Analysis of Bakken Oil Samples

conducted by
Iowa State University
Chemical Instrumentation Facility
July-August 2016

A local landowner obtained a small volume of oil from an employee at an undisclosed well near New Town, North Dakota.

The Bakken oil samples were then sent for analysis at Iowa State University's Chemical Instrumentation Facility.

Tests were performed using a high-resolution gas chromatograph mass spectrometer, and mass defect filters, to determine whether the Bakken oil samples contained cancer-causing compounds like benzene, toluene and ethyl benzene, or aromatic and poly-aromatic hydrocarbons (PAH's).

The tests came back positive for benzene, toluene, ethyl benzene and several other VOC's ("volatile organic compounds") that are known to cause cancer and other serious negative health impacts, including heart, liver, kidney and lung damage.

Any spill on the proposed Dakota Access "Bakken" pipeline into the environment and ground water would release these cancer-causing and otherwise toxic compounds as well.
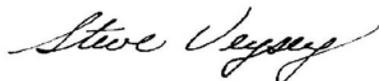
Bottom line: It's nearly impossible to remediate these "volatile organic compounds" like benzene and toulene once they are in the ground water, and it's an expensive and time-consuming process to bring levels to within acceptable thresholds.

Full results of the Bakken oil sample analysis are attached.

1234 Hach Hall
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**Chemical
Instrumentation
Facility**

Memo

To: Tim Hooper

From: Steve Veysey

Steve Veysey

CC: files

Date: 8/23/2016

Re: Crude Oil Analysis

SCOPE

On July 29, 2016, at 2:30 PM I received two samples of "crude oil" from Mr. Tim Hooper. These samples were presented to me in 1L plastic bottles, labeled "1" and "2". I transferred duplicate aliquots of each into glass 10 ml vials with caps. These vials were labeled "1", "1A", "2", and "2A". The vials were then stored in a secure refrigerator in 1238 Hach Hall.

We discussed characterizing whether the samples were authentic Bakken crude. I explained that to do that a certified reference sample would be needed so that GCMS and IR data could be obtained on "reference" and "unknown" samples for comparison.

We discussed characterizing the nature of the unknown samples. I suggested FTIR using ATR sampling as a cost-effective means of obtaining a gross characterization of the samples. I also suggested a basic GCMS analysis as a means of obtaining partial characterization of the components of the mixture. The major chromatographic peaks would be tentatively identified using the mass spec library "search match" program and the mass spec elemental composition program. The data would be available should you also request that we search for specific compound(s). The only specific compound discussed today was benzene.

On August 9, 2016, at 10:30 AM I received two additional samples of "crude oil" from Mr. Tim Hooper. These samples were presented to me in 1L plastic bottles, labeled "1" and "2". It was stated that these were the same bottles presented on July 29. It was stated that these bottles each contained the same oil, taken sequentially from a common source. The bottles were 75% full. I transferred 20 aliquots of each into glass 1.5 ml vials with caps. These vials were each labeled "1" or "2". The vials were then stored in a secure (locked) refrigerator in 1238 Hach Hall.

A quantitative analyses of these samples was requested for benzene, toluene and ethyl benzene. A characterization of the oil was also requested with respect to other compounds in the mixture less saturated than alkenes or alkynes, specifically aromatic and poly-aromatic hydrocarbons (PAH's). This characterization was to be done using chromatograms acquired from the samples received on July 29 or on the samples received August 9. We discussed the use of Chemical Abstract Service (CAS) numbers to provide direction when requesting searches for specific compounds, and we discussed the use of "mass defect filters" to search generally for less saturated and/or aromatic compounds in the mixture.

ANALYSES and RESULTS

FTIR Measurements - July 29.

Aliquots of samples 1A and 2A were transferred with disposable glass pipettes into a Horizontal Attenuated Total Reflectance (HATR) boat assembly; the surface of the germanium crystal was completely covered with material. Infrared spectral data was acquired in the spectral range from 4000 – 850 wavenumbers (cm^{-1}). The instrument used was a Tensor 37 FTIR (Bruker Instruments, Billerica, MA). Data was acquired at 2 cm^{-1} resolution; 16 scans were co-added for the reference (empty boat assembly) and sample single-beam curves. The y-axis was scaled in "ATR Units" (similar to absorbance units).

Both spectra showed features consistent with hydrocarbon molecules. The infrared spectra of the two samples were extremely similar; I was unable to discern differences. The spectrum of 2A was searched against the NIST Vapor Phase Infrared Spectra Library which contains ~3500 entries. The top two matches were with OCTANE and N-DECANE. It should be noted that all n-alkanes of the formula C_nH_{n+2}, regardless of the value of "n", have similar infrared spectra. For example, the match with "Vaseline", petroleum jelly composed of alkanes with n>25, was also good.

GCMS Measurements - August 1

Four GCMS analyses were performed, three on sample 1A and one on sample 2A. All analyses were performed using a Waters GCT high-resolution gas chromatograph mass spectrometer system (GCMS). The gas chromatograph potion of the instrument is an Agilent 6890 GC. MassLynx software was used to acquire and process the data. Neat samples were injected (0.5 to 1 uL) at a split ratio of 100:1. The injector temperature was 280 ^{o}C; the GC oven was programmed from 40 ^{o}C to 310 ^{o}C. The column used for all analyses was an Agilent J&W DB-5MS column (p/n 122-5532) with dimensions 30 meters x 0.25 mm i.d. x 0.25 micron film thickness. Carrier gas was UHP grade helium. The mass spectrometer was scanned over the mass range 35-650 Daltons, at a speed of 0.5 seconds per scan, with a resolution of ~6000 (FWHM). All of the data was acquired with accurate-mass precision (+/- 0.001 Daltons, typical), and one run was acquired with accurate-mass accuracy (data acquired in the presence of an internal lock-mass compound). Complete typical GC and MS configuration details are included in the accompanying instrument log file, Appendix A.

1. A preliminary run of a neat sample taken from vial 1A was obtained by programming at 15 degrees per minute. This data was used to help establish reasonable injection parameters for these samples, including injection volume, GC split ratio, et cetera. The goal was to inject a small enough sample so that the mass spectrometer detector would not saturate. That is difficult with neat samples, but injection parameters and mass spectrometer parameters were adjusted so that most of the hundreds of GC peaks in the mixture were not saturating, or only slightly saturating, the detector.

