

Accurate Mass Analysis of Naphthenic Acids by Argon NCI

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Introduction

Currently naphthenic acid (NA) analysis in oil sands process-affected water (OSPW) and crude is done by evaluating accurate mass spectral patterns which are often difficult to interpret due to chromatographic interference. Two recent approaches to evaluate naphthenic acids are EI/TOF and LC/TOF based. The drawback with EI/TOF analysis is that EI fragmentation leads to a large hump of unresolved compounds of naphthenic acid congeners and fatty acids. The drawback of LC/TOF approaches are the limited chromatographic resolution of UHPLC columns. We use a 20 m GC/MS column to provide a high degree of chromatographic separation with a short acquisition time. We use argon as the reagent gas for ECNI since it provides a softer ionization with minimal fragmentation. Finally, using Kendrick mass defect plots helps identify homologous naphthenic acids.

NAs are water soluble. NA from three "fresh" and one aged tailing pond were aliquoted. Oil sands samples, as well as technical standards from Merichem, Sigma-Aldrich and Arcos were provided to Agilent in a 0.1M aq NaOH solutions for the Oil sands, and 0.05M aq NaOH for the technical standards.

Experimental

Sample Preparation

The NA samples were prepared by extractive alkylation using a perfluoro-derivative. 50µLs of the NA samples were added to 1 mL of dichloromethane (DCM), 1mL of 0.2M NaOH, 1mL of 0.1M tetrabutylammonium hydrogen sulfate, and 80µL of perfluorobenzyl bromide (PFBBR). For the pure technical standard the volumes were the same except for the NA was decreased to 0.2µLs and 25µL for PFBBR. The reaction vials were warmed to 30 °C, and agitated for 30 mins. Then the 1mL of DCM was removed and concentrated under a stream of dry nitrogen to 250µL. 50µL of the concentrated product was taken to dryness by a speed-vac, and reconstituted in 100µL of ethyl acetate. This is a 10-fold dilution from the sample's original concentration.



Figure 1. 7200 series GC/Q-TOF system.

Experimental

GC/MS Acquisition

Table 1 includes the GC/MS parameters as well as configuration utilized in this analysis. The Agilent 7200B GC-QToF was selected for the accurate mass acquisition and fast data acquisition rate. The data was collected at 12 Hz to allow for a more confident deconvolution of this complex sample.

ECNI is very susceptible to reduced ionization efficiency when water is present. To provide the driest environment, the ion source and transfer line were baked out overnight at 350 °C and 310 °C, respectively. The stainless steel lines connected to the ultra high purity argon were heated with a heat-gun, while purging the lines by opening and closing the bottle.

Table 1. GC-QToF Parameters

GC and MS Conditions:	
Column	DB-XLB, 20 m, 0.18 mm ID, 0.18 µm film
Injection volume	2.0 µL
	Low pressure drop split liner w/ wool
Pulsed Split	45 psi for 0.5 min
Inlet temperature	280 °C
Oven temperature program	45 °C for 2 min 40 °C/min to 100 °C 5 °C/min to 240 °C 30 °C/min to 300 for 10 min
Carrier gas	Helium at 1.2 mL/min constant flow
Transfer line temperature	300 °C
Ionization mode	NCI Argon flow at 35 %
Source temperature	150 °C
Quadrupole temperature	150 °C
Scan range	45 to 750 m/z
Spectral acquisition rate	12 Hz, both centroid and profile
Emission	80µA
Ionization parameters used in the method	
2GHz NCI Auto Tune	

Data Analysis

All of the data analysis was performed using MassHunter Qualitative Analysis. This provided deconvolution of the high resolving power data, as well as molecular formula generation for the ions found in the deconvoluted chromatographic peak. Molecular formula generation examines the monoisotopic peak, the isotope peak relative abundances, isotope peak mass accuracy, and isotope peak spacing to provide a calculated elemental composition. Calculate formulas with a score below 60 (Agilent's value) were disregarded.

