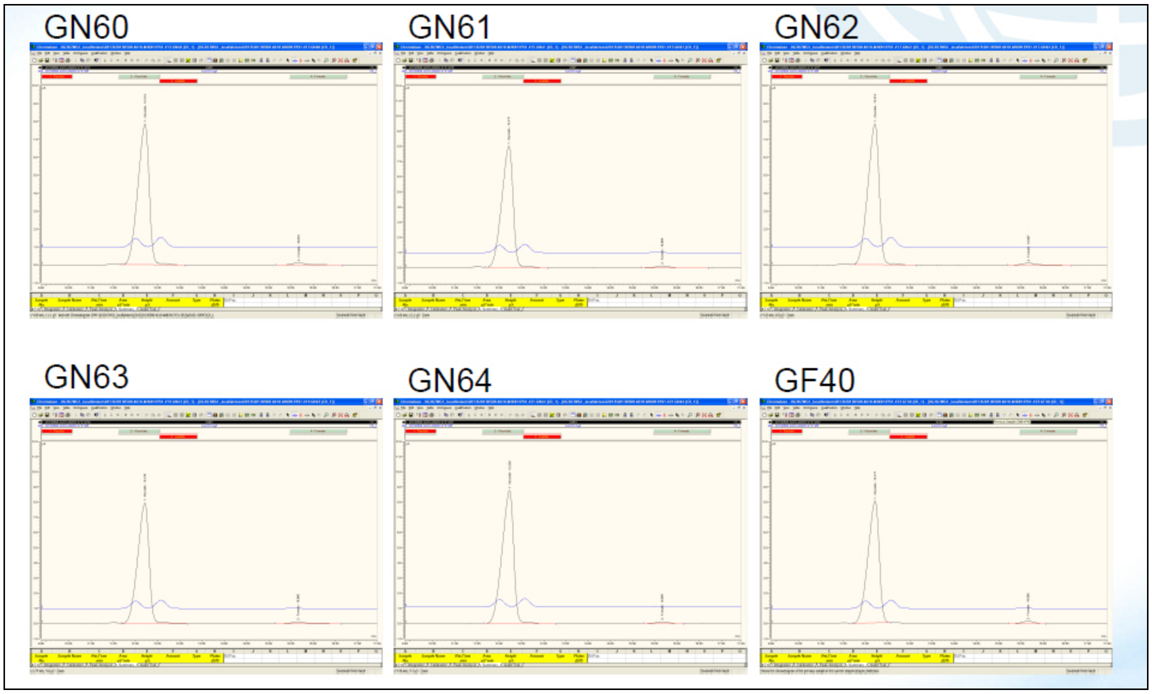


Figure 3-10. Ion chromatograms of various SME product samples. The lack of substantial amounts of acetate is evident.

Presence of Malonate. Malonic acid was identified as a compound that could potentially be present in glycolic acid and SME product but was ruled out by IC analysis as shown in Figures 3-7 and 3-11. In the latter figure, malonic acid was spiked into a SME product in order to determine if it resembled the unknown peak. The result was negative. Modeling using Dionex Virtual Column software was also used to determine where a malonate peak should elute (Figure 3-12) and confirmed the data of Figure 3-11. Malonic acid was also shown not to be present in the glycolic acid technical solution by NMR analysis as discussed in Figure 3-22.

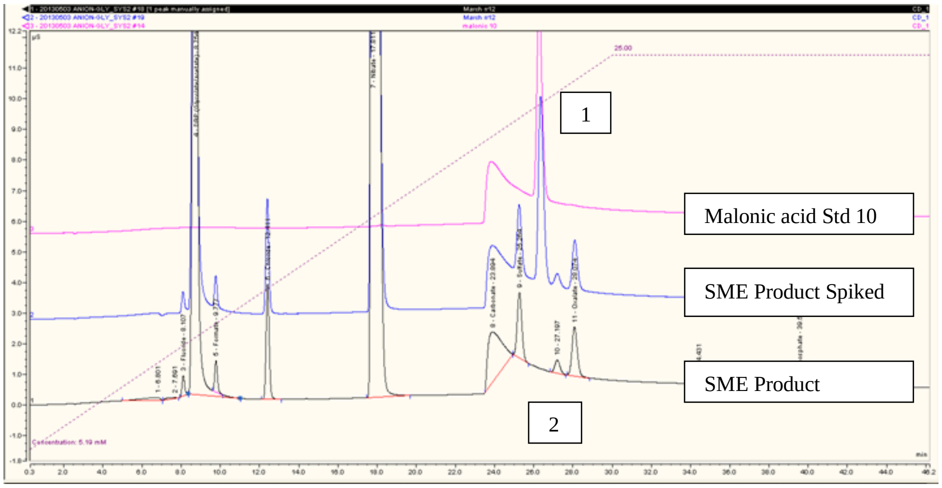
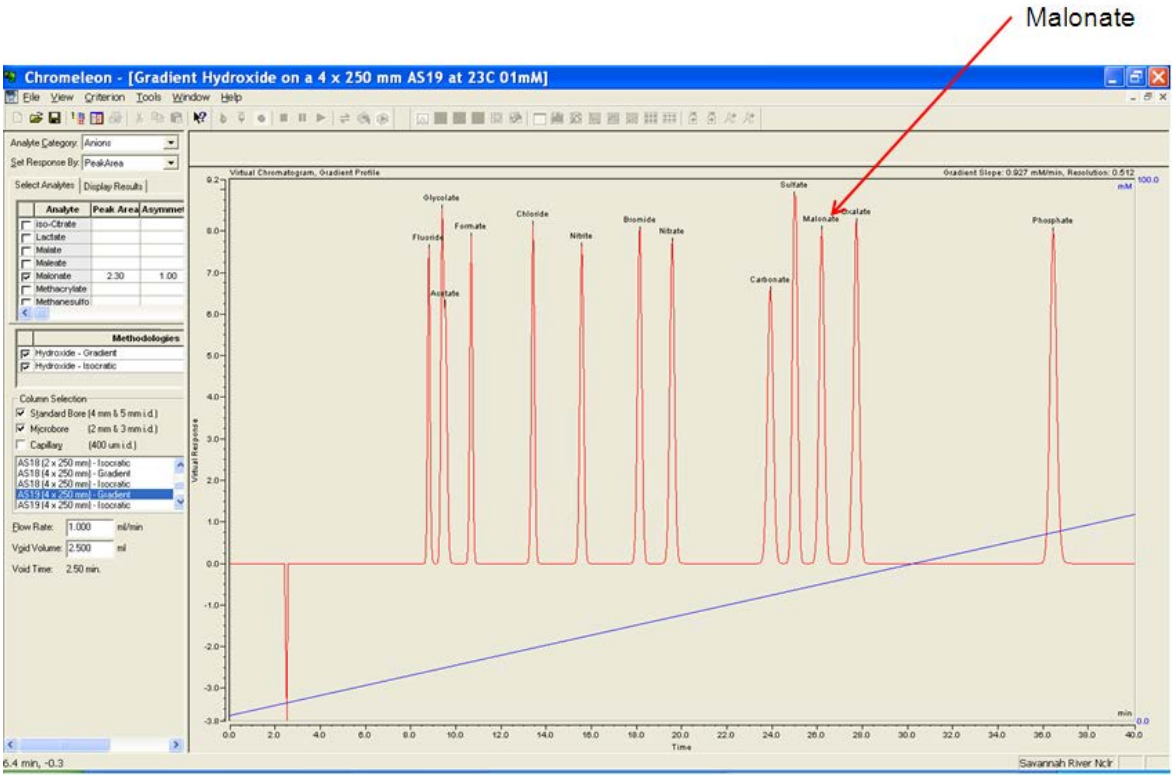


Figure 3-11: Multiple Ion Chromatograms Showing Unknown Peak (2) in SME Product and Malonate (1).

Identification of the unknown peak. Modeling using Dionex Virtual Column as shown in Figure 3-12 determined the unknown peak was likely a diacid and helped with the creation of a list of possible compounds (Table 3-4). Further work (Figure 3-15) showed the best match to be diglycolic acid. This compound is a known impurity in glycolic acid [Glycolic acid, 2000].



Analyte Category: Anions
Set Response By: PeakArea

	Analyte	Peak Area	Asymmet
☐	Iso-Citrate		
☐	Lactate		
☐	Malate		
☐	Maleate		
☑	Malonate	2.30	1.00
☐	Methacrylate		
☐	Methanesulfo		

☑ Hydroxide - Gradient
☑ Hydroxide - Isocratic

☑ Standard Bore (4 mm & 5 mm i.d.)
☑ Microbore (2 mm & 3 mm i.d.)
☐ Capillary (400 um i.d.)

AS18 (2 x 250 mm) - Isocratic
AS18 (4 x 250 mm) - Gradient
AS18 (4 x 250 mm) - Isocratic
AS19 (4 x 250 mm) - Gradient
AS19 (4 x 250 mm) - Isocratic

Flow Rate: 1.000 ml/min
Void Volume: 2.500 ml
Void Time: 2.50 min.

Figure 3-12: Modeling of AS-19 Column Determined Malonate Should Elute Between Sulfate and Oxalate.

Table 3-4: Potential Diacids and Other Analytes Identified by Modeling and VSL.

#	*Name*	*Comment*
1	Glutarate	Diacid
2	Maleate	Diacid
3	Succinate	Diacid
4	Tartrate	Diacid
5	Iodide	Not seen by ICPMS in glycolic acid
6	Selenate	Not seen by ICPMS in glycolic acid
7	Malonate	Suggested by VSL/University of Maryland

Table 3-5 summarizes a review of IC data for the unknown peak and estimates, using the area count of oxalic acid as a surrogate, the concentration to be <500 mg/kg. Thus, in all SME product samples examined, the concentration of the unknown peak was very low relative to glycolic acid. No correlation was observed between noble metals present in the SME product and an increase in the unknown peak area. SME products FN1 and GN51 – GN55 had no noble metals and the unknown peak area was similar to SME products with noble metals.

Table 3-5: Review and Estimate of Unknown Peak to be <500 mg/Kg.

Review of historical Glycolate runs (5/17/12 - 5/14/13)			estimate of Malonate	estimate of unknown peak *(R.T. near oxalate)* **	units
TC #	**LIMS ID**	**Cust ID**			
63934	**300302301**	**12_SB6J_6999 Sludge**	<1	<1	mg/L
63916	**300302215**	**12_GF27_7104**	<10	**~35**	mg/L
63916	**300302216**	**12_GF29_7106**	<100	**~400**	ug/g
63916	**300302217**	**12_GF31_7108**	<100	**~400**	ug/g
63916	**300302218**	**12_GF33A_7110**	<100	**~400**	ug/g
63916	**300302219**	**12_GF35_7112**	<100	< 100	ug/g
63916	**300302221 ***	**12_GF38_7120**	<500	**~450**	ug/g
63916	**300302222 ***	**12_GF40_7121**	<500	**~400**	ug/g
63916	**300302223 ***	**12_GF41_7122**	<500	**~400**	ug/g
64025	**300302567**	**GF40_6**	<500	**~250**	ug/g
64025	**300302568**	**GF40_20**	<500	< 100	ug/g
64025	**300302569**	**GF40_25**	<500	**~250**	ug/g
64025	**300302570**	**GF40_33**	<500	**~300**	ug/g
64025	**300302571**	**GF34_6**	<500	< 100	ug/g
64025	**300302572**	**GF34_29**	<500	< 100	ug/g
64025	**300302573**	**GF34_24**	<500	< 100	ug/g
64025	**300302574**	**GF34_20**	<500	< 100	ug/g
64029	**300302576 ***	**Matrix Matched Sup**	<500	**~250**	ug/g
64093	**300302958**	**13_FN1_7559**	<500	< 100	ug/g
64093	**300302959 ***	**13_GN51_7560**	<500	**~300**	ug/g
64093	**300302960**	**13_GN53_7615**	<500	**~400**	ug/g
64093	**300302961 ***	**13_GN52_7594**	<500	**~350**	ug/g
64139	**300303158**	**13_GN54_7642**	<500	**~350**	ug/g
64139	**300303159**	**13_GN55_7664**	<500	**~350**	ug/g
64140	**300303160**	**12_GN43**	<500	**~400**	ug/g
64140	**300303161**	**12_GN44**	<500	**~400**	ug/g
64140	**300303162**	**12_GN45**	<500	**~450**	ug/g
64140	**300303163**	**12_GN46**	<500	**~450**	ug/g
64140	**300303164**	**12_GN47**	<500	**~400**	ug/g
64140	**300303165**	**12_GN48**	<500	**~400**	ug/g
64140	**300303166**	**12_GN49**	<500	**~350**	ug/g
64140	**300303167**	**12_GN50**	<500	**~350**	ug/g

* small peak observed @ malonate retention time (R.T.)

** rough estimate based upon response of oxalate ion

3.2.3 *Ether Extraction of SME Product*

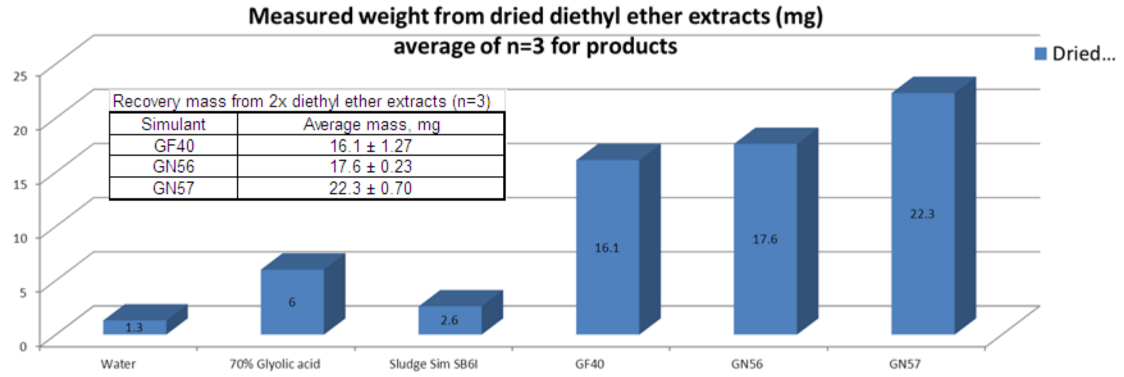
As previously mentioned, supernatants of SME products were subject to extraction protocols with organic solvents in an attempt to: a) determine the presence of non-anionic organics in the aqueous supernate solutions, and b) use NMR spectroscopy for structure elucidation of organics extractable by an organic solvent. Appendix A lists the protocol, developed by VSL, for the diethyl ether extraction (2x) of SME products. Eight milliliters of a SME product sample was filtered, extracted twice with 15 mL of diethyl ether and the extractants were combined and dried; after removal of the solvent, the organics remaining were weighed and analyzed. Table 3-6 shows the solubility of many of the compounds likely to be present in SME product and all are at least partially soluble in diethyl ether. The extraction recoveries were not determined and no attempt to quantify the recovery was made. Rather, these scoping experiments were to determine what ether extractable organic compounds were present.

Table 3-6: Solubility of Many of the Compounds Expected in SME Product

Compound	Diethyl Ether	Water	Notes
Glycolic acid	Soluble	Soluble	From Merck Index
Formic acid	Soluble	Soluble	
Oxalic acid	14 g/L	143 g/L	
Glyoxylic acid	Sparingly Soluble	Soluble	
Acetic acid	Miscible	Miscible	
Other acids	Soluble	See notes	Succinic (58 g/L), malonic (miscible), tartaric (133 g/L), glutaric (639), maleic (788 g/L), etc.
Ethylene glycol	5 g/L	Soluble	
Water	69 g/L	N/A	

SRNL Diethyl Ether Extraction Residue Weights

Each SME product and DuPont glycolic acid 70 wt.% technical solution went through the extraction protocol three times. The controls were water and SB6i; which, as previously mentioned, SB6i is a sludge simulant without organics added. Figure 3-13 shows very little extractable residue results from controls of water and SB6i. However, the extractions of the SME products were significantly higher in extractable residue mass. Table 3-7 shows the average residue weight (n = 3) of the diethyl ether extractions on three different SME products. The weight percent was calculated by dividing the residue weight by the sample weight and multiplying by 100.



Recovery mass from 2x diethyl ether extracts (n=3)

Simulant	Average mass, mg
GF40	16.1 ± 1.27
GN56	17.6 ± 0.23
GN57	22.3 ± 0.70

Figure 3-7: Diethyl Ether Extraction Weights.

Both SME products GF40 and GN57 contained noble metals, mercury, and antifoam while GN56 contained only antifoam (Table 3-1). The SME product GF40 contained 50,000 mg/kg of glycolic acid and 600 mg/kg of antifoam, GN56 contained 28,000 mg/kg of glycolic acid and 2000 mg/kg of antifoam, and GN57 contained 36,000 mg/kg of glycolic acid and 2000 mg/kg of antifoam. The slightly higher amount of organic residue in GN57 versus GN56 seems to be in keeping with a higher glycolic acid addition as observed by both SRNL and VSL by NMR (see Appendix D & E). In addition, GN57 contained noble metals that analytical methods (sections 3.2.3.1 and 3.3.2) show an array of antifoam breakdown products available for extraction. The SME product GF40 was higher in glycolic acid than

GN56 and GN57 but lower in antifoam. The organic residue mass found for GF40 is similar to the masses found for GN56 and GN57 SME product. A comparison of extractable mass cannot be made to VSL because their researchers did not receive GF40 SME product.

Table 3-7: Solubility of Many of the Compounds Expected in SME Product

Sample	Sample Wt. g	Ave. Residue Wt. mg	Wt. (%)
GF40 n=3	8	16.1	0.20
GN56 n=3	8	17.6	0.22
GN57 n=3	8	22.3	0.28

VSL extracted (n = 1) 30 mg or 0.38 wt.% for GN56 SME product and (n = 1) 85 mg or 0.85 wt.% for GN57 SME product [Appendix E]. The higher weight for the VSL GN56 and GN57 residues versus SRNL weights can be partly attributed to the presence to diethyl ether that can be seen in the NMR analysis (Appendix D). There were also differences in drying protocols between SRNL (nitrogen blow down to constant weight) vs. VSL which employed a rotary-evaporation technique. Similar to the results observed by SRNL, GN57 residue weight was higher than the GN56 residue.

3.2.3.1 Analyses of Extracted Residue

Researchers at SRNL analyzed the organic residue from the diethyl ether extracts of SME product as described in Appendix A. For the SVOA analysis, the ether extract was analyzed without blowing down to a residue. Table 3-8 summarizes the results of the analyses. The bulk of the organic was glycolic acid as determined by IC and ^{13}C NMR (GN56 and GN57) as shown in Figure 3-14. The IC analysis also identified lesser amounts of nitrate, oxalate, formate, and unknown peaks. One of the unknown peaks had been observed before in the analysis of SME products and in glycolic acid 70 wt.% technical solution. This peak best matched diglycolic acid as shown in Figure 3-15. This second peak eluted close to where malonic acid lies but is likely another diacid. The ^{1}H and ^{13}C NMR from VSL (Section 3.4) showed malonic acid was not present by spike addition.