2. A slow run under "accurate mass conditions" (programming at 2.5 degrees per minute) was performed for the sample taken from vial #1A. The lock-mass compound used was 2,4,6-*Tris*(*difluoromethyl*)-*1,3,5-triazine*. Data from this run was used to assist in evaluating library search-match results obtained in runs 3 and 4.

3. A slow run under "precise mass conditions" of the same sample taken from vial #1A was performed. This data is more suitable for library "search-match", and can be used in conjunction with the accurate mass data to help suggest compound identifications.

4. A slow run under "precise mass conditions" of a sample taken from vial #2A was performed.

The data was processed with the intent of generally characterizing the two samples, and suggesting identifications for the 20-30 largest peaks in the mixture. The only targeted compound search initially performed was for benzene, however I considered the data acquired to be suitable for later targeted compound searching should that be requested. The chromatograms for samples 1A and 2A were essentially the same when adjusted for the injection amount variability. See Figure 1. Expansions of the chromatogram for sample 2A are shown in Figure 2a thru 2f.
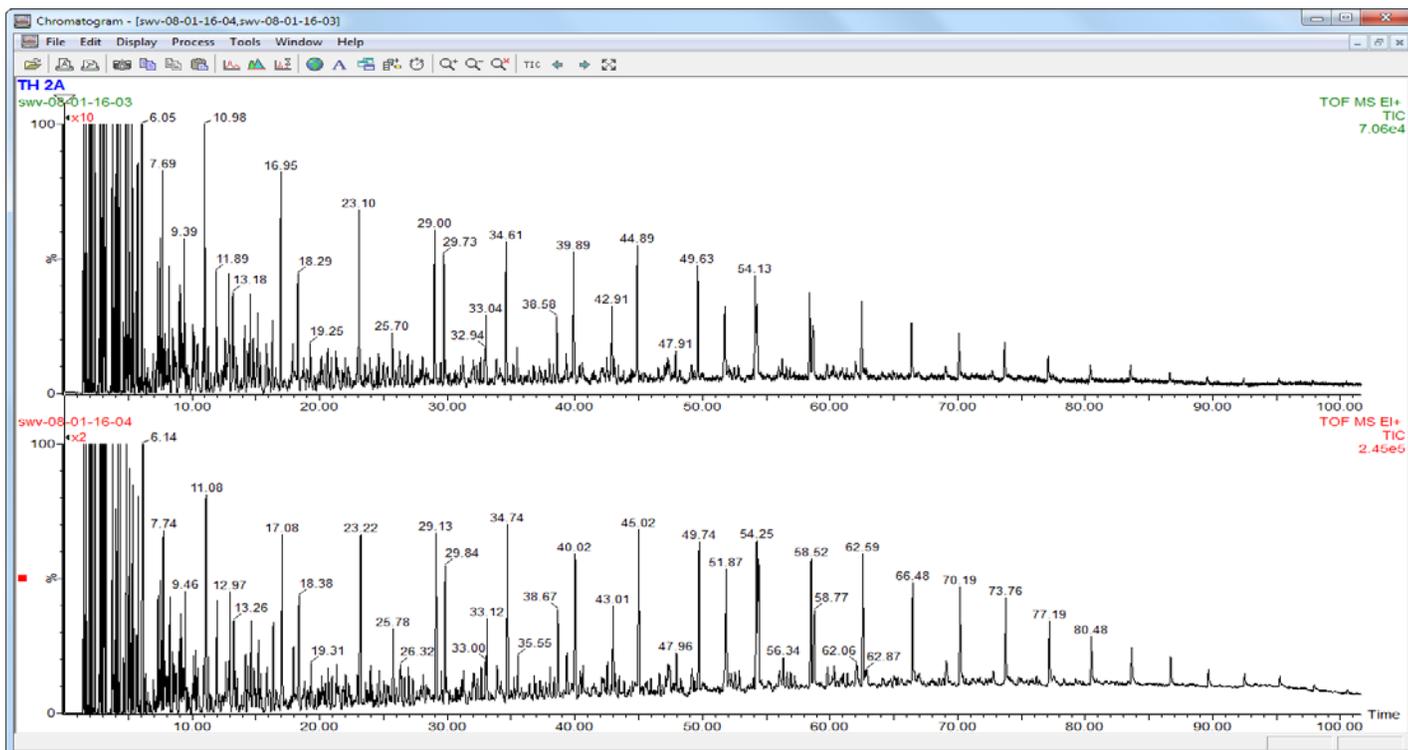
Figure 1 – Chromatographic comparison of sample 1A and 2A. Runs swv-08-01-16-03 and swv-08-01-16-04
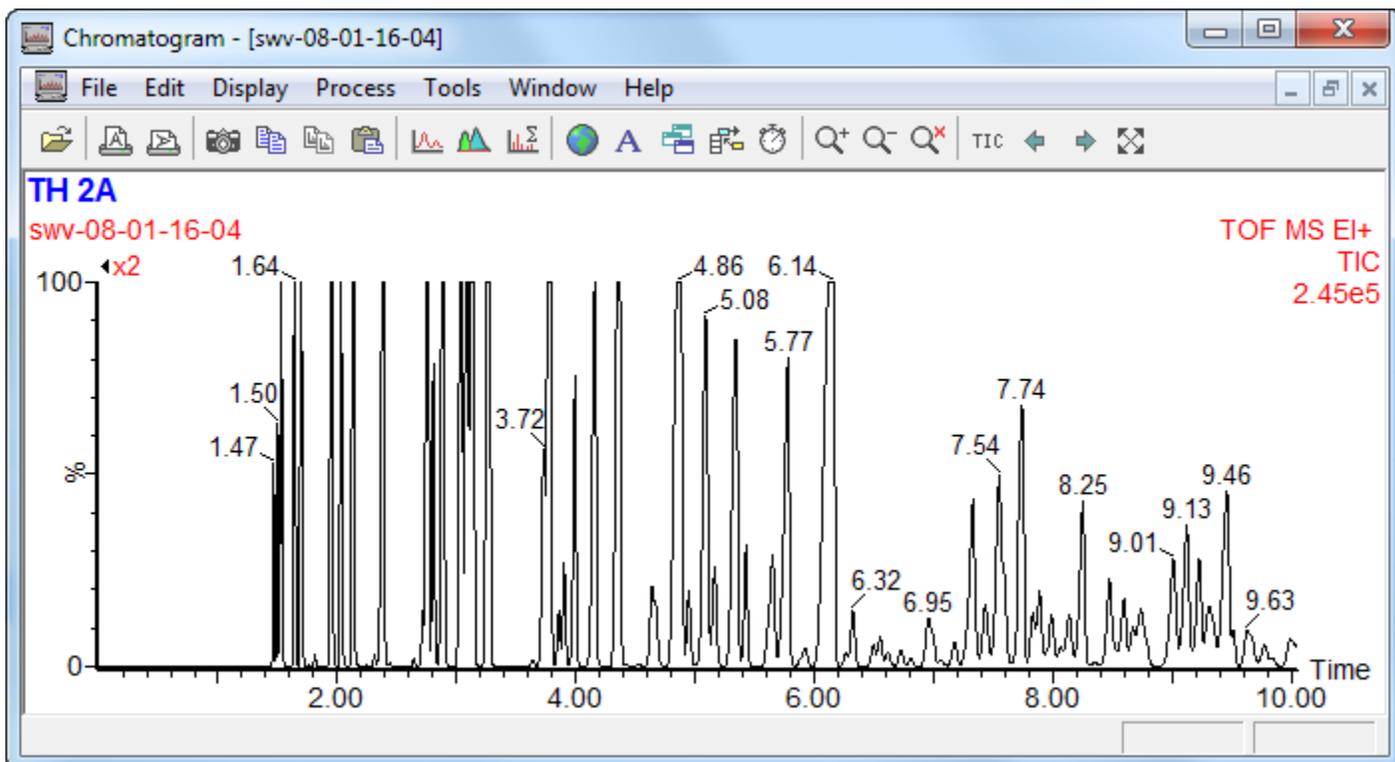