Results and Discussion

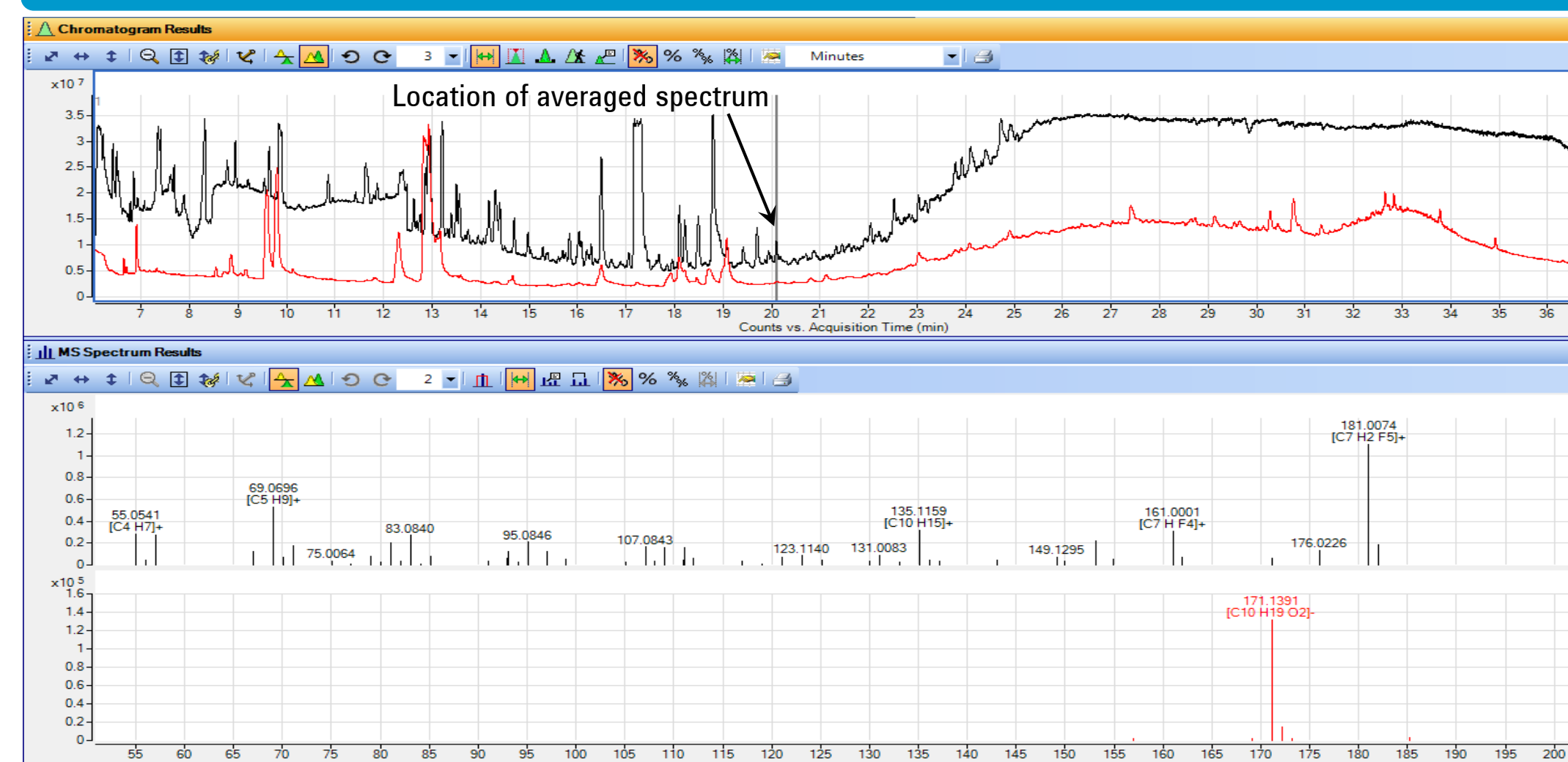


Figure 2. The difference in signal from the EI full scan data (black), and the argon ECNI full scan data (red). The color correlated spectra from the same point in both data files illustrates the ionization of the intact naphthenic acid (red), whereas the EI spectrum only the PFBBR is observed as the base peak (black).