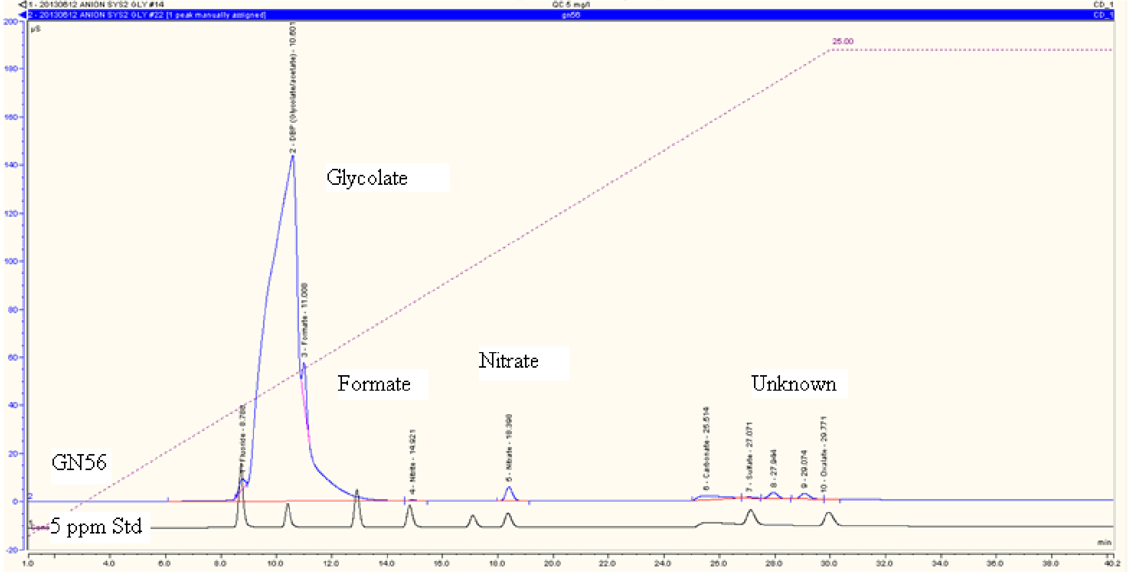


Figure 3-8: GN56 SME Product vs. 5 ppm Standard of Organic Residue from Diethyl Ether Extraction.

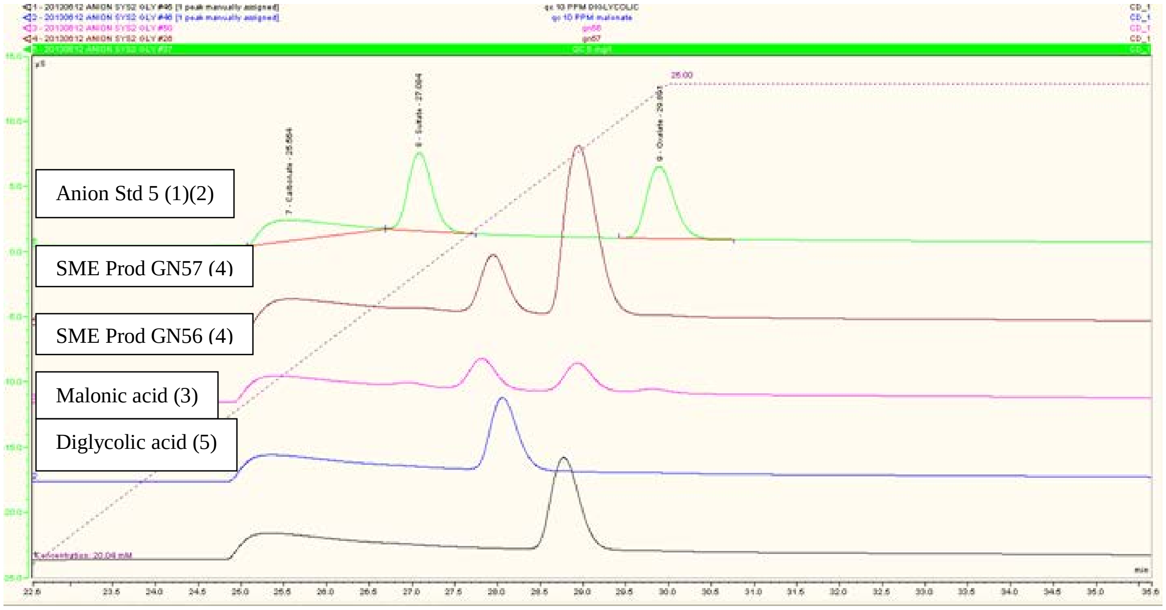
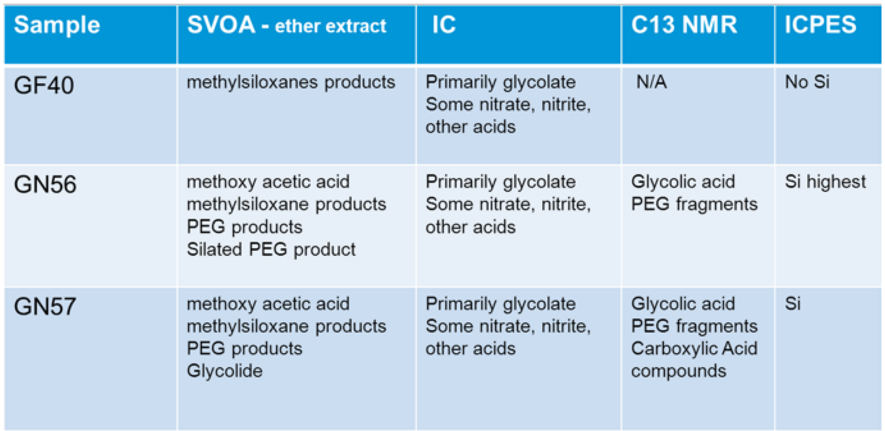


Figure 3-9: Multiple Ion Chromatograms Showing Unknown Peaks (4), Malonate (3), Sulfate (1) and Oxalate (2) from Organic Residue.

The ^{13}C NMR performed at SRNL showed a large variety of antifoam 747 breakdown products especially in GN57 with noble metals. A variety of carbonyl compounds were observed and the spectrum is discussed in Section 3.2.3.3 SRNL NMR Data.

The SVOA analysis of SME products observed low levels of methylsiloxane products and polyethylene glycol (PEG) fragments, which would stem from the breakdown of antifoam 747. Methoxy acetic acid is also possible from antifoam 747 and would arise from the oxidation of the methoxy end capped fragment of the surfactant. The SME product with the highest concentration of glycolic acid, GN57, was positive for the dimer glycolide, which likely formed in the inject port and is an artifact of the SVOA method analysis. The presence of silicon was checked by ICP-AES. This result matched what was observed by NMR at VSL, where GN56 had the largest peaks due to the presence methylsiloxane material. SRNL observed glycolic acid by ^{13}C NMR for GN56.

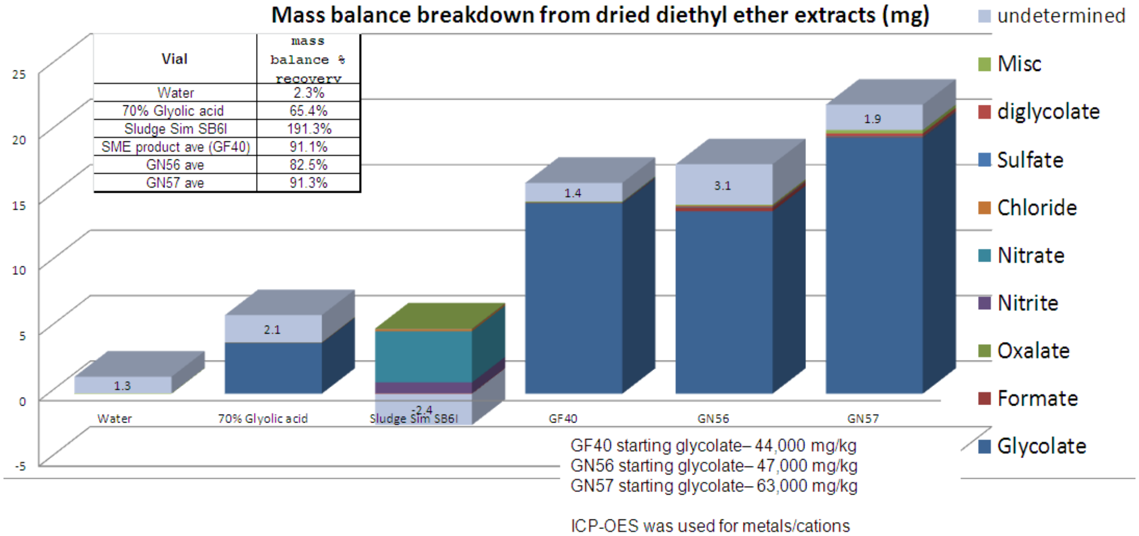
Table 3-8: Summary of Analysis of SME Products.



Sample	SVOA - ether extract	IC	C13 NMR	ICPES
GF40	methylsiloxanes products	Primarily glycolate Some nitrate, nitrite, other acids	N/A	No Si
GN56	methoxy acetic acid methylsiloxane products PEG products Silated PEG product	Primarily glycolate Some nitrate, nitrite, other acids	Glycolic acid PEG fragments	Si highest
GN57	methoxy acetic acid methylsiloxane products PEG products Glycolide	Primarily glycolate Some nitrate, nitrite, other acids	Glycolic acid PEG fragments Carboxylic Acid compounds	Si

Figure 3-16 shows the mass balance of the extracted organic residues. The y-axis is in mg and the x-axis is sample identification. The recoveries were calculated by summing the analyses, dividing by the weight of the residue, and multiplying by 100 (Appendix A). Deionized water (n=1) was the control and a trace amount of residue was measured weighing 1.2 mg. Extracting and drying glycolic acid 70 wt.% technical solution (n=1) yielded a 65% recovery and the amount of residue was measured weighing 6.0 mg where the missing 35% of the mass balance, 2.1 mg of material, was similar to the mass obtained extracting deionized water alone. This amount is represented in Figure 3-16 as the gray box or the amount in mg on top of the column. This can also be considered the remainder of the mass balance not accounted for by the measurement techniques.

Sludge simulant SB6i contained no noble metals, mercury, or antifoam. The bulk of the material observed in the extraction by IC was nitrate with some nitrite and chloride. The recovery was higher than expected at 191% likely due to analyzing the sample by back extraction rather than dissolving a residue. One sample of sludge simulant SB6i was extracted, blown down to constant weight, and weighed to give the residue weight. This residue was not analyzed. A second sample was extracted 2x with diethyl ether, the extracts combined, the ether was back extracted with 5 mM KOH, and the water was analyzed by IC. For all SME products, the residues were dissolved and analyzed giving more reasonable recoveries. These SME products gave recoveries on average (n = 3) of 82 to 91% and the bulk material was glycolic acid. Miscellaneous (Misc.) is the sum of species from ICPES and butylated hydroxytoluene (BHT) by SVOA from the diethyl ether extractant.



Vial	mass balance % recovery
Water	2.3%
70% Glyolic acid	65.4%
Sludge Sim SB6I	191.3%
SME product ave (GF40)	91.1%
GN56 ave	82.5%
GN57 ave	91.3%

GF40 starting glycolate– 44,000 mg/kg
GN56 starting glycolate– 47,000 mg/kg
GN57 starting glycolate– 63,000 mg/kg

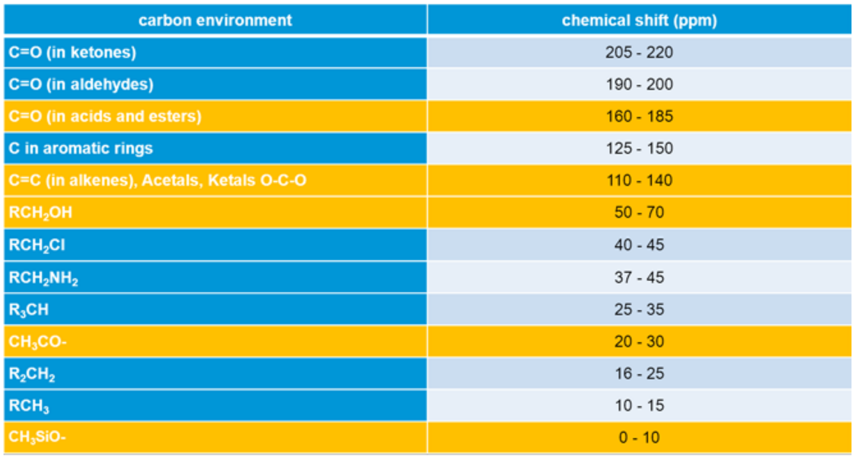
ICP-OES was used for metals/cations

Figure 3-10: Mass Balance Chart of three SME products with controls.

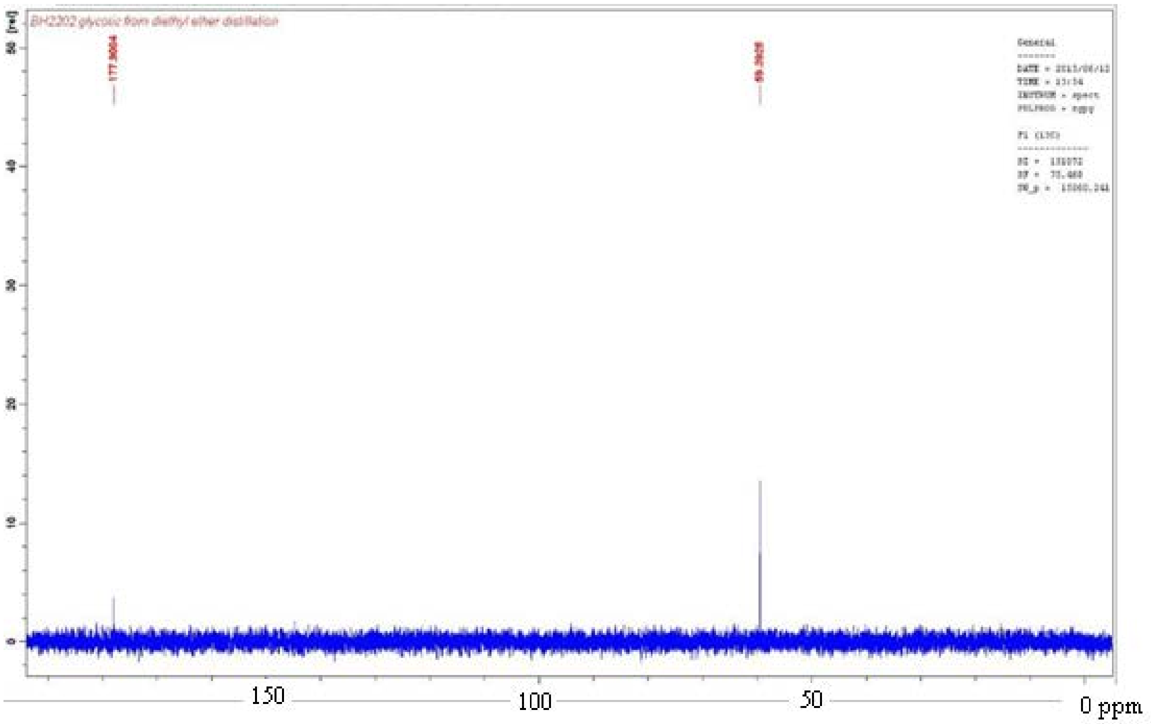
3.2.3.2 SRNL NMR Data

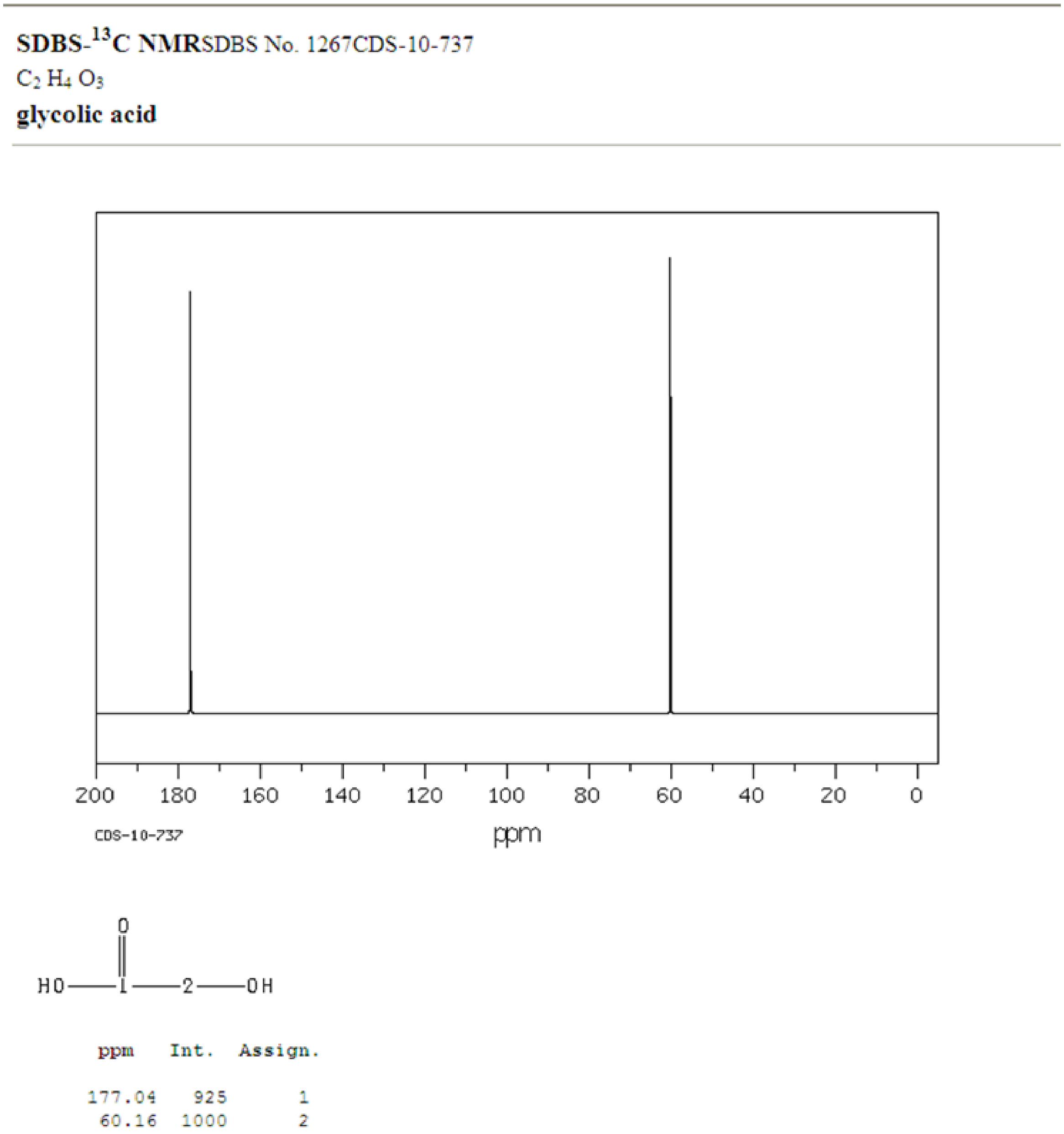
Table 3-9 shows typical ^{13}C NMR chemical shifts. The ^{13}C NMR analysis of the organic residue of glycolic acid 70 wt.% technical solution is shown in Figure 3-17. This spectrum matched well with a literature spectrum from Spectral Database for Organic Compounds (SDBS)[SBDS, 2013]. The low intensity of the peaks is a result of the small mass (~ 6 mg) analyzed. Figure 3-18 is a spectrum of antifoam 747.