Figure 2a – Chromatographic expansion of sample 2A; 0 – 10 minutes.. Run swv-08-01-16-04
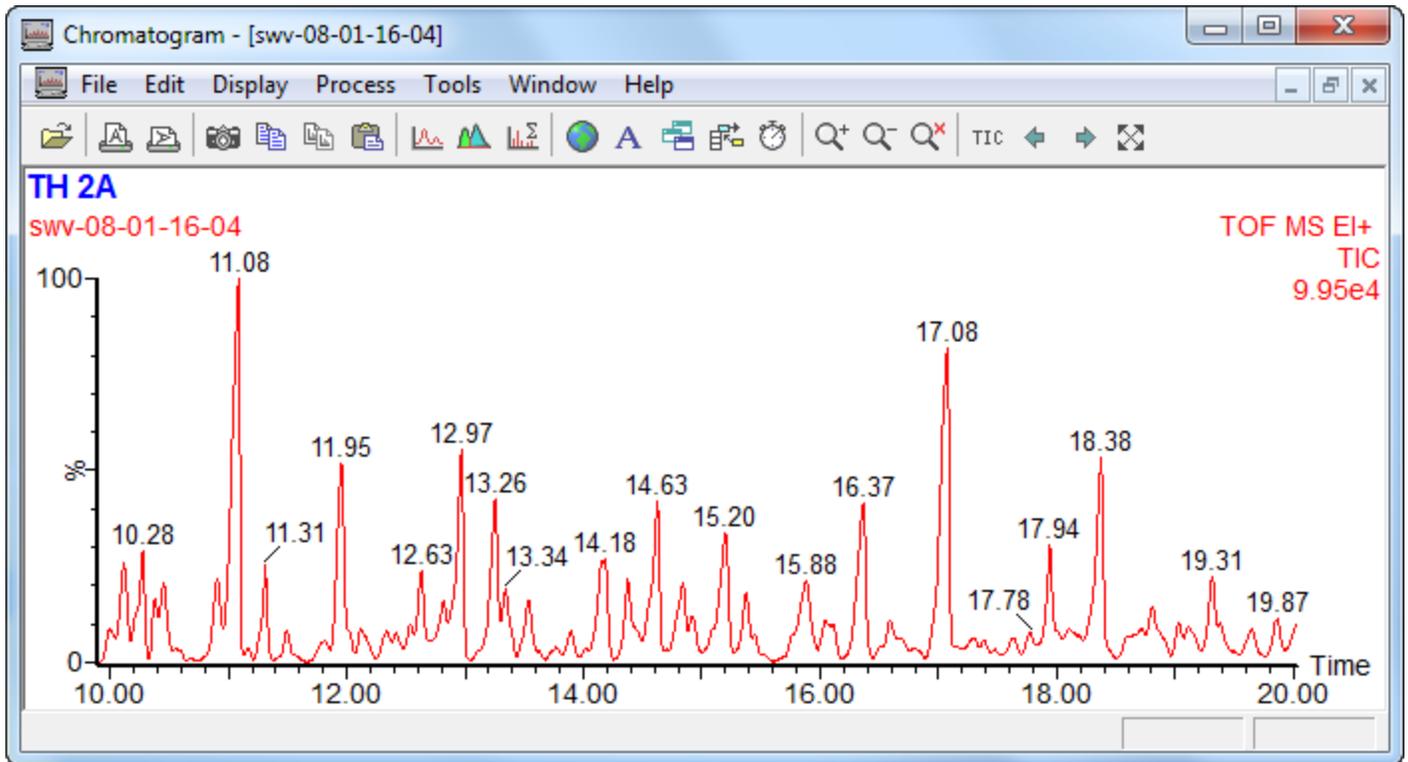
● Page 3