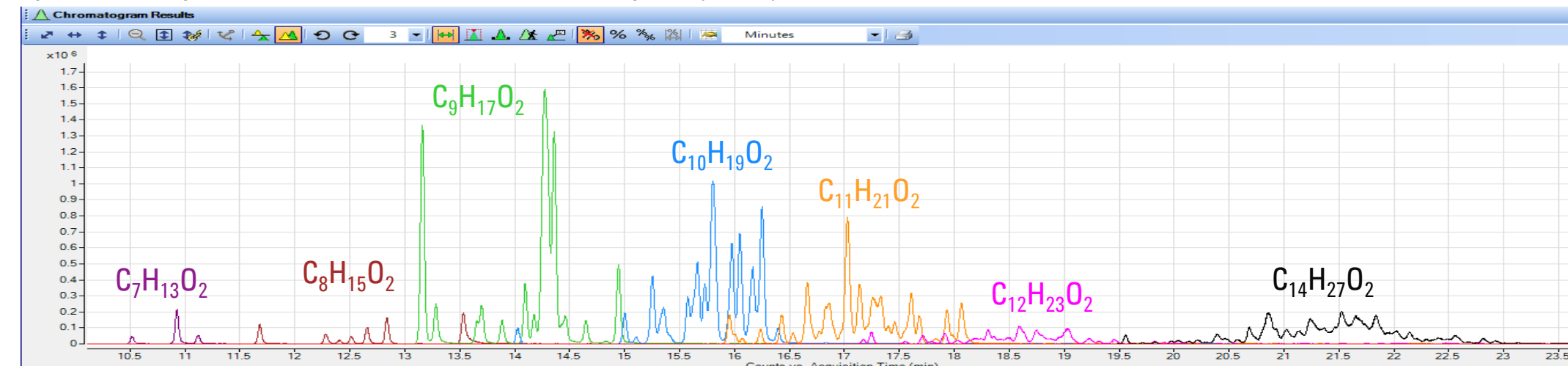


Figure 3. Argon ECNI extracted ion chromatograms for the different alkane isomer groups. During the ionization of the analyte loses the PFBBR group while the charge is retained on the naphthenic acid.

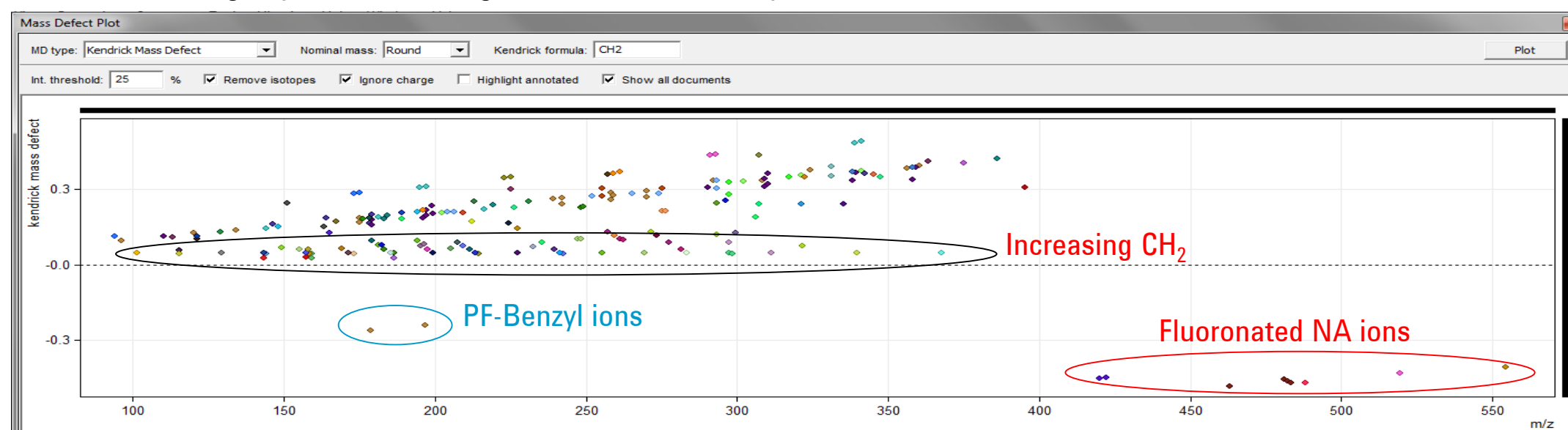


Figure 4. The pure Sigma Technical standard derivatized sample was diluted 1000x in ethyl acetate, to produce the extracted ion chromatogram for the m/z 185.1547 isomer groups, to observe the detection limits for these analytes using argon ECNI.