Table 3-9: Summary of ^{13}C NMR Chemical Shifts



carbon environment	chemical shift (ppm)
C=O (in ketones)	205 - 220
C=O (in aldehydes)	190 - 200
C=O (in acids and esters)	160 - 185
C in aromatic rings	125 - 150
C=C (in alkenes), Acetals, Ketals O-C-O	110 - 140
RCH_2OH	50 - 70
RCH_2Cl	40 - 45
RCH_2NH_2	37 - 45
R_3CH	25 - 35
CH_3CO-	20 - 30
R_2CH_2	16 - 25
RCH_3	10 - 15
CH_3SiO-	0 - 10





SDBS-^{13}C NMRSDBS No. 1267CDS-10-737
$C_2H_4O_3$
glycolic acid

ppm	Int.	Assign.
177.04	925	1
60.16	1000	2

Figure 3-11: Glycolic acid extractant residue.

The ^{13}C NMR spectrum of antifoam 747 showed strong peaks in the regions where carbon is bound to Si and O which is the bulk of the surfactant. In addition, peaks of carbon bound to carbon are observed. Degradation and loss of methylsiloxane fragments would lower the intensity of the peaks near 0 ppm and oxidation would cause an increase in peaks observed in the carbonyl range after 150 ppm.

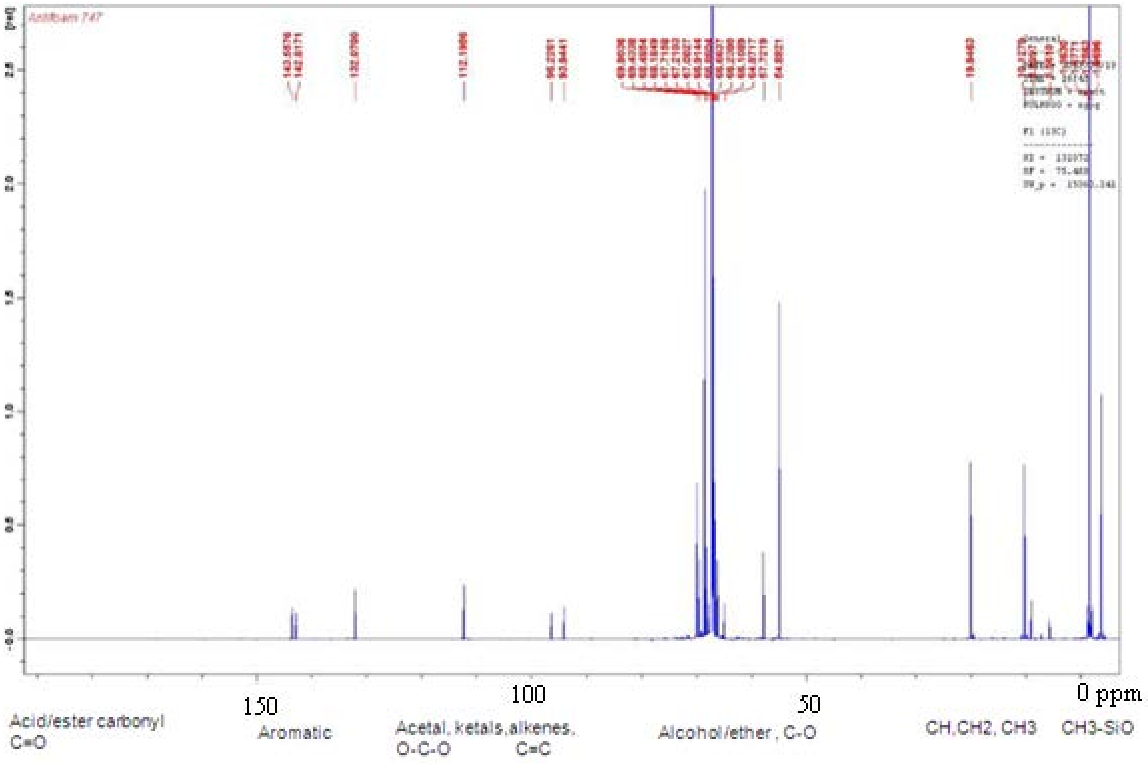


Figure 3-12: 13C NMR of Antifoam 747.

The ^{13}C NMR analysis of the organic residue of GN56 SME product (~18 mg) is shown in Figure 3-19. This spectrum shows glycolic acid as the primary analyte. Trace peaks can be seen in the alcohol/ether region indicating the presence of glycols.

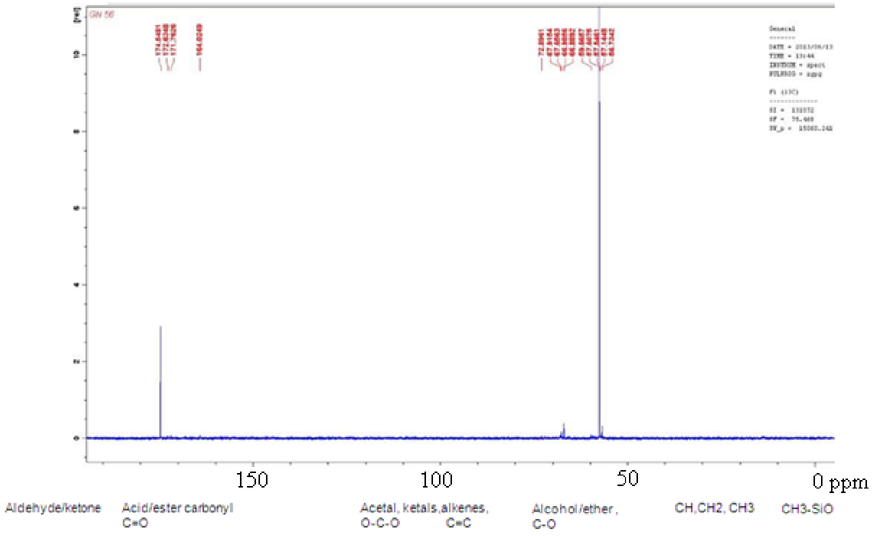


Figure 3-13: GN56 SME Product Extractant Residue.

The ^{13}C NMR analysis of the organic residue of GN57 SME product is shown in Figure 3-20. This spectrum shows glycolic acid as the primary analyte but a number of carbonyl compounds have arisen consistent with the breakdown of antifoam 747 [Nikolov, 2011]. Some likely acids present include formic, diglycolic, oxalic, and methoxyacetic acid as well as glycols.

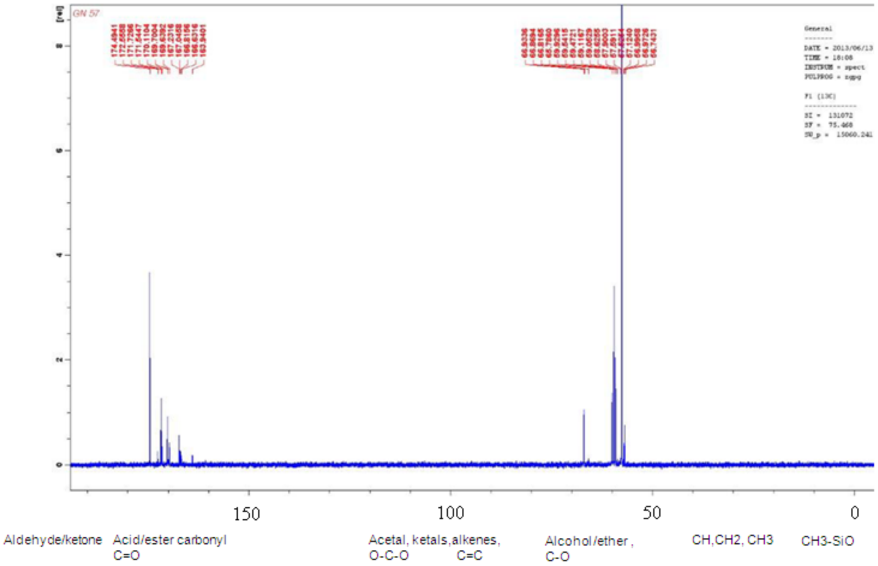


Figure 3-14: GN57 SME Product Extractant Residue.

3.3 VSL NMR Results

SME product simulated waste samples GN56 and GN57 were extracted using diethyl ether and the solvent was removed yielding a product of mixed organics and some inorganics. The residue was analyzed using ^{1}H NMR and ^{13}C NMR. DuPont glycolic acid 70 wt.% technical solution was also analyzed by NMR. The only potential decomposition product that utilized spike addition analysis was malonic acid and was found not to be present. All other compounds were determined by comparing to literature standards in the SDBS.

3.3.1 *DuPont 70 wt.% technical grade glycolic acid*

^{13}C and ^{1}H NMR of glycolic acid spectra are shown in Appendix D. Figure 3-21 show the ^{1}H NMR spectrum with a major glycolic acid signal at 4.1 ppm; the remaining peaks are attributed to polymerization products including diglycolic acid and glycolide. Some formic acid is observed above 8 ppm and no acetic acid is present (2.1 ppm). Malonic acid was not observed and this was confirmed by spike addition. The ^{1}H NMR shows no peak at 2.0 ppm and 3.4 ppm in the glycolic acid spectrum (Figure 3-21). The ^{13}C NMR also demonstrates no malonic acid is present (Figure 3-22).

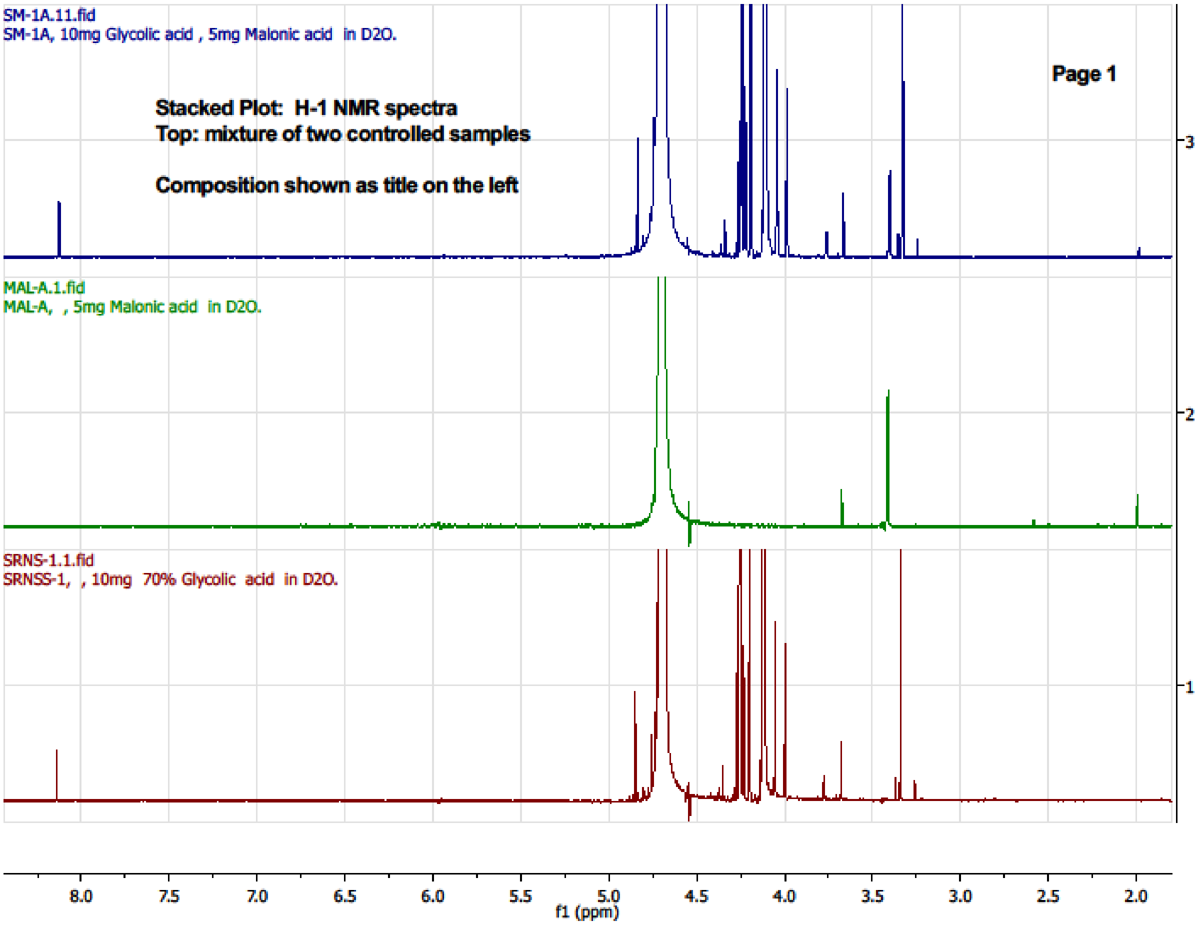


Figure 3-15: ^{1}H NMR Spectrum of Glycolic Acid and Malonic acid (top), Malonic Acid (middle), and 70% Glycolic Acid (bottom).

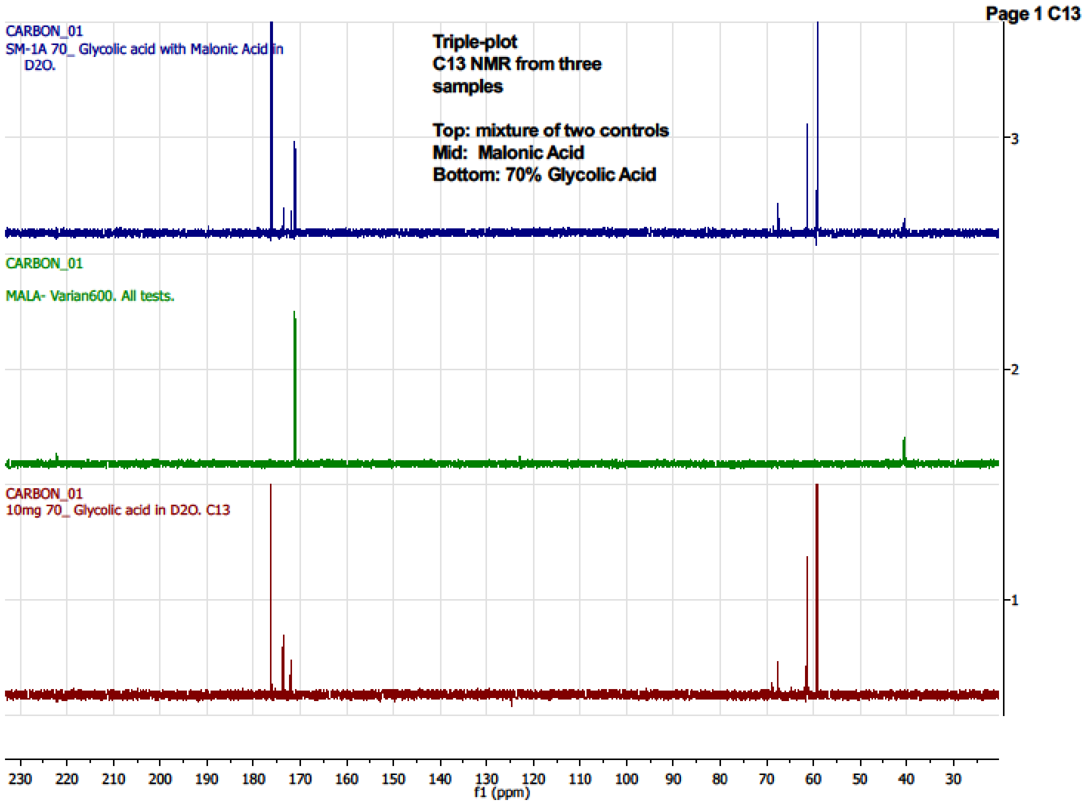


Figure 3-22: ^{13}C NMR Spectrum of Glycolic Acid and Malonic acid (top), Malonic Acid (middle), and 70% Glycolic Acid (bottom)

3.3.2 *Ether Extractions*

In Appendix D, the ^{13}C and ^{1}H NMR spectra of GN56 and GN57 show a number of compounds present. Some are due to the extraction method such as diethyl ether, chloroform, and potentially the reaction of glycols with carbonyls in ether to form peaks in the aldol/ketal region of the NMR. Many of the other peaks are in keeping with compounds from the decomposition of antifoam such as PEG fragments or glycols, formic acid, other acids, and methylsiloxane compounds. Figure 3-23 shows an interesting trend. The GN56 SME product extract shows methylsiloxane compounds in both the ^{1}H and ^{13}C NMR while GN57 SME product extract does not. Also, GN57 SME product showed more peaks in the area where PEG fragments would be expected. This implies the surfactant is decomposed more readily in the presence of noble metals and mercury.

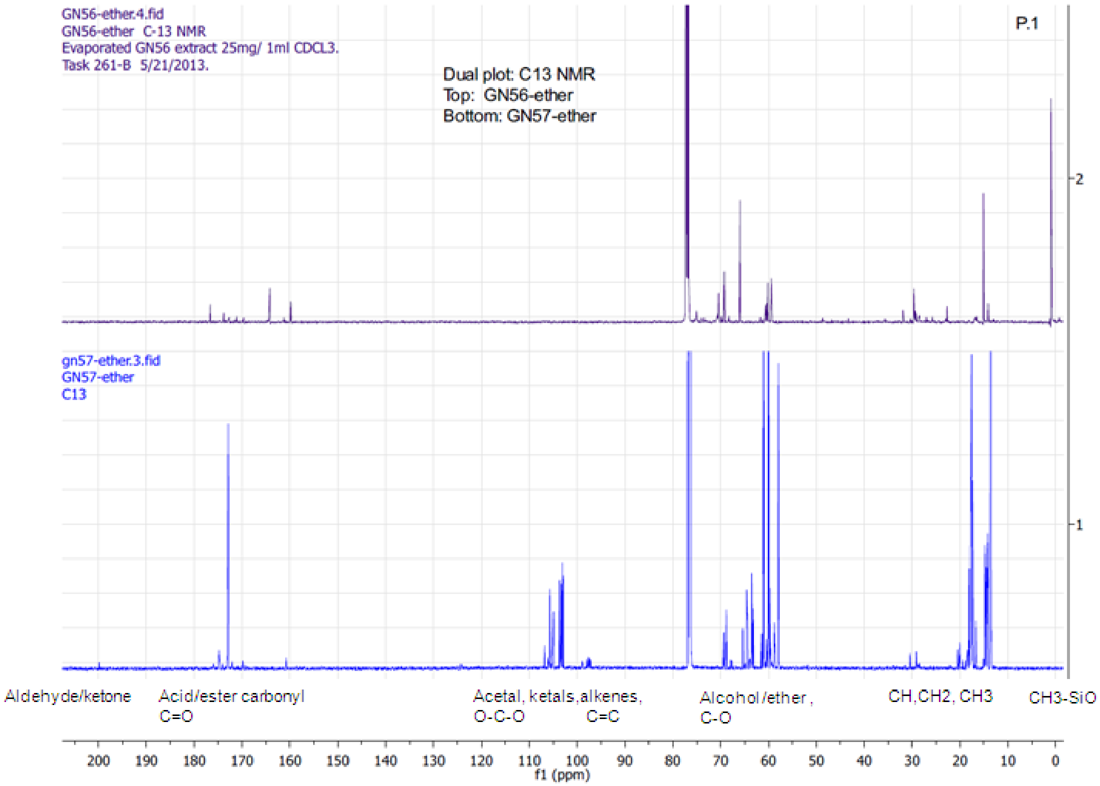


Figure 3-16: ^{13}C NMR Spectrum of GN56 SME Product Extract (top) and GN57 SME Product Extract (bottom).