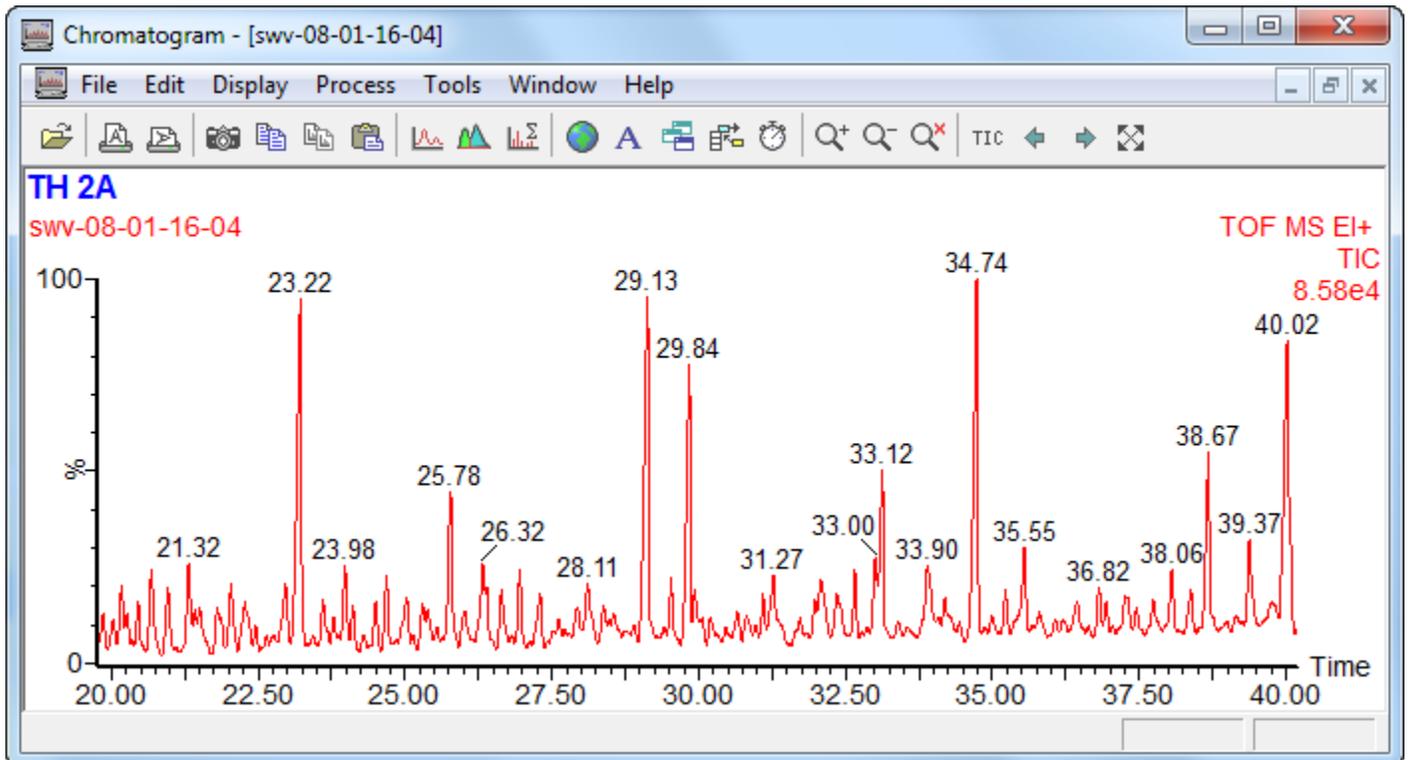*Figure 2b – Chromatographic expansion of sample 2A; 10 – 20 minutes.. Run swv-08-01-16-04*