Results and Discussion

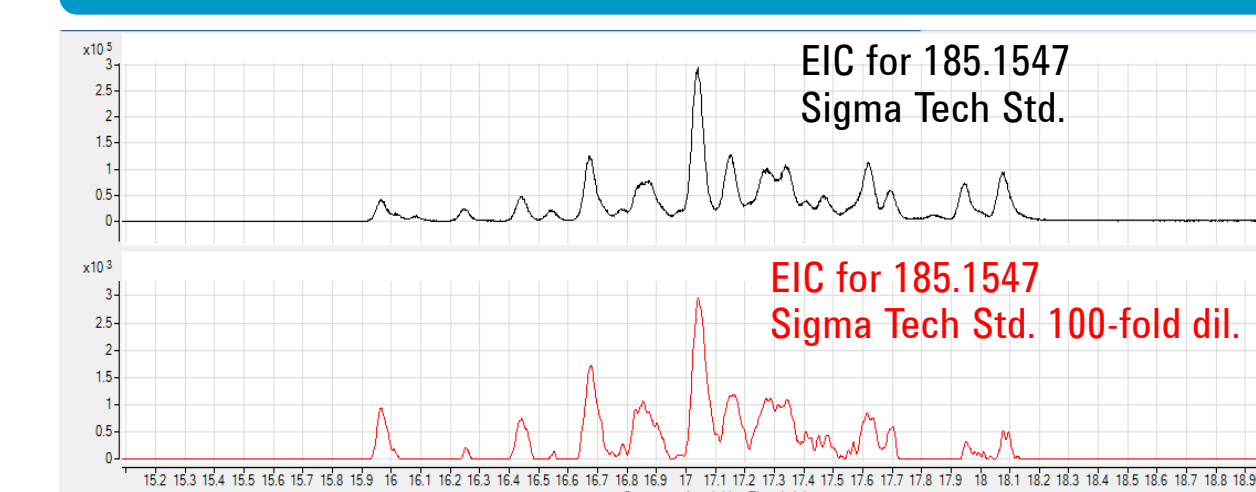


Figure 6. The pure Sigma Technical standard derivatized sample was diluted 100x in ethyl acetate, to produce the extracted ion chromatogram for the m/z 185.1547 isomer groups, to observe the detection limits.