4.0 Summary

Analysis of SME products by a number of techniques suggest the following:

1. Glycolic acid is the major organic compound present in the MFT waste feed.

2. Minor amounts of formate, oxalate, and diglycolic acid are also expected but no acetate. Formic and diglycolic acids are impurities present in the DuPont commercially available technical solution of glycolic acid, currently used in the flowsheet. Oxalate originates in the tank farm waste.

3. Numerous other organics, at very low concentrations are additionally observed as a result of the degradation of antifoam 747. Some of these degradation products include PEG fragments, methylsiloxane fragments, and carboxylic acids. This suggests that identification of a more chemically stable superwetter (similar to Silwet L-77) might lead to greatly improved antifoam effectiveness. The presence of noble metals, as seen in analysis of GN57 SME product, accelerates the breakdown of antifoam 747.

4. No organics were found at concentrations above 500 mg/kg that would significantly impact the REDOX prediction of the SRAT or SME melter feed. Malonic acid was not observed in the SME products. Acetic acid was not observed although it has a higher detection limit of 1250 mg/kg due the high glycolate concentration.

5. Development of an analytical method that is able to track antifoam 747 breakdown products for inclusion into flammability calculations and REDOX equations may be useful and may assist in the identification of a more chemically stable, and thus more effective, superwetter. Possible methods for tracking antifoam 747 degradation include Si NMR spectroscopy and monitoring of PEG fragments via a GC-MS SVOA technique that involves extraction or prior derivatization of these fragments.

5.0 References

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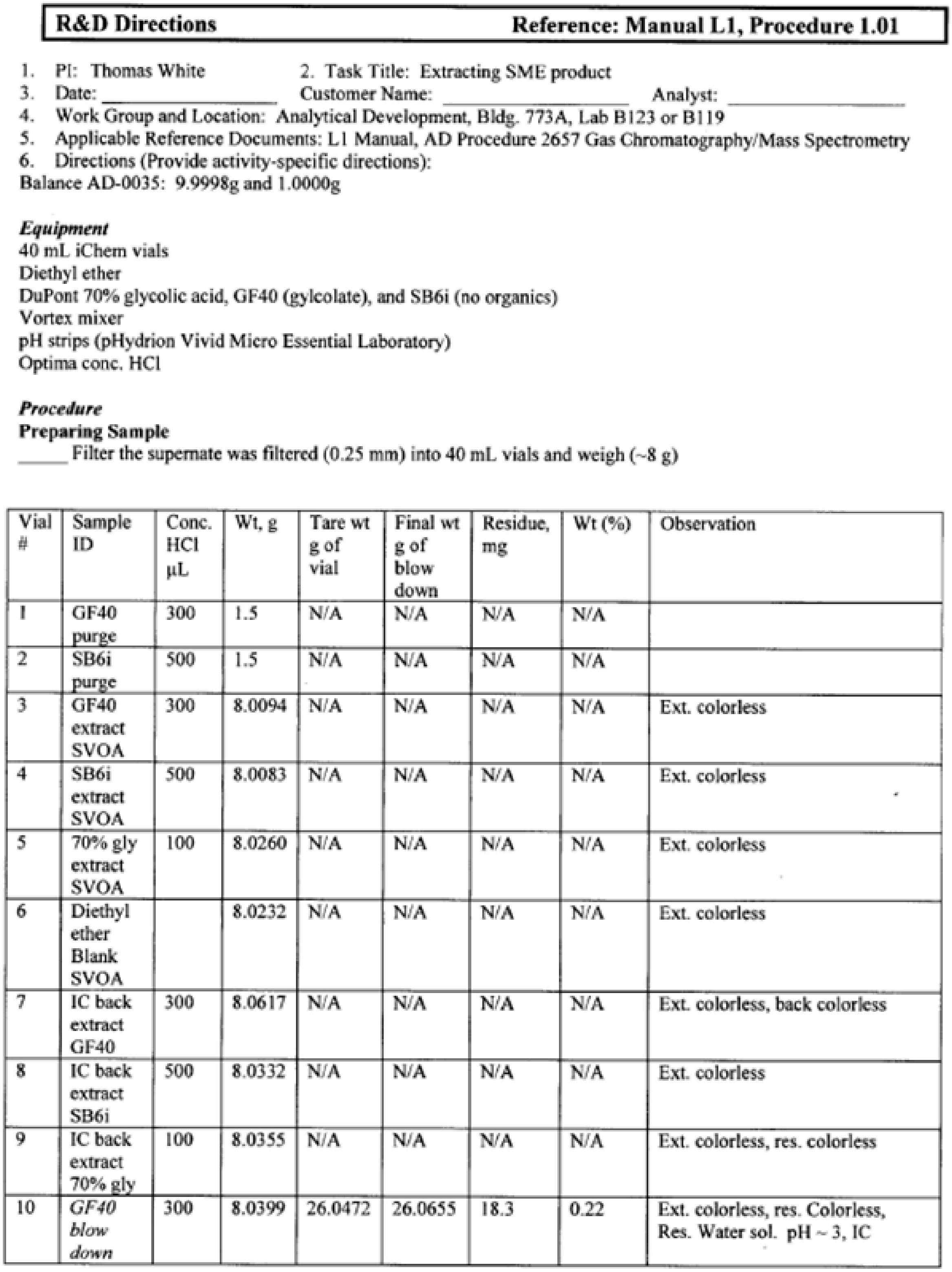
6.0 Appendix A – Diethyl Ether Extraction Protocol

A.1 VSL Diethyl Ether Protocol

Procedure for Extraction of Slurry Mix Evaporator (SME) Products at VSL
The Slurry Mix Evaporator (SME) product was homogenized and a sample was centrifuged (3800 rpm for 15 min). The supernatant was filtered (0.45 µm) and the filtrate was acidified with concentrated HCl to a final pH of about 2. The acidified solution was extracted with diethyl ether (2× with 15 mL each for ≈10 g of solution). The organic fractions were combined and dried with $MgSO_4$ overnight. Following filtration of $MgSO_4$, the solvent was removed using a Rotavac.

A.2 SRNL Diethyl Ether Extraction Protocol



R&D Directions **Reference: Manual L1, Procedure 1.01**

1. PI: Thomas White 2. Task Title: Extracting SME product
3. Date: ____________ Customer Name: ____________ Analyst: ____________
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B123 or B119
5. Applicable Reference Documents: L1 Manual, AD Procedure 2657 Gas Chromatography/Mass Spectrometry
6. Directions (Provide activity-specific directions):

Balance AD-0035: 9.9998g and 1.0000g

Equipment

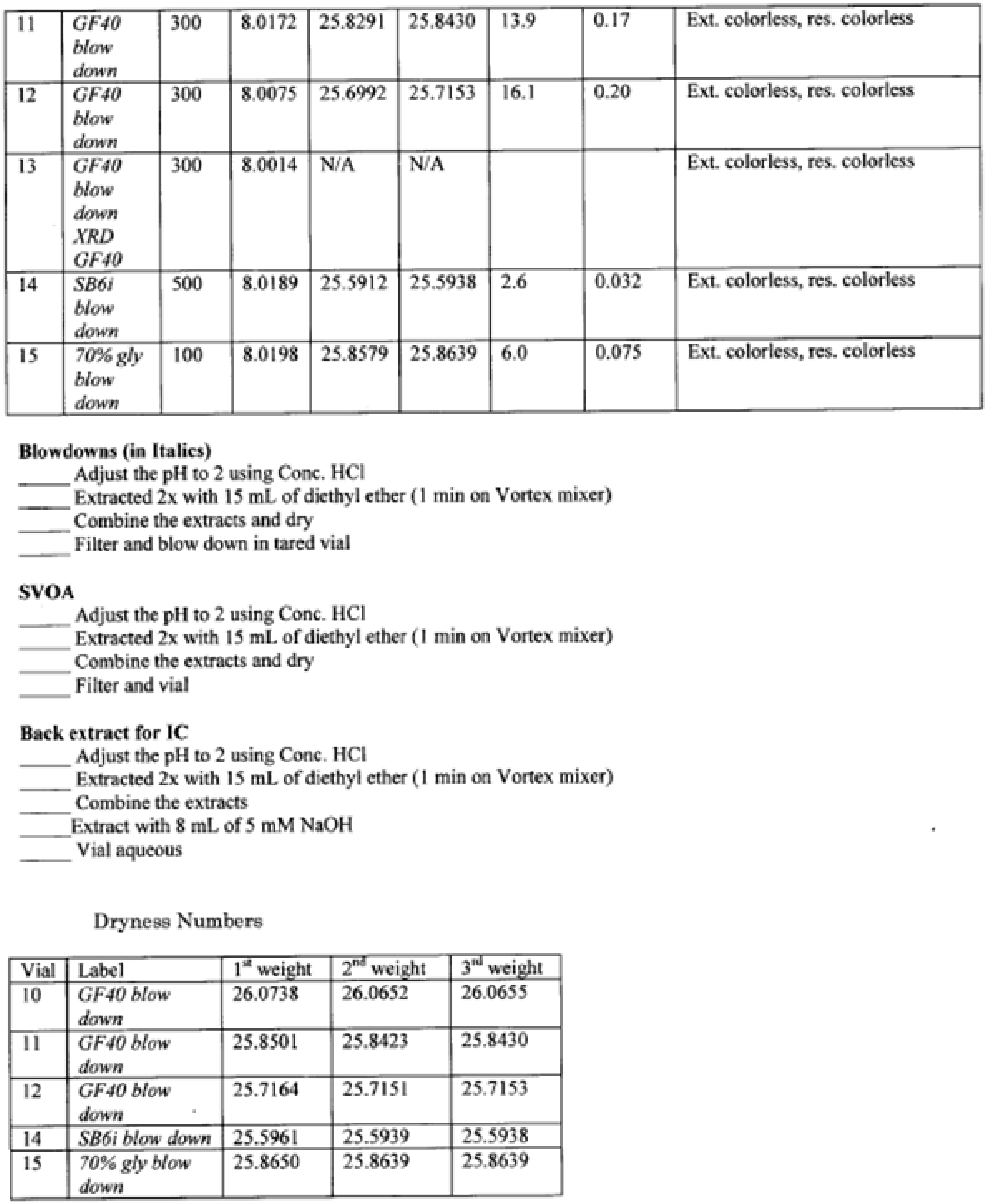
40 mL iChem vials
Diethyl ether
DuPont 70% glycolic acid, GF40 (gylcolate), and SB6i (no organics)
Vortex mixer
pH strips (pHydrion Vivid Micro Essential Laboratory)
Optima conc. HCl

Procedure

Preparing Sample

_____ Filter the supernate was filtered (0.25 mm) into 40 mL vials and weigh (~8 g)

Vial #	Sample ID	Conc. HCl µL	Wt, g	Tare wt g of vial	Final wt g of blow down	Residue, mg	Wt (%)	Observation
1	GF40 purge	300	1.5	N/A	N/A	N/A	N/A	
2	SB6i purge	500	1.5	N/A	N/A	N/A	N/A	
3	GF40 extract SVOA	300	8.0094	N/A	N/A	N/A	N/A	Ext. colorless
4	SB6i extract SVOA	500	8.0083	N/A	N/A	N/A	N/A	Ext. colorless
5	70% gly extract SVOA	100	8.0260	N/A	N/A	N/A	N/A	Ext. colorless
6	Diethyl ether Blank SVOA		8.0232	N/A	N/A	N/A	N/A	Ext. colorless
7	IC back extract GF40	300	8.0617	N/A	N/A	N/A	N/A	Ext. colorless, back colorless
8	IC back extract SB6i	500	8.0332	N/A	N/A	N/A	N/A	Ext. colorless
9	IC back extract 70% gly	100	8.0355	N/A	N/A	N/A	N/A	Ext. colorless, res. colorless
10	*GF40 blow down*	300	8.0399	26.0472	26.0655	18.3	0.22	Ext. colorless, res. Colorless, Res. Water sol. pH ~ 3, IC



11	*GF40 blow down*	300	8.0172	25.8291	25.8430	13.9	0.17	Ext. colorless, res. colorless
12	*GF40 blow down*	300	8.0075	25.6992	25.7153	16.1	0.20	Ext. colorless, res. colorless
13	*GF40 blow down XRD GF40*	300	8.0014	N/A	N/A			Ext. colorless, res. colorless
14	*SB6i blow down*	500	8.0189	25.5912	25.5938	2.6	0.032	Ext. colorless, res. colorless
15	*70% gly blow down*	100	8.0198	25.8579	25.8639	6.0	0.075	Ext. colorless, res. colorless

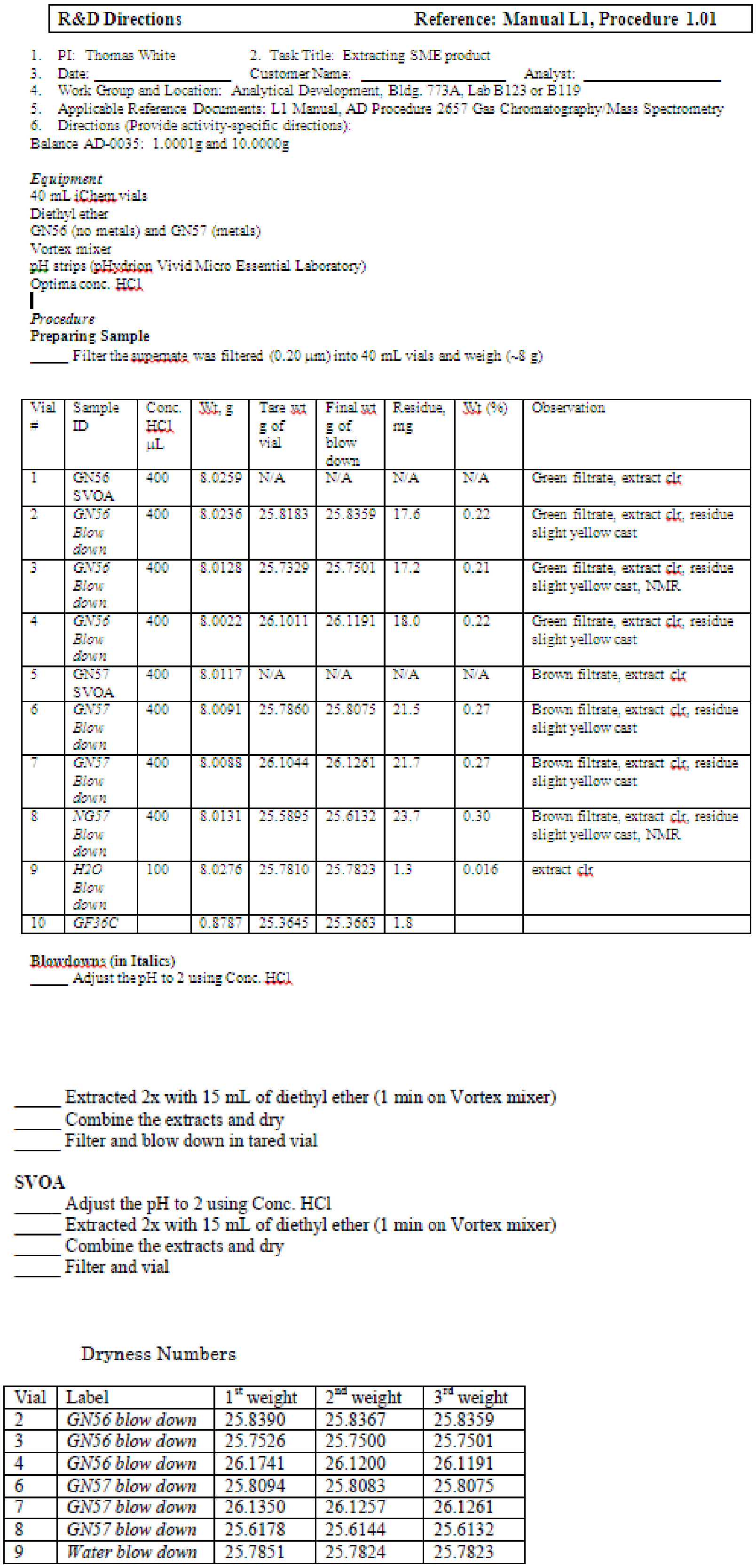
Blowdowns (in Italics)
_____ Adjust the pH to 2 using Conc. HCl
_____ Extracted 2x with 15 mL of diethyl ether (1 min on Vortex mixer)
_____ Combine the extracts and dry
_____ Filter and blow down in tared vial

SVOA
_____ Adjust the pH to 2 using Conc. HCl
_____ Extracted 2x with 15 mL of diethyl ether (1 min on Vortex mixer)
_____ Combine the extracts and dry
_____ Filter and vial

Back extract for IC
_____ Adjust the pH to 2 using Conc. HCl
_____ Extracted 2x with 15 mL of diethyl ether (1 min on Vortex mixer)
_____ Combine the extracts
_____Extract with 8 mL of 5 mM NaOH
_____ Vial aqueous

Dryness Numbers

Vial	Label	1st weight	2nd weight	3rd weight
10	*GF40 blow down*	26.0738	26.0652	26.0655
11	*GF40 blow down*	25.8501	25.8423	25.8430
12	*GF40 blow down*	25.7164	25.7151	25.7153
14	*SB6i blow down*	25.5961	25.5939	25.5938
15	*70% gly blow down*	25.8650	25.8639	25.8639



R&D Directions **Reference: Manual L1, Procedure 1.01**

1. PI: Thomas White 2. Task Title: Extracting SME product
3. Date: ______________ Customer Name: ______________ Analyst: ______________
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B123 or B119
5. Applicable Reference Documents: L1 Manual, AD Procedure 2657 Gas Chromatography/Mass Spectrometry
6. Directions (Provide activity-specific directions):

Balance AD-0035: 1.0001g and 10.0000g

Equipment
40 mL iChem vials
Diethyl ether
GN56 (no metals) and GN57 (metals)
Vortex mixer
pH strips (pHydrion Vivid Micro Essential Laboratory)
Optima conc. HCl