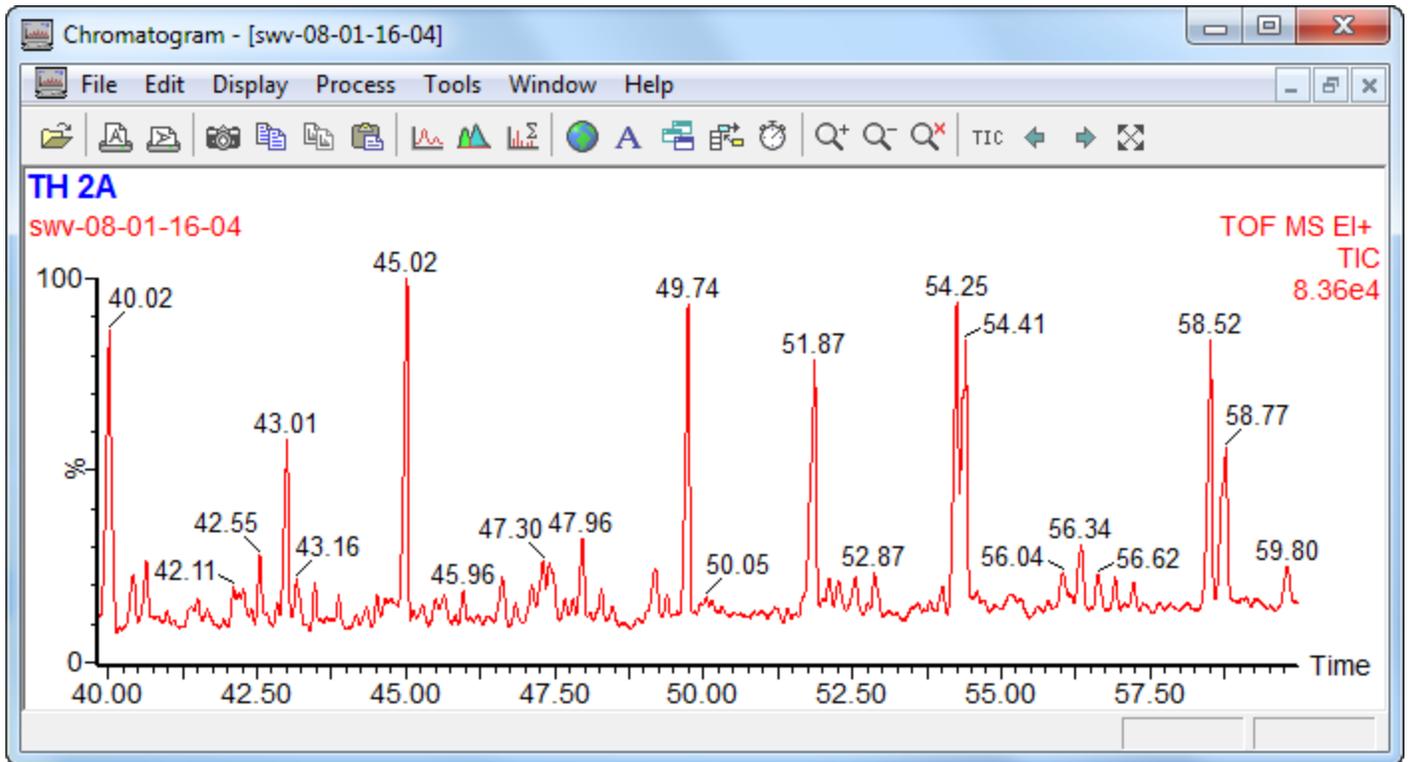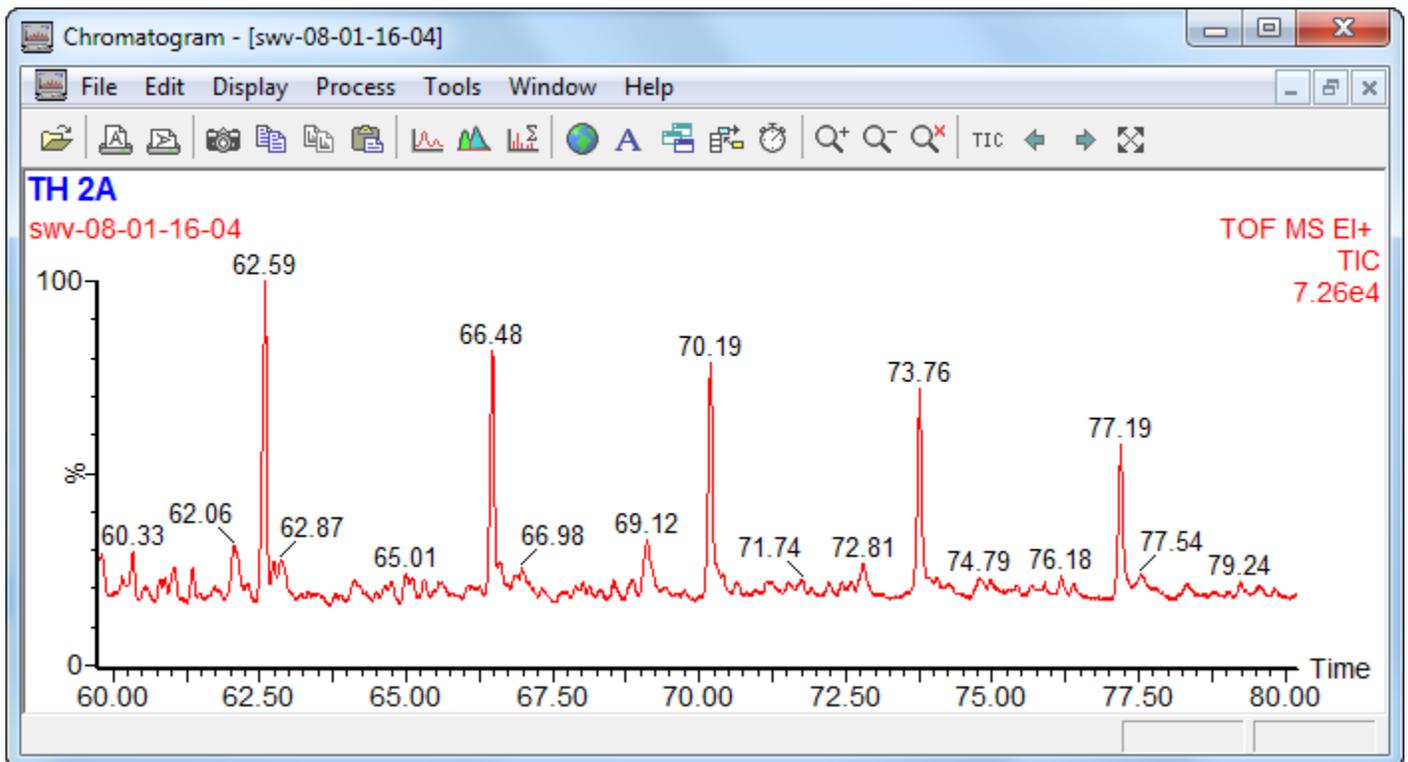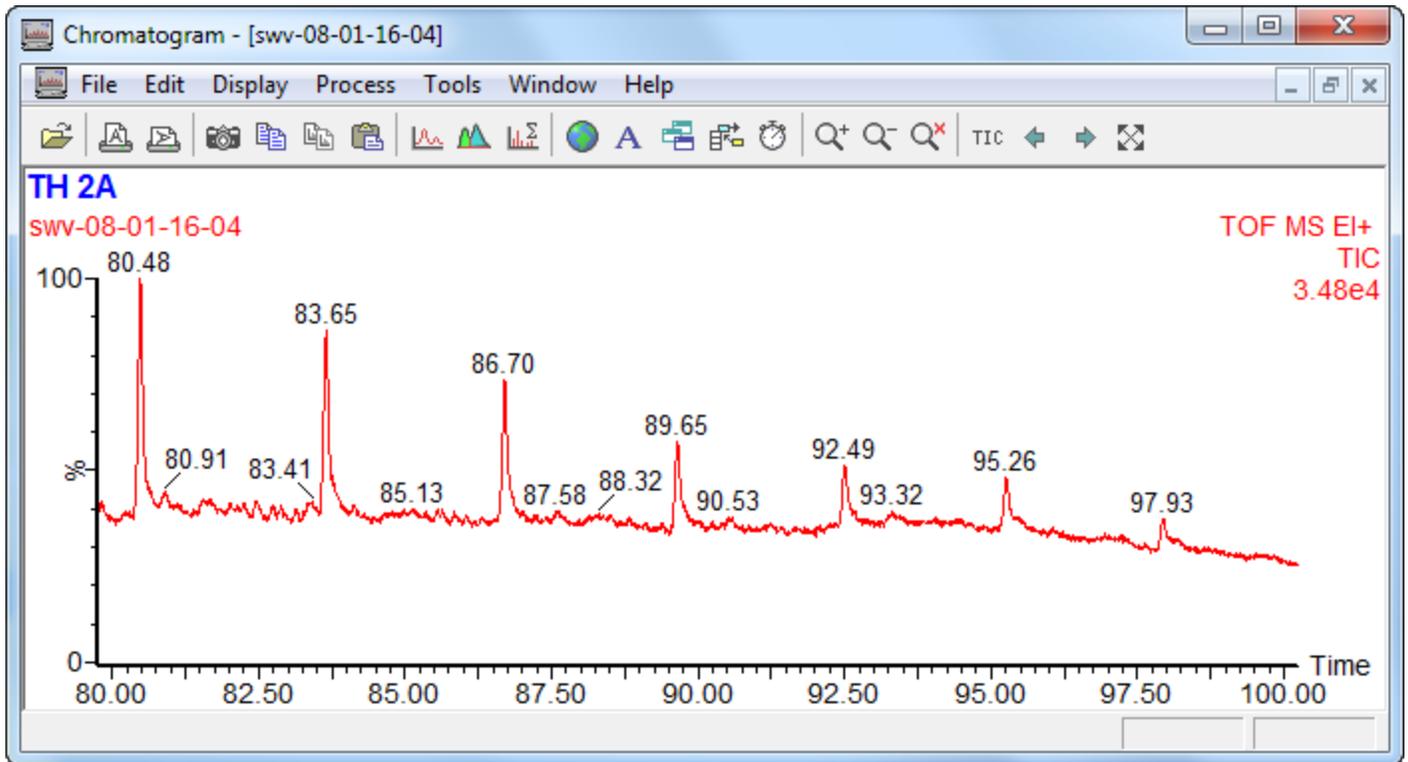*Figure 2c – Chromatographic expansion of sample 2A; 20 – 30 minutes.. Run swv-08-01-16-04*