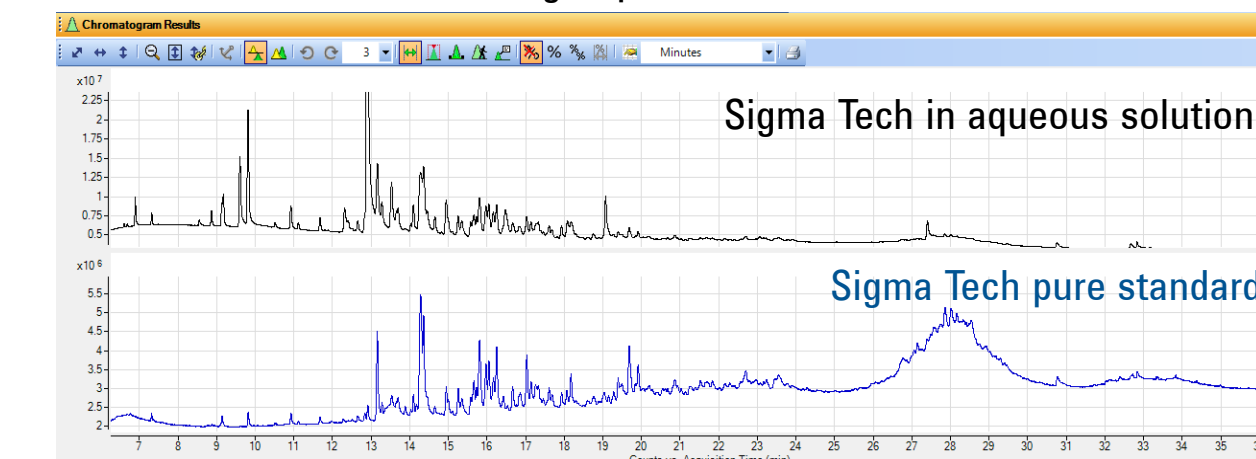


Figure 7. Top chromatogram was produced from the sigma technical standard provided to Agilent in a 0.05M NaOH solution, while the bottom is the pure sigma technical standard (not concentrated after derivatization). The two chromatograms are similar to show the derivatization is not hindered by an aqueous solution.

Table 2. A fraction of the elemental compositions calculated, in MassHunter, from deconvoluted compounds including the score and mDa error.

RT	Formula	Score	Mass	Mass (MFG)	Diff (MFG, mDa)	Area
30.768	C16 H31 O2	96.38	255.2347	255.2324	-2.28	3871627
32.829	C18 H35 O2	95.78	283.2665	283.2637	-2.81	1592032
13.524	C8 H16 O2	93.27	144.1142	144.115	0.78	5262718
8.869	C21 H6 O2 S	89.44	322.0096	322.0089	-0.72	3911148
9.178	C18 H8 O3 S	89.15	304.0169	304.0194	2.55	7784007
14.264	C9 H18 O2	88.93	158.1314	158.1307	-0.73	12030779
19.825	C11 H19 O2	85.79	183.14	183.1385	-1.48	231210
17.61	C11 H19 O2	85.72	183.14	183.1385	-1.5	3420229
20.69	C11 H19 O2	85.67	183.14	183.1385	-1.48	791530
16.764	C11 H19 O2	85.57	183.14	183.1385	-1.48	107855
16.249	C10 H20 O2	85.12	172.1462	172.1463	1.13	11063154
14.095	C9 H18 O2	85.01	158.1316	158.1307	-0.95	10820099
21.628	C14 H21 O	84.98	205.1606	205.1592	-1.39	207309
17.246	C11 H19 O2	84.86	183.14	183.1385	-1.47	955306
18.893	C11 H19 O2	84.74	183.14	183.1385	-1.46	245642
14.942	C9 H18 O2	84.55	158.1316	158.1307	-0.92	19064967
20.618	C13 H25 O3	84.5	229.182	229.1804	-1.59	658418
32.695	C17 H21 O2	84.45	257.1557	257.1542	-1.54	1373230
26.022	C14 H15 F4 O3	83.89	307.0968	307.0957	-1.1	25637
31.911	C17 H23 O2	81.83	259.1714	259.1698	-1.58	192731
33.782	C20 H27 O2	81.44	299.2039	299.2011	-2.8	62518
21.178	C11 H19 O2	81.02	183.1399	183.1385	-1.43	136082

Conclusions

- The sample preparation of extractive alkylation with a perfluoro-bromo derivative provided a quick, simple, one-pot reaction for the analysis of naphthenic acid extracts. This reduces the signal from the non-carboxylic acid analytes within the sample.
- Argon ECNI produced spectra that represented the intact naphthenic acid with the loss of the PFBBR group. This simplified the identification to the original analyte.
- Argon is a clean reagent gas, to allow for continuous analysis without deposit build-up found with other reagents.
- Figure 2 illustrates the decrease in complexity when analyzing the naphthenic acid samples with argon ECNI when compared to the EI full scan data.
- The Kendrick mass defect plot provides a visual representation of the different NA groups when using the mass defect in the nominal mass of CH₂ versus the exact mass (figure 4).
- A 100-fold dilution of the Sigma Tech standard exhibits a proof of concept limit of detection.

Future Work

- The 20m DB-XLB provided adequate separation, but a different phase or longer column will be ran in the future to increase the separation of the isomers.
- Optimizing the ion source to keep the derivatized molecule intact during the ionization process.
- Analyze some of the analytes by MS/MS to increase the confidence in the element and structural assignment.
- Pure standards of individual naphthenic acids will be derivative to provide a clear method detection limit.