Procedure

Preparing Sample

_____ Filter the supernate was filtered (0.20 µm) into 40 mL vials and weigh (~8 g)

Vial #	Sample ID	Conc. HCl µL	Wt, g	Tare wt g of vial	Final wt g of blow down	Residue, mg	Wt (%)	Observation
1	GN56 SVOA	400	8.0259	N/A	N/A	N/A	N/A	Green filtrate, extract clr
2	*GN56 Blow down*	400	8.0236	25.8183	25.8359	17.6	0.22	Green filtrate, extract clr, residue slight yellow cast
3	*GN56 Blow down*	400	8.0128	25.7329	25.7501	17.2	0.21	Green filtrate, extract clr, residue slight yellow cast, NMR
4	*GN56 Blow down*	400	8.0022	26.1011	26.1191	18.0	0.22	Green filtrate, extract clr, residue slight yellow cast
5	GN57 SVOA	400	8.0117	N/A	N/A	N/A	N/A	Brown filtrate, extract clr
6	*GN57 Blow down*	400	8.0091	25.7860	25.8075	21.5	0.27	Brown filtrate, extract clr, residue slight yellow cast
7	*GN57 Blow down*	400	8.0088	26.1044	26.1261	21.7	0.27	Brown filtrate, extract clr, residue slight yellow cast
8	*NG57 Blow down*	400	8.0131	25.5895	25.6132	23.7	0.30	Brown filtrate, extract clr, residue slight yellow cast, NMR
9	*H2O Blow down*	100	8.0276	25.7810	25.7823	1.3	0.016	extract clr
10	*GF36C*		0.8787	25.3645	25.3663	1.8		

Blowdowns (in Italics)
_____ Adjust the pH to 2 using Conc. HCl

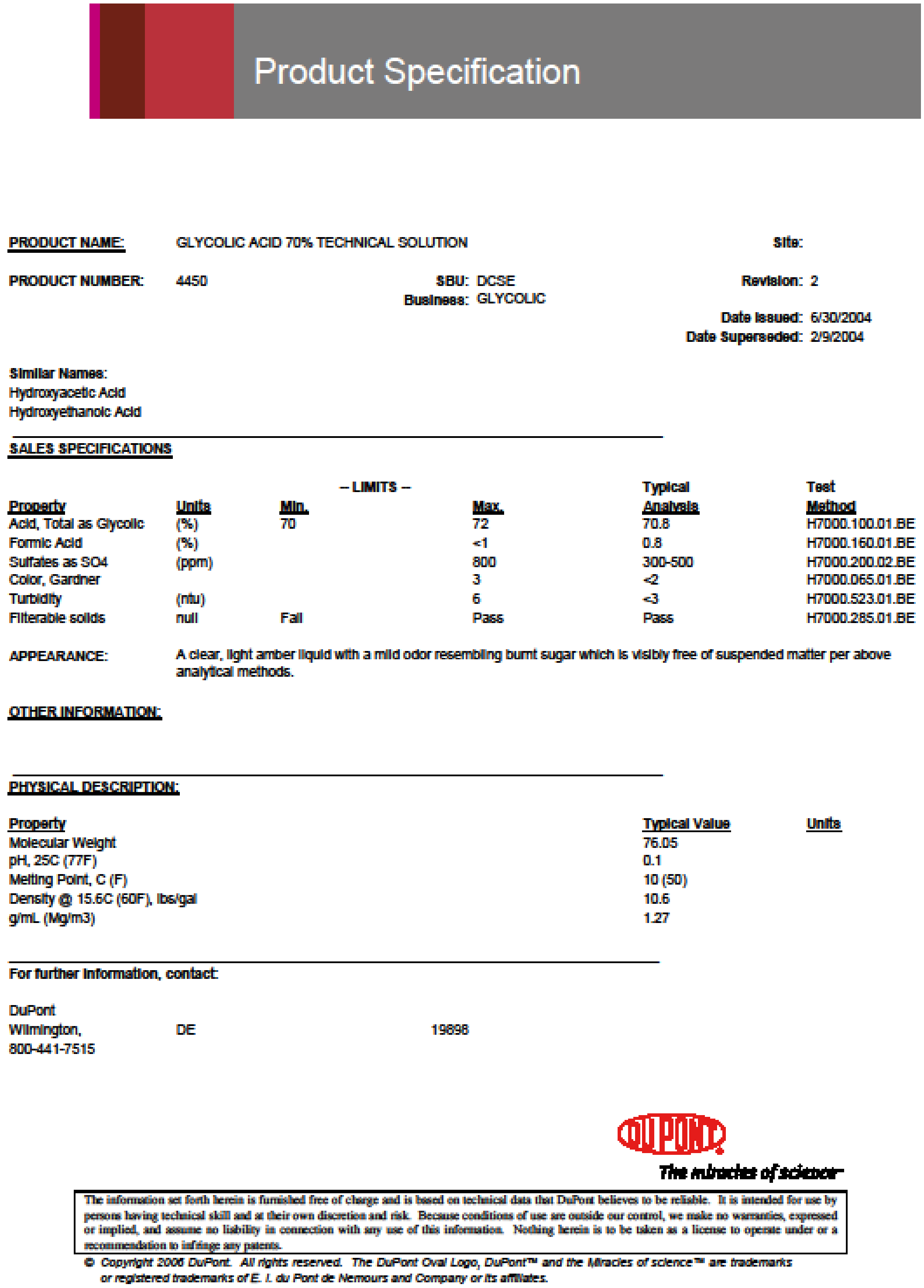
_____ Extracted 2x with 15 mL of diethyl ether (1 min on Vortex mixer)
_____ Combine the extracts and dry
_____ Filter and blow down in tared vial

SVOA
_____ Adjust the pH to 2 using Conc. HCl
_____ Extracted 2x with 15 mL of diethyl ether (1 min on Vortex mixer)
_____ Combine the extracts and dry
_____ Filter and vial

Dryness Numbers

Vial	Label	1st weight	2nd weight	3rd weight
2	*GN56 blow down*	25.8390	25.8367	25.8359
3	*GN56 blow down*	25.7526	25.7500	25.7501
4	*GN56 blow down*	26.1741	26.1200	26.1191
6	*GN57 blow down*	25.8094	25.8083	25.8075
7	*GN57 blow down*	26.1350	26.1257	26.1261
8	*GN57 blow down*	25.6178	25.6144	25.6132
9	*Water blow down*	25.7851	25.7824	25.7823

7.0 Appendix B – DuPont Glycolic Acid 70% Technical Solution



Product Specification

PRODUCT NAME: GLYCOLIC ACID 70% TECHNICAL SOLUTION

Site:

PRODUCT NUMBER: 4450

SBU: DCSE
Business: GLYCOLIC

Revision: 2

Date Issued: 6/30/2004
Date Superseded: 2/9/2004

Similar Names:
Hydroxyacetic Acid
Hydroxyethanoic Acid

SALES SPECIFICATIONS

		– LIMITS –		Typical	Test
Property	**Units**	**Min.**	**Max.**	**Analysis**	**Method**
Acid, Total as Glycolic	(%)	70	72	70.8	H7000.100.01.BE
Formic Acid	(%)		<1	0.8	H7000.160.01.BE
Sulfates as SO4	(ppm)		800	300-500	H7000.200.02.BE
Color, Gardner			3	<2	H7000.065.01.BE
Turbidity	(ntu)		6	<3	H7000.523.01.BE
Filterable solids	null	Fail	Pass	Pass	H7000.285.01.BE

APPEARANCE: A clear, light amber liquid with a mild odor resembling burnt sugar which is visibly free of suspended matter per above analytical methods.

OTHER INFORMATION:

PHYSICAL DESCRIPTION:

Property	**Typical Value**	**Units**
Molecular Weight	76.05	
pH, 25C (77F)	0.1	
Melting Point, C (F)	10 (50)	
Density @ 15.6C (60F), lbs/gal	10.6	
g/mL (Mg/m3)	1.27	

For further information, contact:

DuPont
Wilmington, DE 19898
800-441-7515

The miracles of science

8.0 Appendix C – Simulated SME Product SB6i, GF40, GN56, and GN57

C.1 SB6i

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Process Science Analytical Laboratory
Customer: William King
Date: 1/12/13
Sample ID: SB6I Simulant - Blue Grass Chemicals
Lab ID: 13-0037

elemental wt%

Sample ID	Lab ID	Al	Ba	Ca	Ce	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Si	Ti	Zn	Zr
SB6I Simulant (A)	13-0037	14.2	0.135	1.34	0.188	0.186	0.115	22.1	0.247	0.942	7.03	13.3	3.05	0.133	<0.010	0.252	1.29	<0.100	0.114	0.271
SB6I Simulant (B)	13-0037	14.3	0.134	1.15	0.190	0.182	0.145	22.3	0.246	0.949	7.13	13.0	3.10	0.129	<0.010	0.249	1.27	<0.100	0.114	0.257

oxide wt%

Sample ID	Lab ID	Al2O3	BaO	CaO	CeO2	Cr2O3	Cu2O	Fe2O3	K2O	MgO	MnO2	Na2O	NiO	P2O5	PbO	SO4	SiO2	TiO2	ZnO	ZrO2	Sum Oxides
SB6I Simulant (A)	13-0037	26.8	0.151	1.88	0.231	0.271	0.129	31.6	0.296	1.564	11.1	17.9	3.87	0.304	0.000	0.757	2.75	0.000	0.141	0.366	100.2
SB6I Simulant (B)	13-0037	27.1	0.150	1.61	0.234	0.266	0.164	31.9	0.295	1.575	11.3	17.6	3.94	0.295	0.000	0.748	2.72	0.000	0.141	0.347	100.3

Units: mg/Kg

Sample ID	Lab ID	F	Cl	NO2	NO3	SO4	C2O4	HCO2	PO4
SB6I Simulant (A)	13-0037	<100	<100	4790	5300	650	157	<100	<100
SB6I Simulant (B)	13-0037	<100	<100	4760	5310	654	156	<100	<100

Weight % Solids Calculations

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Total Solids	Wet Wt	Dry Wt	Insoluble Solids	Cruc Wt+ Calcined	Wt % Calcined
SB6I Simulant (A)	13-0037	44.3087	49.8481	45.3004	17.9%	5.539	0.992	12.90%	45.0239	12.9%
SB6I Simulant (B)	13-0037	43.8300	49.3701	44.8245	18.0%	5.540	0.995	13.00%	44.5440	12.9%
SB6I Simulant (C)	13-0037	42.7069	48.2392	43.6981	17.9%	5.532	0.991	12.91%	43.4200	12.9%
									0.1290	

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Uncorr	Soluble Solids	pH	Slurry Density	Supernate Density
SB6I Simulant (A)	13-0037	44.1356	48.2552	44.3722	5.74%	5.00%	12.5	1.1197	1.0426
SB6I Simulant (B)	13-0037	44.8435	49.3370	45.0991	5.69%	4.95%		1.1196	1.0426
SB6I Simulant (C)	13-0037	43.1941	47.8453	43.4614	5.75%	5.00%			

Supernate mg/L

Sample ID	Lab ID	Al	Ba	Ca	Ce	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Si	Ti	Zn	Zr
SB6I Simulant (A)	13-0037	854	<0.100	1.32	<0.100	1.11	<0.100	<0.100	549.0	<0.100	<0.100	21000	<0.100	46.7	<0.100	542	<1.00	<0.100	<0.100	<0.100
SB6I Simulant (B)	13-0037	853	<0.100	1.32	<0.100	1.06	<0.100	<0.100	550.0	<0.100	<0.100	20900	<0.100	45.3	<0.100	542	<1.00	<0.100	<0.100	<0.100

Total Base		pH - 7.0 Result (mmol/gram)	*pH - 5.5* Result (mmol/gram)
0.0973 mmol/gram NaOH Standard		0.0948	
SB6I Simulant (A)	13-0037	0.3953	0.4595
SB6I Simulant (B)	13-0037	0.3961	0.4600
SB6I Simulant (C)	13-0037	0.3992	0.4602
0.0973 mmol/gram NaOH Standard		0.0944	

C.2 GF40

Process Science Analytical Laboratory
Customer: Dan Lambert
Date: 6/15/12
Sample ID: 12-GF40
Lab ID: 12-0697-0700

elemental wt%- calcined 1100C

Sample ID	Lab ID	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Pd	Rh	Ru	S	Si	Ti	Zn	Zr
12-GF40-6615 (A)	12-0697	<0.100	14.7	<0.100	0.091	0.615	0.025	0.031	14.2	0.421	<0.100	0.303	4.52	22.9	1.95	<0.100	<0.010	<0.100	<0.100	<0.100	0.295	1.43	0.022	0.046	0.201
12-GF40-6615 (B)	12-0697	<0.100	14.7	<0.100	0.089	0.587	0.025	0.029	14.2	0.402	<0.100	0.293	4.50	23.1	1.95	<0.100	<0.010	<0.100	<0.100	<0.100	0.289	1.40	0.022	0.048	0.198
12-GF40-6621 (A)	12-0699	<0.100	5.03	1.51	0.027	0.328	0.017	0.013	4.08	0.172	2.32	0.116	1.35	11.2	0.576	<0.100	<0.010	<0.100	<0.100	<0.100	0.076	24.8	0.064	0.016	0.180
12-GF40-6621 (B)	12-0699	<0.100	5.09	1.49	0.027	0.279	0.017	0.012	4.08	0.175	2.30	0.114	1.36	11.2	0.578	<0.100	<0.010	<0.100	<0.100	<0.100	0.073	25.1	0.064	0.017	0.183

oxide wt% - calcined 1100C		Ag2O	Al2O3	B2O3	BaO	CaO	Cr2O3	Cu2O	Fe2O3	K2O	Li2O	MgO	MnO2	Na2O	NiO	P2O5	PbO2	PdO	RhO2	RuO2	SO4	SiO2	TiO2	ZnO	ZrO2	Totals
12-GF40-6615 (A)	12-0697	0.0	27.8	0.0	0.102	0.861	0.037	0.035	20.3	0.505	0.0	0.503	7.14	30.9	2.48	0.000	0.000	0.000	0.000	0.000	0.885	3.06	0.037	0.057	0.271	95.0
12-GF40-6615 (B)	12-0697	0.0	27.8	0.0	0.100	0.822	0.037	0.033	20.3	0.482	0.0	0.486	7.11	31.2	2.48	0.000	0.000	0.000	0.000	0.000	0.867	3.00	0.037	0.060	0.267	95.0
12-GF40-6621 (A)	12-0699	0.0	9.51	4.86	0.030	0.459	0.025	0.015	5.83	0.206	4.99	0.193	2.13	15.1	0.732	0.000	0.000	0.000	0.000	0.000	0.228	53.1	0.107	0.020	0.243	97.8
12-GF40-6621 (B)	12-0699	0.0	9.62	4.80	0.030	0.391	0.025	0.014	5.83	0.210	4.95	0.189	2.15	15.1	0.734	0.000	0.000	0.000	0.000	0.000	0.219	53.7	0.107	0.021	0.247	98.4

Units: mg/Kg

Sample ID	Lab ID	F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
12-GF40-6615 (A)	12-0697	<500	<500	<500	60300	61600	1370	13500	<500	<500
12-GF40-6615 (B)	12-0697	<500	<500	<500	59600	62700	1370	13500	<500	<500
12-GF40-6621 (A)	12-0699	<500	<500	<500	47800	48800	1780	17000	<500	<500
12-GF40-6621 (B)	12-0699	<500	<500	<500	48600	49500	1780	17000	<500	<500

Weight % Solids Calculations

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Total Solids	Wet Wt	Dry Wt	Insoluble Solids	Cruc Wt+ Calcined	Wt % Calcined
12-GF40-6615 (A)	12-0697	43.6776	49.7619	45.3722	27.9%	6.084	1.695	10.6%	44.5557	14.4%
12-GF40-6615 (B)	12-0697	45.3634	51.4724	47.0298	27.3%	6.109	1.666	9.85%	46.2364	14.3%
12-GF40-6621 (A)	12-0699	44.4473	51.5461	48.0055	50.1%	7.099	3.558	37.2%	47.1550	38.1%
12-GF40-6621 (B)	12-0699	43.1374	50.1919	46.6328	49.5%	7.055	3.495	36.6%	45.8039	37.8%

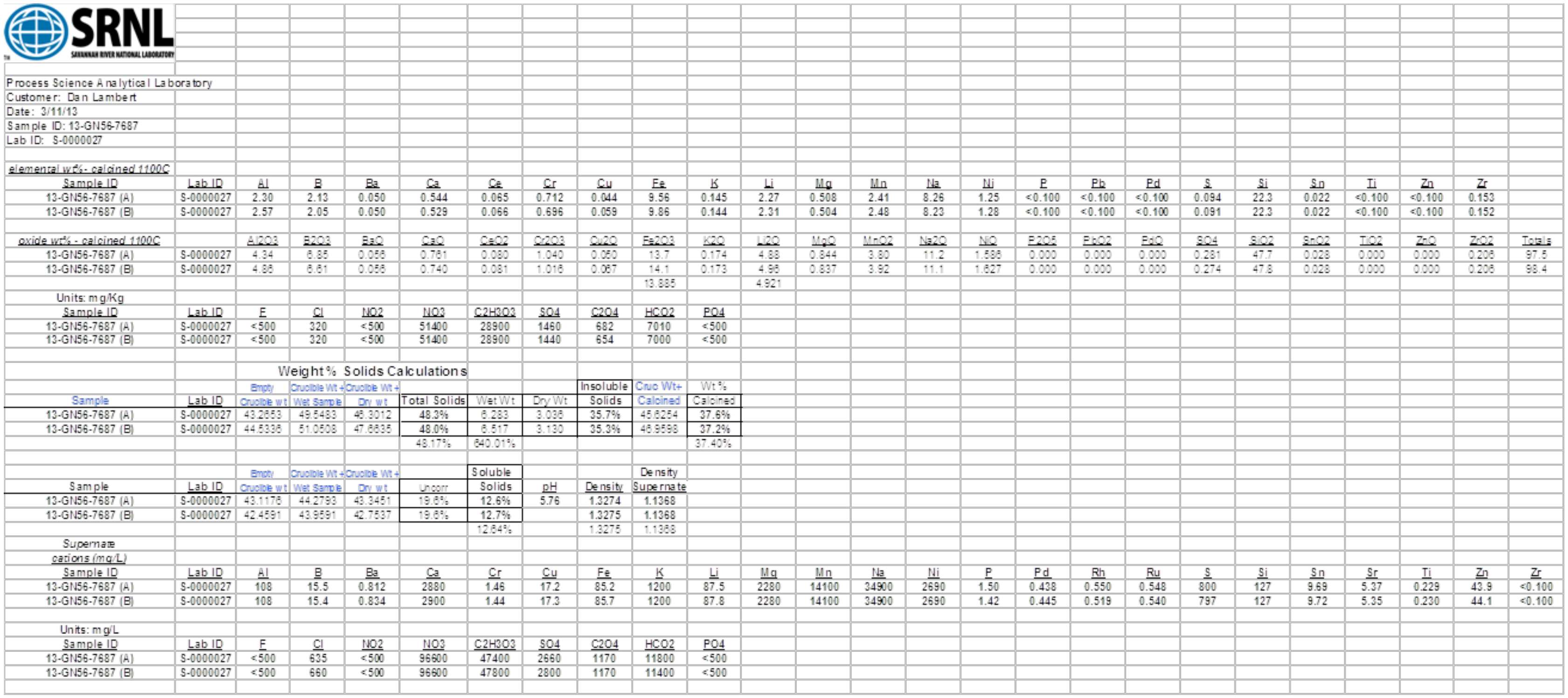
Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Uncorr	Soluble Solids	pH	Supernate Density	Slurry Density
12-GF40-6615 (A)	12-0697	45.2953	46.4688	45.5222	19.34%	17.3%	4.84	1.1282	1.2079
12-GF40-6615 (B)	12-0697	45.9420	47.1074	46.1673	19.33%	17.4%			
12-GF40-6621 (A)	12-0699	43.5134	44.6708	43.7514	20.56%	12.9%	4.76	1.1367	1.2432
12-GF40-6621 (B)	12-0699	42.8413	43.9758	43.0733	20.45%	13.0%			