Figure 2d – Chromatographic expansion of sample 2A; 40 – 60 minutes.. Run swv-08-01-16-04

Figure 2e – Chromatographic expansion of sample 2A; 60 – 80 minutes.. Run swv-08-01-16-04

Figure 2f – Chromatographic expansion of sample 2A; 80 – 100 minutes.. Run swv-08-01-16-04

Spectra and library match results for approximately thirty of the largest peaks were provided shortly after these initial runs were performed.

As seen in the chromatograms, this sample is an extremely complex mixture. Upon inspection, many of the chromatographic peaks shown above consist of overlapping, unresolved peaks. A reasonable estimate of the number of compounds in this sample would be >500.

The quantitative analysis for three compounds present in the oil was conducted on August 16 and August 17. Standards were reagent grade obtained from Fisher Scientific and from Sigma Aldrich. The internal standard chosen was fully deuterated benzene (D6 benzene). Dilution was in diethyl ether. The purity of all of the standards was verified by GCMS. See Figure 3.
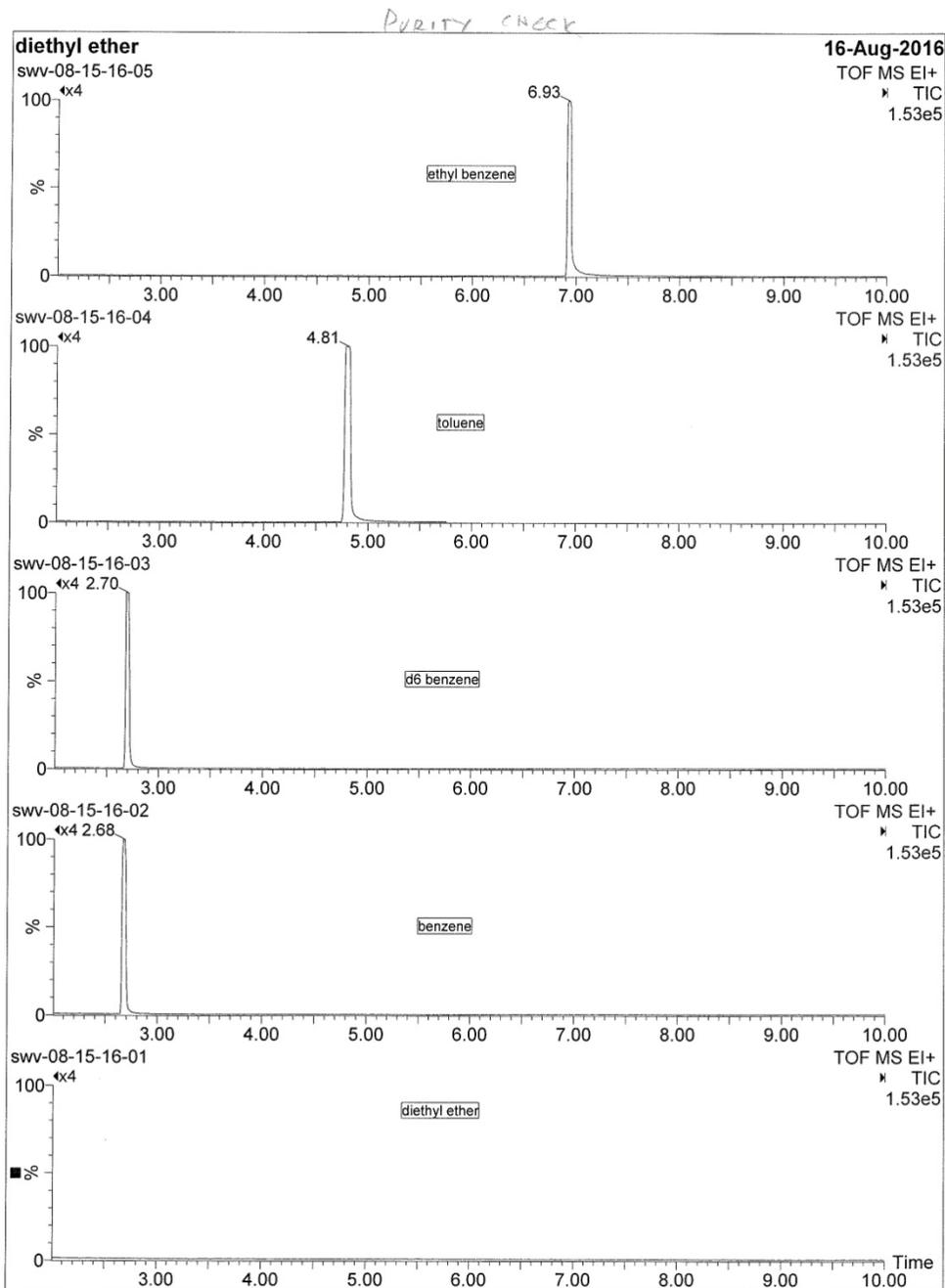

Figure 3 Testing purity of the quantitation standards and diethyl ether solvent.

The spectra of the standards were evaluated to determine appropriate quantitation ion(s). Since benzene and D6 benzene partially co-elute, the spectra were examined to ensure suitable quantitation ions. See Figures 4-5
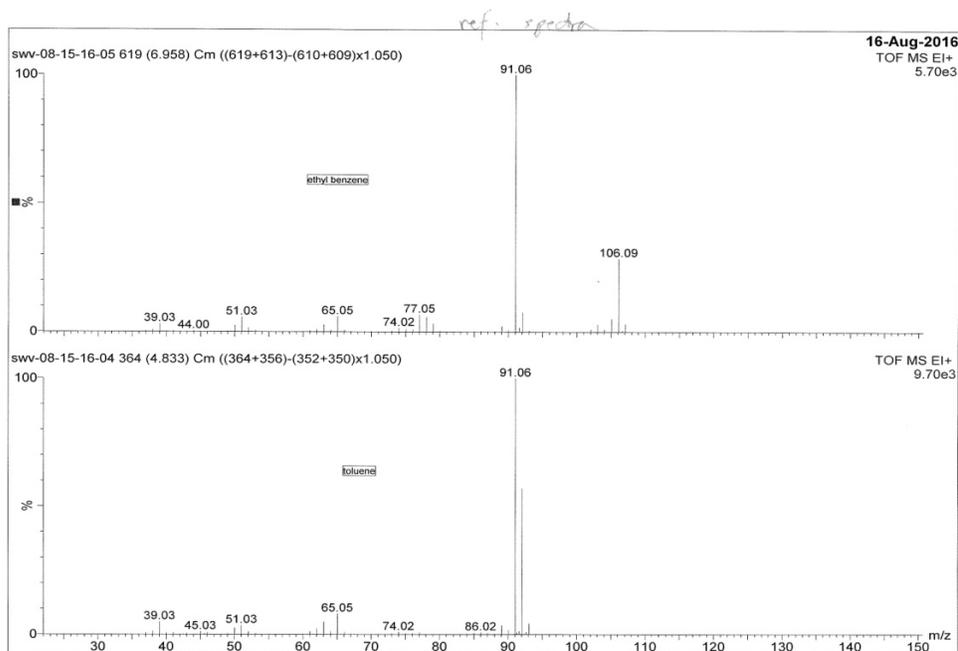
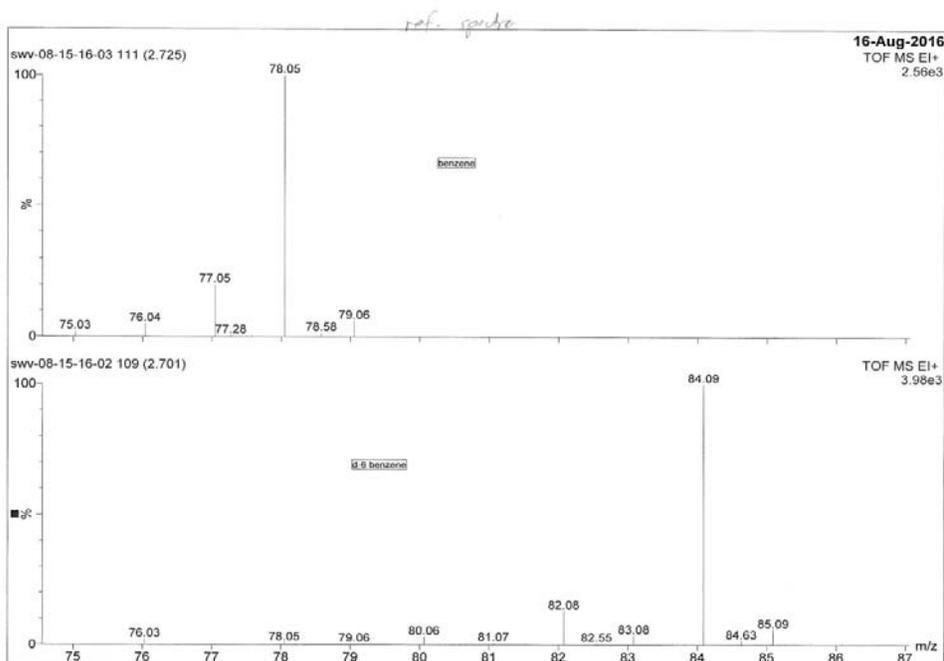Figure 4 Spectra of ethyl benzene and toluene standards

Figure 5   Spectra of benzene and D6-benzene standards

The quantitation ions chosen were:

- Benzene   m/z 78.043 +/- 0.05   R.T. = 2.70 min
- D6 benzene   m/z 84.08 +/- 0.05   R.T. = 2.67 min
- Toluene   m/z 92.061 +/- 0.05   R.T. = 4.80 min
- Ethyl benzene   m/z 106.078 +/- 0.05   R.T. = 7.67 min