Supernate cations (mg/L)

Sample ID	Lab ID	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	K	Hg	Li	Mg	Mn	Na	Ni	P	Pb	Pd	Rh	Ru	S	Si	Ti	Zn	Zr
12-GF40-6615 (A)	12-0697	<0.100	1710	<10.0	9.35	369	27.4	19.4	5500	916	<10.0	<10.0	281	5120	44800	733	14.2	6.79	<1.00	30.6	54.2	584	43.8	0.686	22.3	195
12-GF40-6615 (B)	12-0697	<0.100	1720	<10.0	9.38	368	27.4	19.4	5510	920	<10.0	<10.0	280	5130	43800	730	14.0	6.66	<1.00	30.3	54.0	582	44.9	0.680	22.5	195
12-GF40-6621 (A)	12-0699	<0.100	2240	<10.0	14.3	396	35.3	27.0	10100	991	<10.0	<10.0	353	5230	45300	1070	10.1	15.8	<1.00	36.5	84.8	713	62.6	0.938	41.8	260
12-GF40-6621 (B)	12-0699	<0.100	2240	<10.0	14.3	401	35.3	27.1	10100	991	<10.0	<10.0	352	5230	47300	1070	10.4	15.7	<1.00	36.9	85.6	716	61.9	0.937	42.0	262

		F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
12-GF40-6615 (A)	12-0697	<500	<500	<500	75900	49700	1910	11100	<500	<500
12-GF40-6615 (B)	12-0697	<500	<500	<500	75800	50800	1910	11100	<500	<500
12-GF40-6621 (A)	12-0699	<500	<500	<500	93600	60500	2330	10400	<500	<500
12-GF40-6621 (B)	12-0699	<500	<500	<500	94500	60300	2330	10400	<500	<500

C.3 GN56



Process Science Analytical Laboratory
Customer: Dan Lambert
Date: 3/11/13
Sample ID: 13-GN56-7687
Lab ID: S-0000027

elemental wt% - calcined 1100C

Sample ID	Lab ID	Al	B	Ba	Ca	Ce	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Pd	S	Si	Sn	Ti	Zn	Zr
13-GN56-7687 (A)	S-0000027	2.30	2.13	0.050	0.544	0.065	0.712	0.044	9.56	0.145	2.27	0.508	2.41	8.26	1.25	<0.100	<0.100	<0.100	0.094	22.3	0.022	<0.100	<0.100	0.153
13-GN56-7687 (B)	S-0000027	2.57	2.05	0.050	0.529	0.066	0.696	0.059	9.86	0.144	2.31	0.504	2.48	8.23	1.28	<0.100	<0.100	<0.100	0.091	22.3	0.022	<0.100	<0.100	0.152

oxide wt% - calcined 1100C		Al2O3	B2O3	BaO	CaO	CeO2	Cr2O3	Cu2O	Fe2O3	K2O	Li2O	MgO	MnO2	Na2O	NiO	P2O5	PbO2	PdO	SO4	SiO2	SnO2	TiO2	ZnO	ZrO2	Totals
13-GN56-7687 (A)	S-0000027	4.34	6.85	0.056	0.761	0.080	1.040	0.050	13.7	0.174	4.88	0.844	3.80	11.2	1.586	0.000	0.000	0.000	0.281	47.7	0.028	0.000	0.000	0.206	97.5
13-GN56-7687 (B)	S-0000027	4.86	6.61	0.056	0.740	0.081	1.016	0.067	14.1	0.173	4.96	0.837	3.92	11.1	1.627	0.000	0.000	0.000	0.274	47.8	0.028	0.000	0.000	0.206	98.4
									13.885		4.921														

Units: mg/Kg

Sample ID	Lab ID	F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
13-GN56-7687 (A)	S-0000027	<500	320	<500	51400	28900	1460	682	7010	<500
13-GN56-7687 (B)	S-0000027	<500	320	<500	51400	28900	1440	654	7000	<500

Weight % Solids Calculations

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Total Solids	Wet Wt	Dry Wt	Insoluble Solids	Cruc Wt+ Calcined	Wt % Calcined
13-GN56-7687 (A)	S-0000027	43.2653	49.5483	46.3012	48.3%	6.283	3.036	35.7%	45.6254	37.6%
13-GN56-7687 (B)	S-0000027	44.5336	51.0508	47.6635	48.0%	6.517	3.130	35.3%	46.9598	37.2%
					48.17%	640.01%				37.40%

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Uncorr	Soluble Solids	pH	Density	Density Supernate
13-GN56-7687 (A)	S-0000027	43.1176	44.2793	43.3451	19.6%	12.6%	5.76	1.3274	1.1368
13-GN56-7687 (B)	S-0000027	42.4591	43.9591	42.7537	19.6%	12.7%		1.3275	1.1368
						12.64%		1.3275	1.1368

Supernate
cations (mg/L)

Sample ID	Lab ID	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pd	Rh	Ru	S	Si	Sn	Sr	Ti	Zn	Zr
13-GN56-7687 (A)	S-0000027	108	15.5	0.812	2880	1.46	17.2	85.2	1200	87.5	2280	14100	34900	2690	1.50	0.438	0.550	0.548	800	127	9.69	5.37	0.229	43.9	<0.100
13-GN56-7687 (B)	S-0000027	108	15.4	0.834	2900	1.44	17.3	85.7	1200	87.8	2280	14100	34900	2690	1.42	0.445	0.519	0.540	797	127	9.72	5.35	0.230	44.1	<0.100

Units: mg/L

Sample ID	Lab ID	F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
13-GN56-7687 (A)	S-0000027	<500	635	<500	96600	47400	2660	1170	11800	<500
13-GN56-7687 (B)	S-0000027	<500	660	<500	96600	47800	2800	1170	11400	<500

C.4 GN57

Process Science Analytical Laboratory
Customer: Dan Lambert
Date: 3/19/13
Sample ID: 13-GN57-S-92
Lab ID: S-0000092

elemental wt%- calcined 1100C

Sample ID	Lab ID	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pd	S	Si	Sn	Ti	Zn	Zr
13-GN57-S-92 (A)	S-0000092	5.53	2.74	0.056	0.421	0.072	0.059	8.32	0.155	2.31	0.239	2.54	7.36	1.09	<0.100	<0.100	0.096	21.6	0.027	0.025	0.045	0.109
13-GN57-S-92 (B)	S-0000092	5.51	2.76	0.058	0.371	0.070	0.076	8.37	0.160	2.32	0.238	2.50	7.12	1.08	<0.100	<0.100	0.088	21.6	0.027	0.029	0.044	0.100

oxide wt% - calcined 1100C		Al2O3	B2O3	BaO	CaO	Cr2O3	Cu2O	Fe2O3	K2O	Li2O	MgO	MnO2	Na2O	NiO	P2O5	PdO	SO4	SiO2	SnO2	TiO2	ZnO	ZrO2	Totals
13-GN57-S-92 (A)	S-0000092	10.5	8.82	0.062	0.590	0.105	0.066	11.90	0.186	4.962	0.397	4.01	9.94	1.384	0.000	0.000	0.287	46.2	0.035	0.041	0.055	0.148	99.6
13-GN57-S-92 (B)	S-0000092	10.4	8.88	0.065	0.519	0.102	0.086	11.97	0.192	4.979	0.395	3.95	9.61	1.369	0.000	0.000	0.264	46.2	0.034	0.048	0.055	0.135	99.3

Units: mg/Kg

Sample ID	Lab ID	F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
13-GN57-S-92 (A)	S-0000092	<500	733	<500	58400	36200	1680	2870	<500	<500
13-GN57-S-92 (B)	S-0000092	<500	752	<500	58300	36300	1690	2970	<500	<500

Weight % Solids Calculations

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Total Solids	Wet Wt	Dry Wt	Insoluble Solids	Cruc Wt+ Calcined	Wt % Calcined
13-GN57-S-92 (A)	S-0000092	44.0844	51.0269	47.4803	48.9%	6.943	3.396	35.1%	46.6675	37.2%
13-GN57-S-92 (B)	S-0000092	42.6623	49.7373	46.1299	49.0%	7.075	3.468	35.2%	45.3059	37.4%

Sample	Lab ID	Empty Crucible wt	Crucible Wt + Wet Sample	Crucible Wt + Dry wt	Uncorr	Soluble Solids	pH	Density	Density Supernate
13-GN57-S-92 (A)	S-0000092	44.0912	45.2465	44.3375	21.32%	13.8%	4.7	1.3990	1.1523
13-GN57-S-92 (B)	S-0000092	42.7612	43.9159	43.0079	21.36%	13.9%		1.3990	1.1523

Supernate
cations (mg/L)

Sample ID	Lab ID	Al	B	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pd	Rh	Ru	S	Si	Sn	Ti	Zn	Zr
13-GN57-S-92 (A)	S-0000092	432	155	3.85	2880	3.16	133	1038	1151	199	2379	16249	36400	4026	3.23	0.374	29.9	129	1061	54.8	11.6	0.690	118	<0.100
13-GN57-S-92 (B)	S-0000092	434	154	3.82	2897	3.10	135	1029	1165	199	2384	16394	36500	4033	3.55	0.376	30.0	129	1060	54.4	11.6	0.693	117	<0.100

Units: mg/L

Sample ID	Lab ID	F	Cl	NO2	NO3	C2H3O3	SO4	C2O4	HCO2	PO4
13-GN57-S-92 (A)	S-0000092	<500	1420	<500	111000	63100	2950	4250	<500	<500
13-GN57-S-92 (B)	S-0000092	<500	1420	<500	110000	63200	2970	4250	<500	<500

9.0 Appendix D – NMR

D.1 VSL ^{1}H NMR

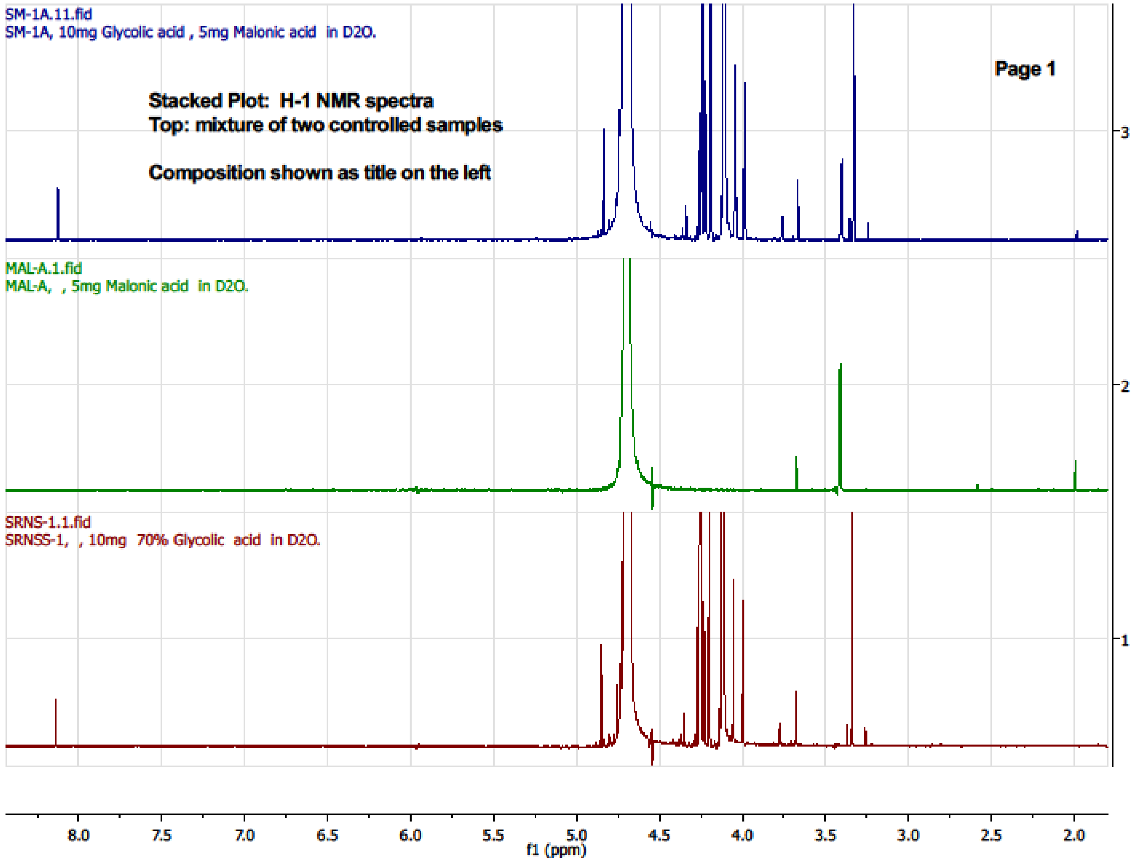


Figure D.1-1 ^{1}H NMR Spectrum of Glycolic Acid and Malonic acid (top), Malonic Acid (middle), and 70% Glycolic Acid (70% Glycolic Acid)

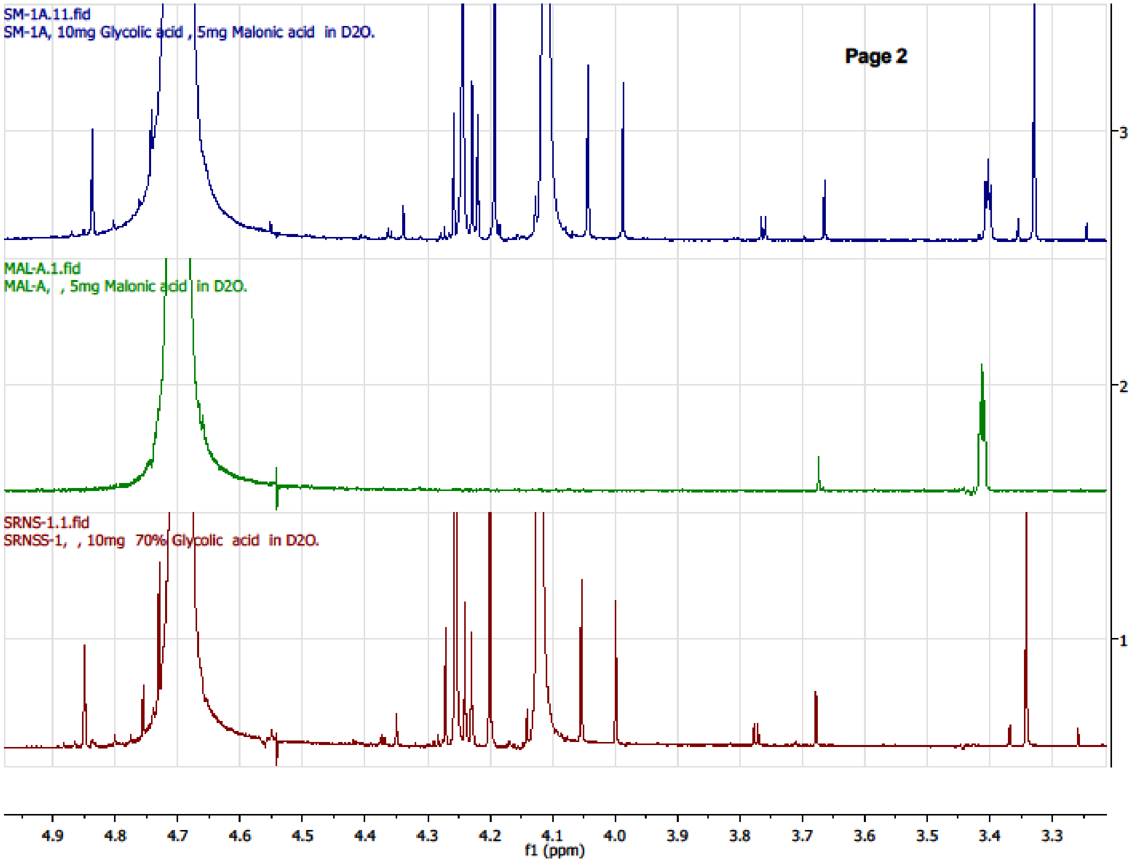


Figure D.1-2 Expanded ^{1}H NMR Spectrum of Glycolic Acid and Malonic acid (top), Malonic Acid (middle), and 70% Glycolic Acid (bottom)

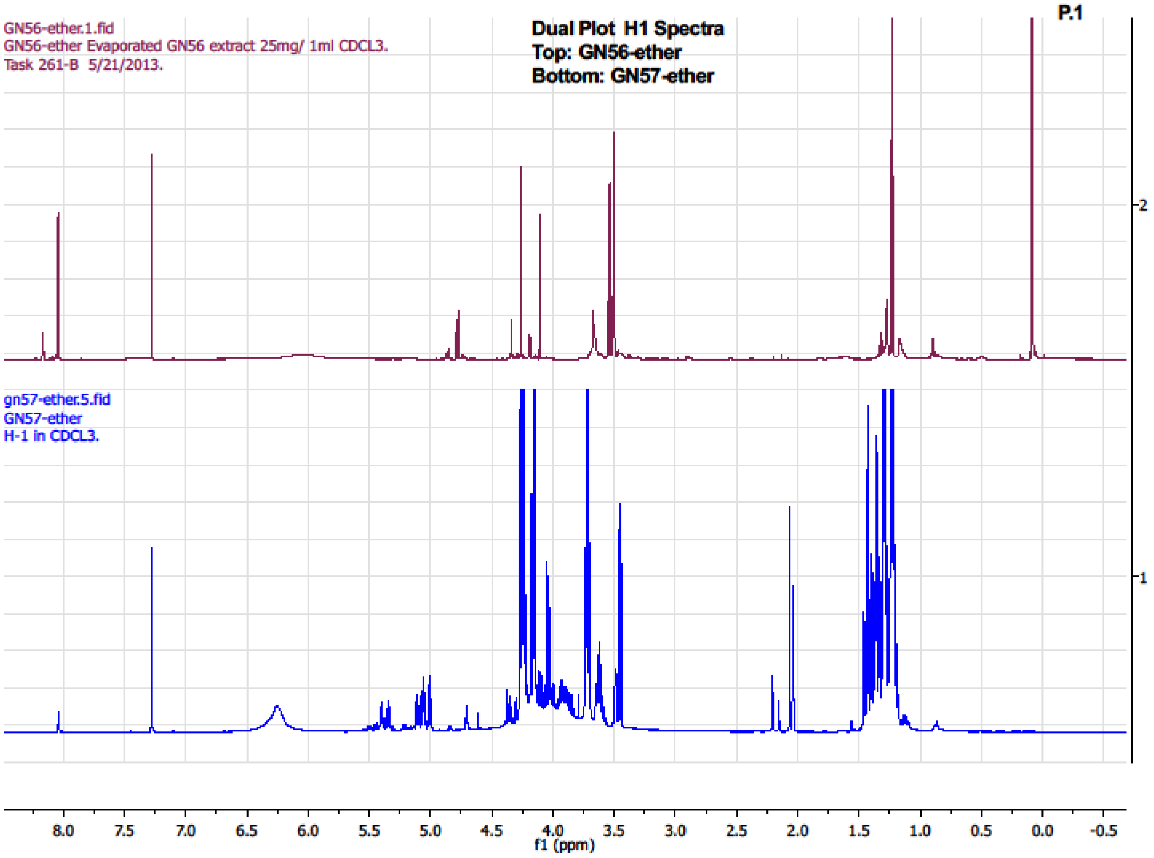


Figure D.1-3 ^{1}H NMR Spectrum of GN56 ether extract (top) and GN57 ether extract (bottom)

D.2 VSL ^{13}C NMR

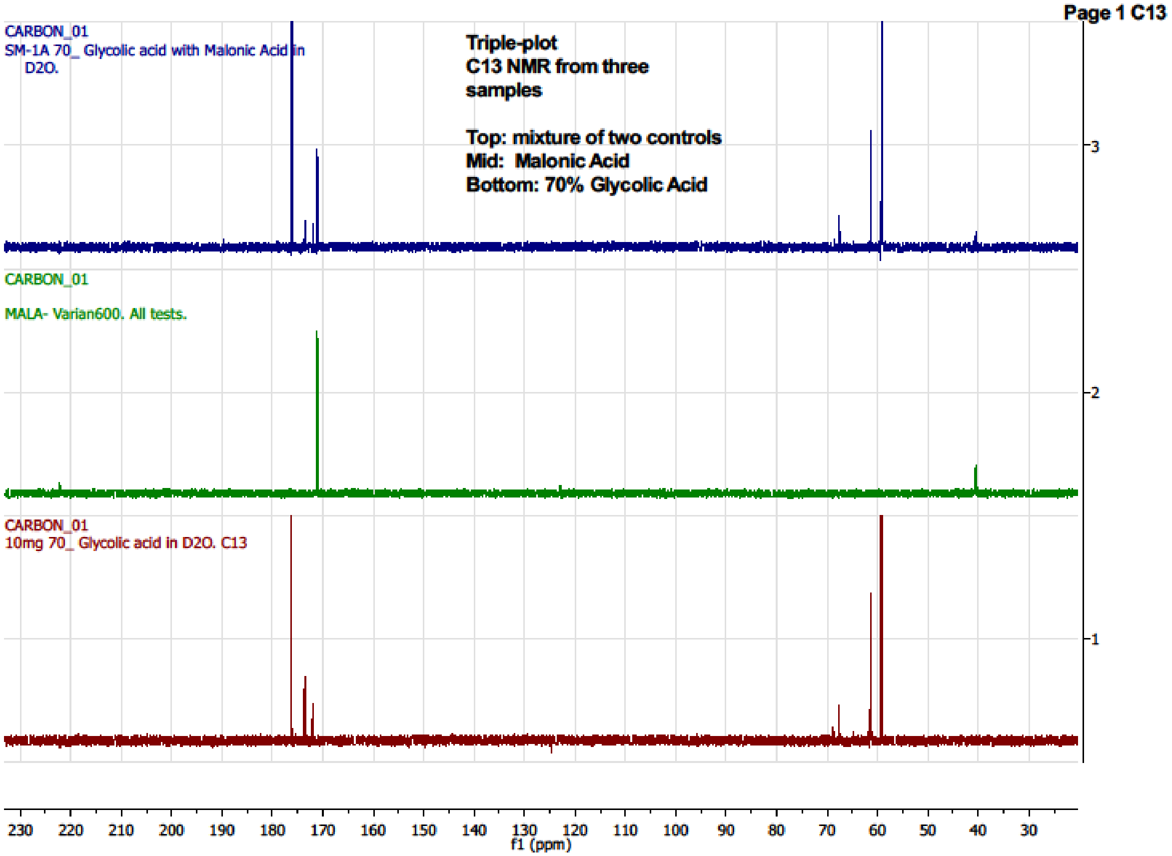


Figure D.2-1 ^{13}C NMR Spectrum of Glycolic Acid and Malonic acid (top), Malonic Acid (middle), and 70% Glycolic Acid (bottom)

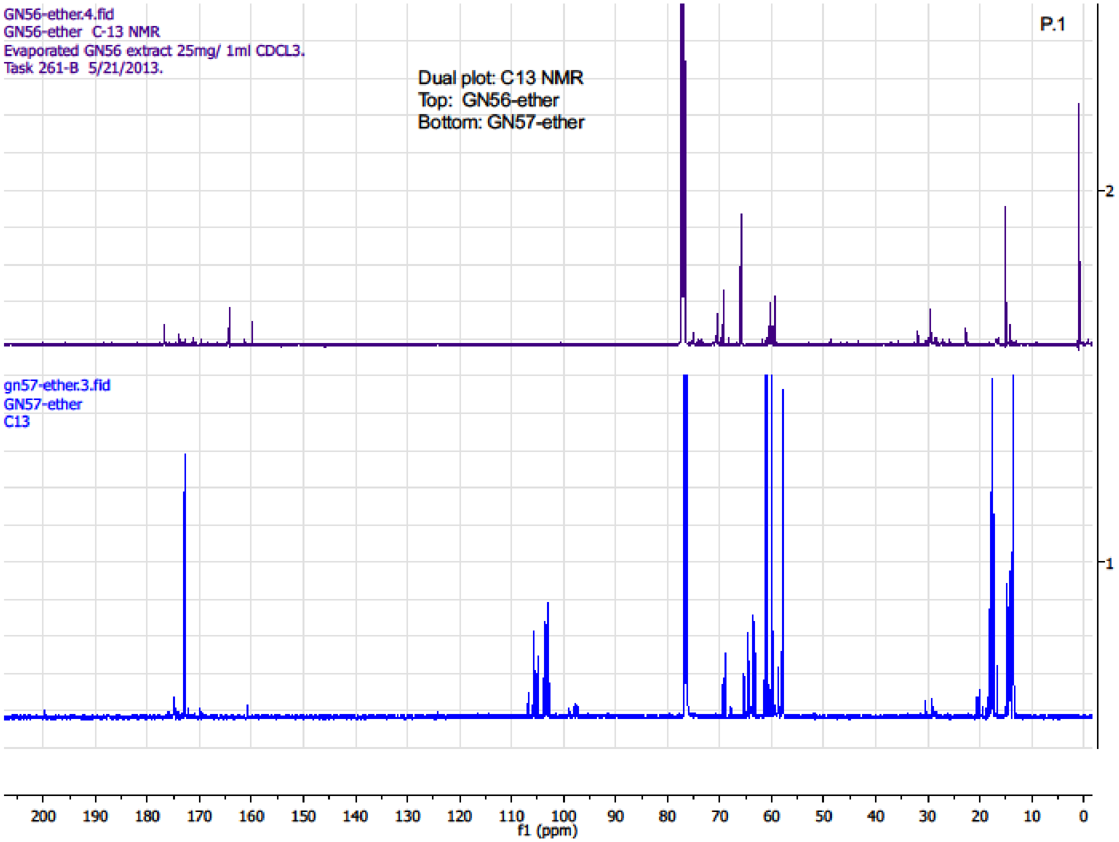
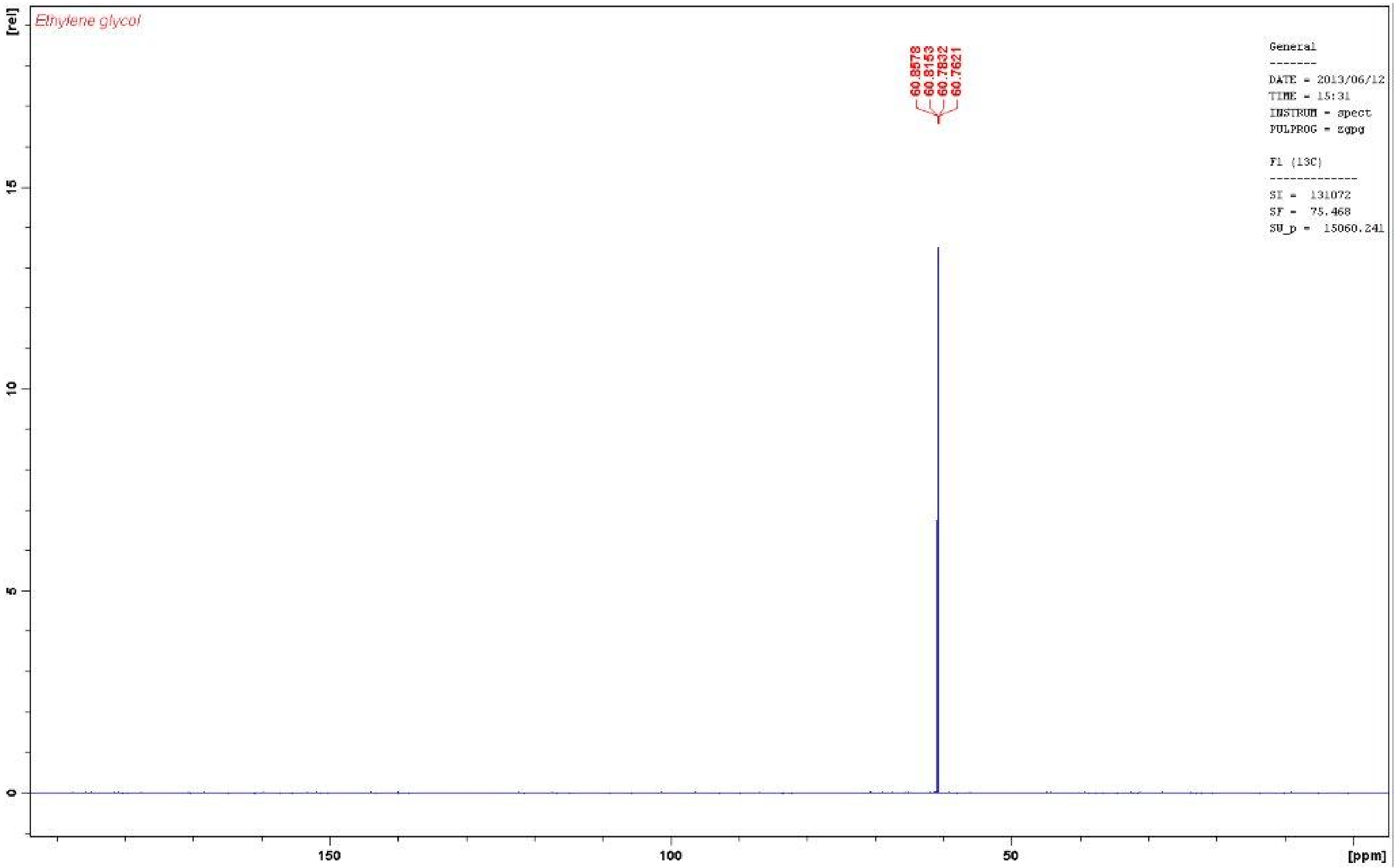


Figure D.2-2 ^{13}C NMR Spectrum of GN56 ether extract (top) and GN57 ether extract (bottom)

D.3 SNRL ^{13}C NMR



General

DATE = 2013/06/12
TIME = 15:31
INSTRUM = spect
PULPROG = zgpg

F1 (13C)

SI = 131072
SF = 75.468
SW_p = 15060.241

Figure D.3-1 ^{13}C NMR Spectrum of Ethylene Glycol

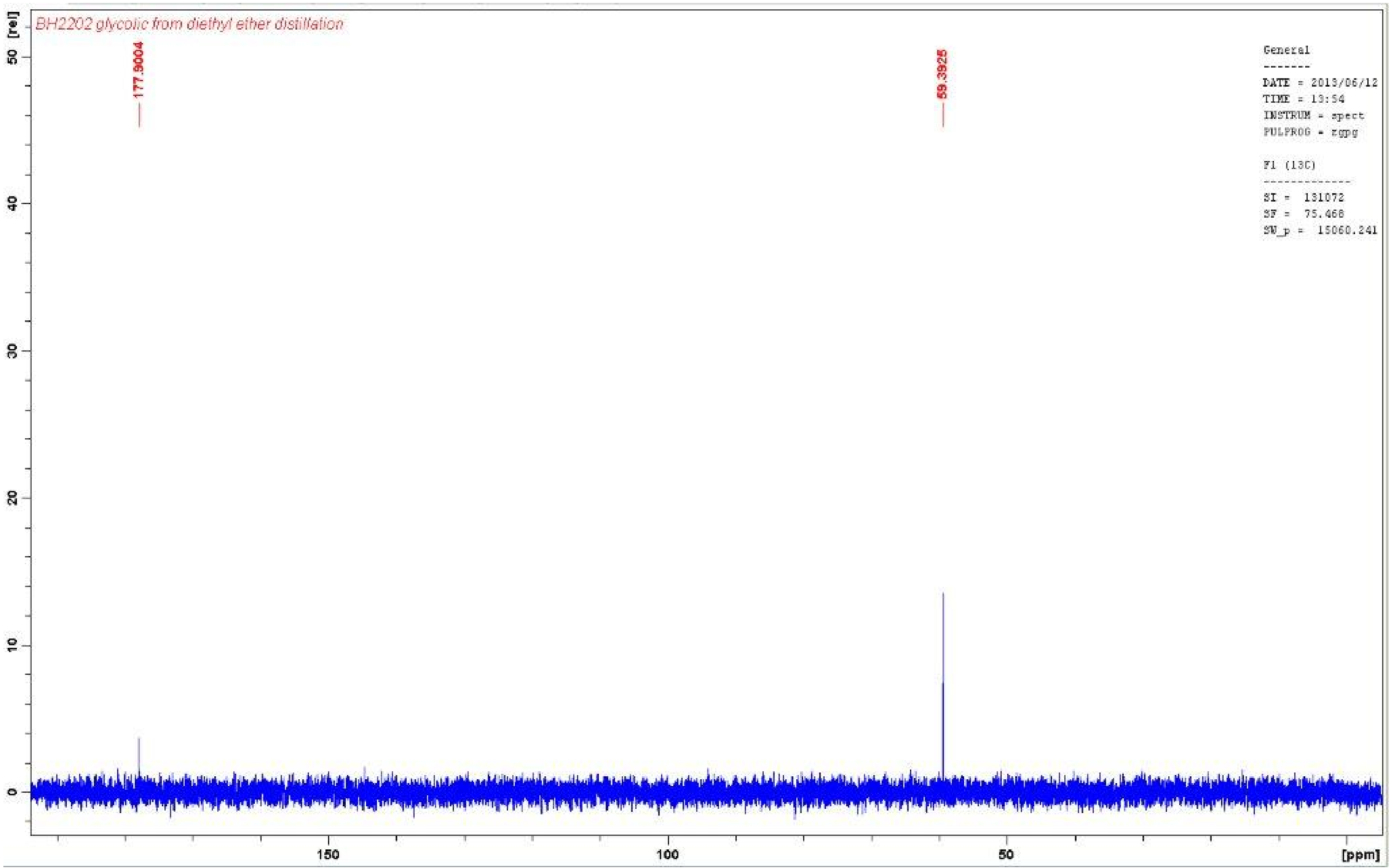


Figure D.3-2 ^{13}C NMR Spectrum of Glycolic acid from Diethyl Ether Extracts

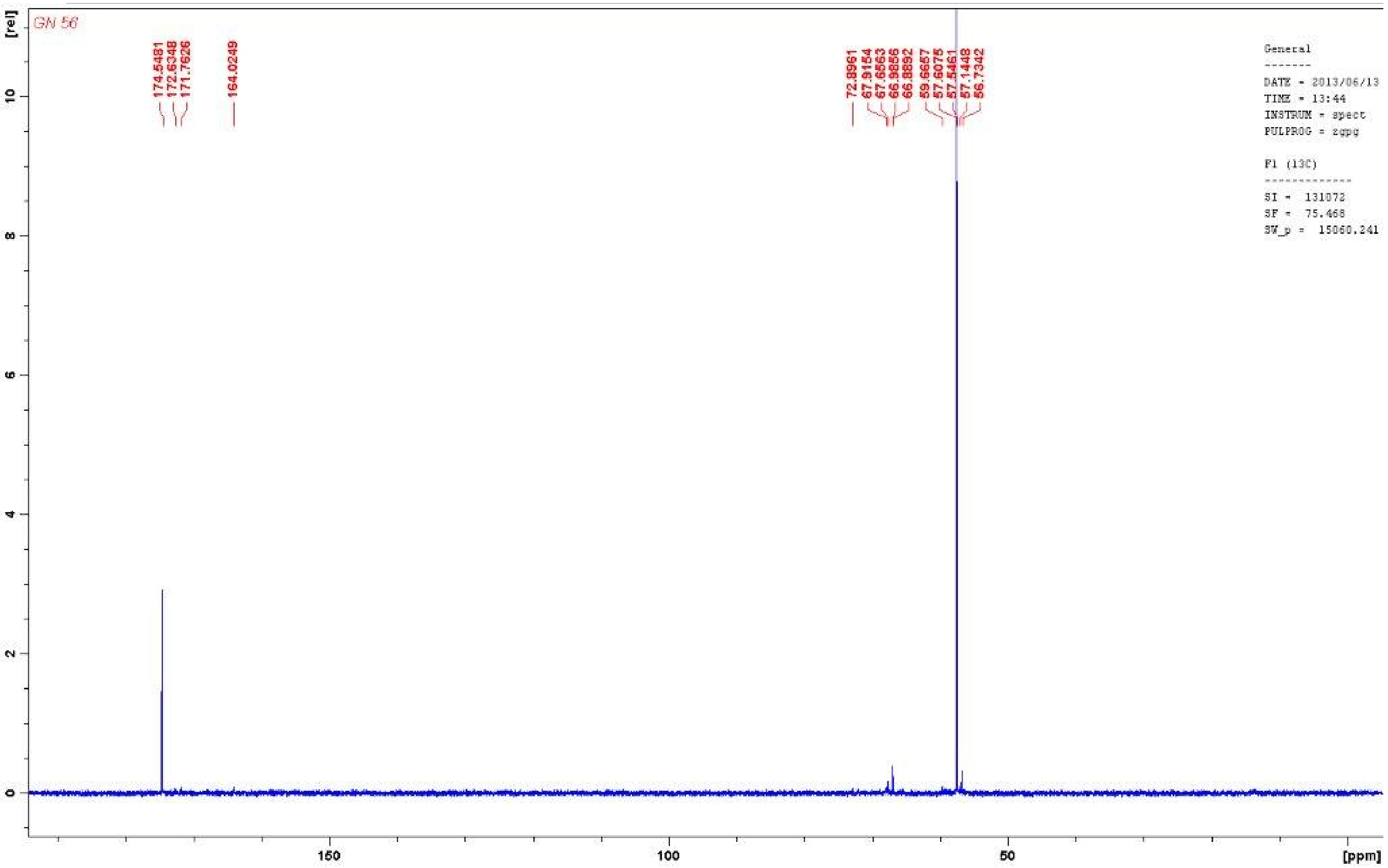


Figure D.3-3 ^{13}C NMR Spectrum of GN56 Diethyl Ether Extracts

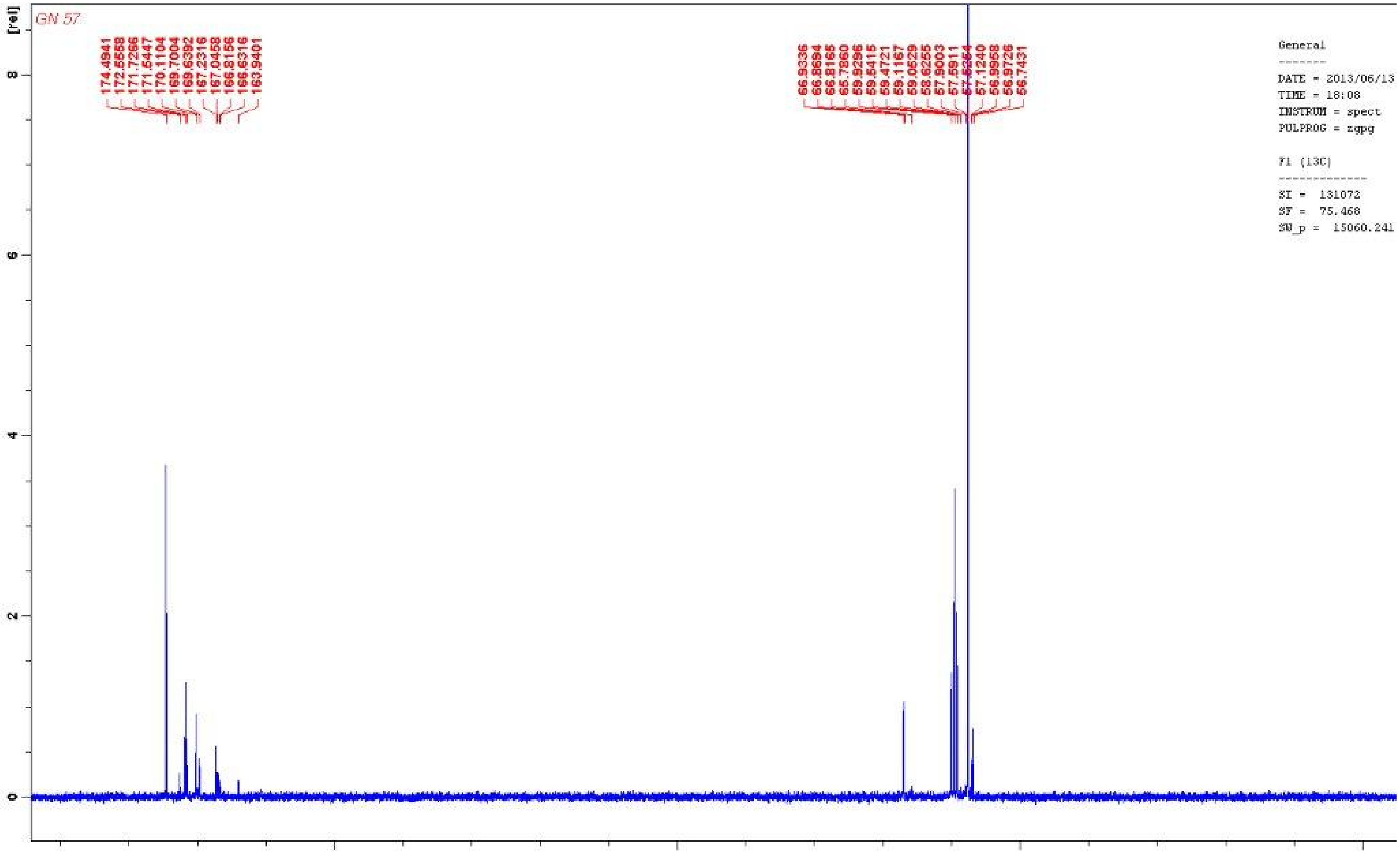


Figure D.3-4 ^{13}C NMR Spectrum of GN57 Diethyl Ether Extracts

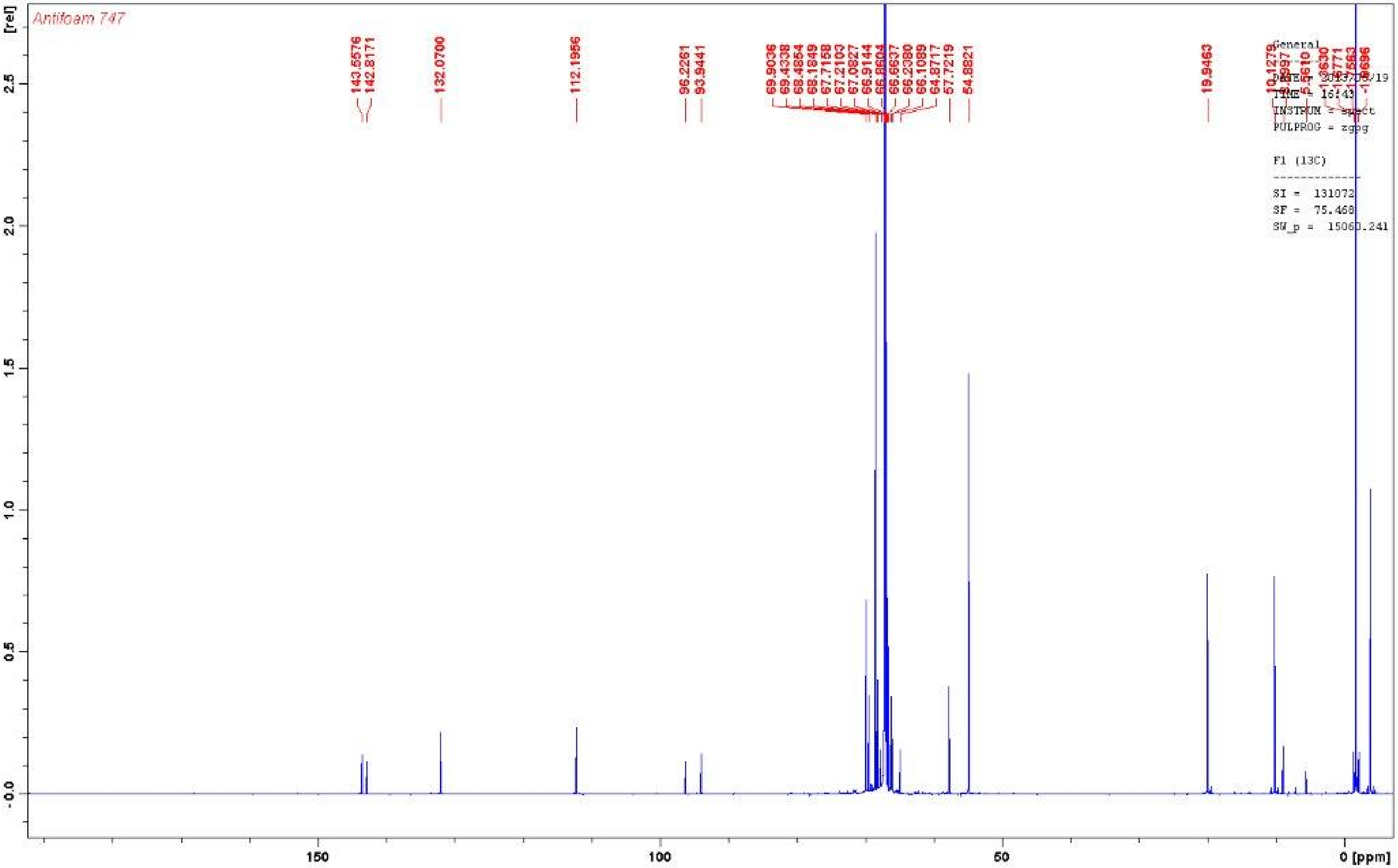


Figure D.3-5 ^{13}C NMR Spectrum of 747 Antifoam

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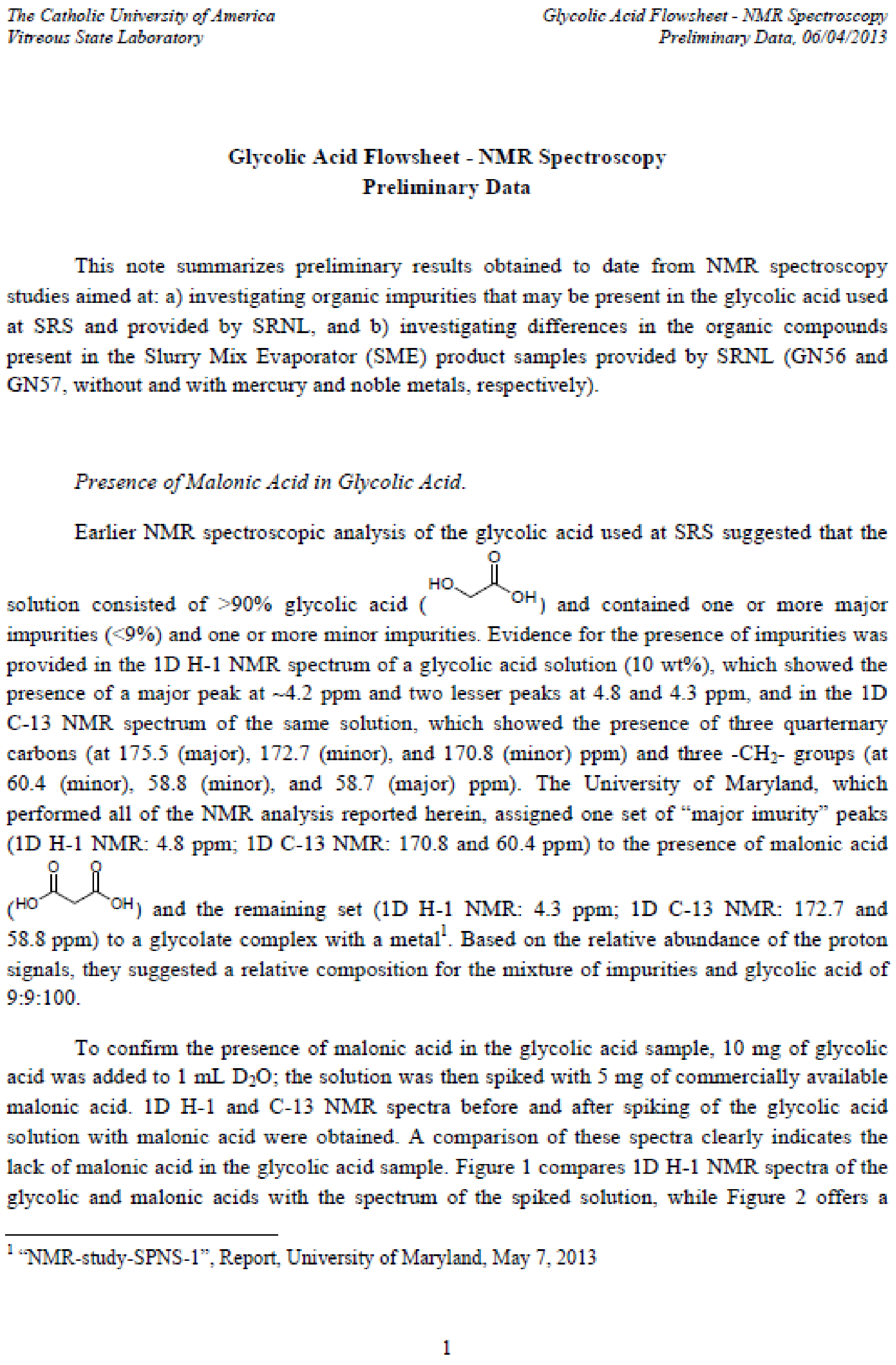
10.0 Appendix E: Email from VSL dated 06/04/13



The Catholic University of America
Vitreous State Laboratory

Glycolic Acid Flowsheet - NMR Spectroscopy
Preliminary Data, 06/04/2013

Glycolic Acid Flowsheet - NMR Spectroscopy
Preliminary Data

This note summarizes preliminary results obtained to date from NMR spectroscopy studies aimed at: a) investigating organic impurities that may be present in the glycolic acid used at SRS and provided by SRNL, and b) investigating differences in the organic compounds present in the Slurry Mix Evaporator (SME) product samples provided by SRNL (GN56 and GN57, without and with mercury and noble metals, respectively).

Presence of Malonic Acid in Glycolic Acid.

Earlier NMR spectroscopic analysis of the glycolic acid used at SRS suggested that the solution consisted of >90% glycolic acid ( ) and contained one or more major impurities (<9%) and one or more minor impurities. Evidence for the presence of impurities was provided in the 1D H-1 NMR spectrum of a glycolic acid solution (10 wt%), which showed the presence of a major peak at ~4.2 ppm and two lesser peaks at 4.8 and 4.3 ppm, and in the 1D C-13 NMR spectrum of the same solution, which showed the presence of three quarternary carbons (at 175.5 (major), 172.7 (minor), and 170.8 (minor) ppm) and three -CH_2- groups (at 60.4 (minor), 58.8 (minor), and 58.7 (major) ppm). The University of Maryland, which performed all of the NMR analysis reported herein, assigned one set of "major imurity" peaks (1D H-1 NMR: 4.8 ppm; 1D C-13 NMR: 170.8 and 60.4 ppm) to the presence of malonic acid ( ) and the remaining set (1D H-1 NMR: 4.3 ppm; 1D C-13 NMR: 172.7 and 58.8 ppm) to a glycolate complex with a metal[1]. Based on the relative abundance of the proton signals, they suggested a relative composition for the mixture of impurities and glycolic acid of 9:9:100.

To confirm the presence of malonic acid in the glycolic acid sample, 10 mg of glycolic acid was added to 1 mL D_2O; the solution was then spiked with 5 mg of commercially available malonic acid. 1D H-1 and C-13 NMR spectra before and after spiking of the glycolic acid solution with malonic acid were obtained. A comparison of these spectra clearly indicates the lack of malonic acid in the glycolic acid sample. Figure 1 compares 1D H-1 NMR spectra of the glycolic and malonic acids with the spectrum of the spiked solution, while Figure 2 offers a

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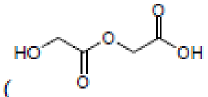
[1] "NMR-study-SPNS-1", Report, University of Maryland, May 7, 2013

similar comparison of the expanded region between 5 and 3 ppm. Similarly, Figure 3 compares 1D C-13 NMR spectra of the two acids with the corresponding spectrum of the spiked solution. Figures 1 and 2 show that the signal assigned to the protons of the methylene group in malonic acid (3.4 ppm) is absent from the spectrum of the glycolic acid, while Figure 3 show that the C-13 spectrum of glycolic acid lacks the peaks associated with the quaternary carbon (~170 ppm) and the methylene carbon (~41 ppm) of malonic acid.

Although the University of Maryland assigned proton signals 4.8 and 4.3 ppm to different compounds (malonic acid and glycolate complex, respectively) their report clearly suggested that the two signals were related. Related proton signals belong to the same compound and are separated by 2 or more bonds. Glycolic acid is known to polymerize. Min et al.[2] have reported the proton signals associated with the methylene groups of the glycolic dimmer ( or HO-(CH_2COO)$_2$-H) to be 4.78 and 4.28 ppm and suggested that the corresponding signals of the glycolic tetramer were 4.90, 4.87, 4.78, and 4.30 ppm. It is thus entirely possible that the compound present as ~10% impurity in the glycolic acid solution is a glycolic dimmer. The 1D H-1 and C-13 NMR spectra of the glycolic acid in Figures 1-3 also indicate the presence of additional minor impurities (<1%). It is conceivable that some of these impurities are glycolic acid polymers with various degrees of polymerization.

Comparison of Etheric Extracts of GN56 and GN57.

The SME products GN56 and GN57 provided by SRNL (without and with mercury and noble metals, respectively) were subjected to extraction with diethyl ether using the following experimental protocol:

The SME product was homogenized and a sample was centrifuged (3800 rpm for 15 min). The supernatant was filtered (0.45 µm) and the filtrate was acidified with concentrated HCl to a final pH of about 2. The acidified solution was extracted with diethyl ether (2× with 15 mL each for ≈10 g of solution). The organic fractions were combined and dried with $MgSO_4$ overnight. Following filtration to remove the $MgSO_4$, the solvent was removed using a Rotavac.

SME product GN56 yielded ~30 mg of organic material from 8 g of initial filtrate, while GN57 yielded ~85 mg of organic material from 10 g of initial filtrate. Subsamples of these materials, 25 mg of the GN56 extract and 50 mg of the GN57 extract, were subjected to NMR

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[2] "Free Acid Effect and NMR Study of Glycolide," B. Min et al., Bull. Korean Chem. Soc. 21(6), 635-637 (2000).

analysis using $CDCl_3$ as a solvent. 1D H-1 and C-13 NMR spectra revealed that both extracts were complex mixtures that differed significantly in composition, as evident in Figures 4 and 5, which compare the H-1 and C-13 spectra of the two extracts, respectively. Analysis of these spectra is in progress. However, a number of general observations can be made from the above figures:

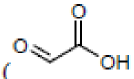
a) The spectra of the two extracts show many differences and rather few similarities.

b) The GN57 extract appears to be more compositionally complex than GN56 extract.

c) GN57 contains unique groups of signals in both H-1 (5.5 - 5.0 and 2.0 - 2.5 ppm) and C-13 (110 - 95 ppm) NMR spectra.

d) While the presence of residual diethyl ether can be clearly seen in the spectra of GN56 extract (for example, as signals with identical intensity at ~15 and ~67 ppm in the 1D C-13 NMR spectrum) such presence is less evident in the GN57 extract.

e) While these compounds may have been produced in the SRAT/SME process, it is still possible that some of the compositional complexity of both extracts may be attributed to minor or previously unseen impurities found in glycolic acid since the etheric extraction process is expected to concentrate and, thus, amplify signals from such constituents, especially if they are less water soluble than glycolic acid. In this regard, it may be useful to perform the same diethyl ether extraction and NMR analysis on the glycolic acid sample for comparison.

f) The presence of a number of alkyl carbons (as evident from proton peaks in the region of 2.0 - 1.0 ppm or carbon peaks in the region of 20 - 10 ppm) is surprising. It is possible that these are groups associated with antifoam agents or previously unseen impurities of glycolic acid. It is also conceivable that they are products of redox reactions involving glycolic acid. For example, enzymatic reactions are known whereby glycolic acid can be oxidized to glyoxylic acid ( usually existing as the corresponding hydrate or $(HO)_2CHCO_2H$), which in turn can be oxidized to oxalic acid or $(COOH)_2$.

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. R. Click, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
M. J. Barnes, 773-A
Records Administration (EDWS)

J. M. Bricker, 704-30S
T. L. Fellinger, 704-27S
E. J. Freed, 704-S
J. M. Gillam, 766-H
B. A. Hamm, 766-H
E. W. Holtzscheiter, 704-15S
J. F. Iaukea, 704-27S
R.N. Mahannah, 704-28S
D. W. McImoyle, 766-H
D. K. Peeler, 999-W
J. W. Ray, 704-S
P. J. Ryan, 704-30S
A. Samadi, 704-27S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
M. E. Stone, 999-W

P. R. Jackson, DOE-SR, 703-46A
V. Jain, 766-H

T. L. White, 773-A
B. J. Wiedenman, 773-A
D. P. Lambert, 999-W
S. L. Crump, 773-A
F. F. Fondeur, 773-A

L.H. Connelly, 773-A
C.M. Gregory, 773-A
C.M. Jantzen, 773-A
M.J. Hart, 210-S
J. D. Newell, 999-W
J. M. Pareizs, 773-A
W. T. Riley, 999-W
R. H. Young, 773-A
J. R. Zamecnik, 999-W
D. R. Best, 999-W
C. J. Coleman, 773-A