The response factors used were the average of four runs. Relative response factors were then calculated with respect to the internal standard, D6-benzene. A typical response factor chromatogram is shown in Figure 6.
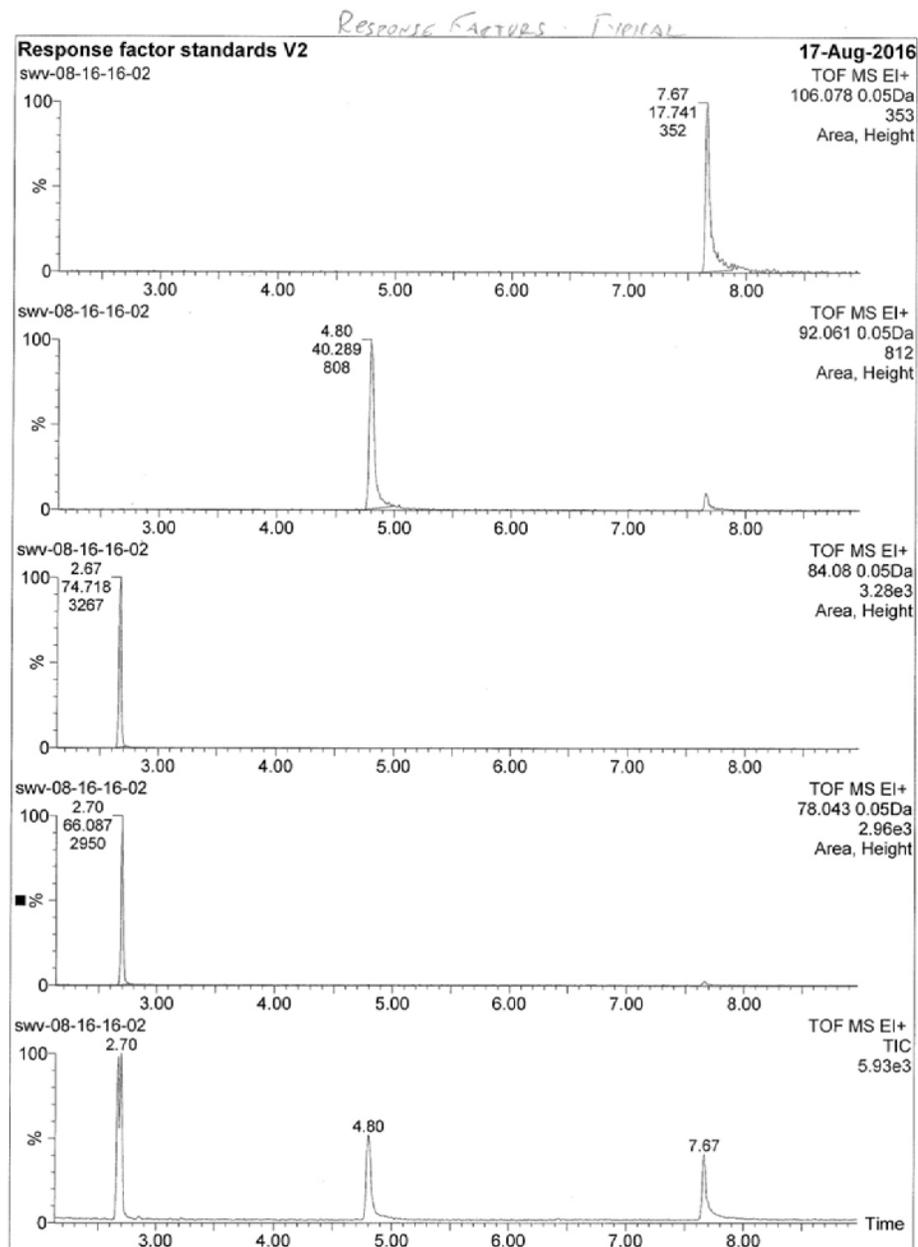

Figure 6 Typical response factor chromatogram (four replicates were performed)

Table 1   Response Factor and R R F Calculations

swv-18-16-16-01

Compound - quant mass	RT (min)	Pk Ht	Pk Area	Area Ratio	Resp. Fac.	Rel. Resp. Fac
Benzene - 78.04	2.699	3334	72.92	0.881	0.834	0.958
D6 benzene - 84.08	2.666	3638	82.74	1.000	0.871	1.000
Toluene - 92.06	4.808	803	40.26	0.487	0.465	0.534
Ethyl benzene - 106.08	7.658	375	20.62	0.249	0.238	0.273

swv-18-16-16-02

Compound	RT (min)	Pk Ht	Pk Area	Area Ratio	Resp. Fac.	Rel. Resp. Fac
Benzene - 78.04	2.699	2950	66.09	0.884	0.756	0.961
D6 benzene - 84.08	2.674	3267	74.72	1.000	0.787	1.000
Toluene - 92.06	4.799	808	40.29	0.539	0.466	0.592
Ethyl benzene - 106.08	7.667	352	17.74	0.237	0.205	0.260

swv-18-16-16-03

Compound	RT (min)	Pk Ht	Pk Area	Area Ratio	Resp. Fac.	Rel. Resp. Fac
Benzene - 78.04	2.700	3259	73.98	0.880	0.846	0.957
D6 benzene - 84.08	2.675	3481	84.07	1.000	0.885	1.000
Toluene - 92.06	4.800	908	40.56	0.482	0.469	0.530
Ethyl benzene - 106.08	7.667	375	20.79	0.247	0.240	0.271

swv-18-16-16-04

Compound	RT (min)	Pk Ht	Pk Area	Area Ratio	Resp. Fac.	Rel. Resp. Fac
Benzene - 78.04	2.700	2819	65.46	0.885	0.749	0.962
D6 benzene - 84.08	2.667	3087	73.97	1.000	0.779	1.000
Toluene - 92.06	4.800	876	41.28	0.558	0.477	0.613
Ethyl benzene - 106.08	7.659	366	18.67	0.252	0.215	0.277

	Density	Amt (ul)	Mass (mg)	Vol (mL)	Conc (ug/mL)
Benzene	0.874	10.0	8.74	100.0	87.400
D6 benzene	0.950	10.0	9.50	100.0	95.000
Toluene	0.865	10.0	8.65	100.0	86.500
Ethyl benzene	0.867	10.0	8.67	100.0	86.700

	RRf (avg)	RRf (stdev)
Benzene	0.959	0.003
D6 benzene	1.000	0.000
Toluene	0.567	0.042
Ethyl benzene	0.270	0.007

Response factors (Rf)are in units of area/weight per unit volume

Two vials of crude oil #1 obtained on August 9 were weighed into a volumetric flask and diluted with diethyl ether. A D6-benzene standard was prepared in diethyl ether and an aliquot was added to the crude oil volumetric. This solution was analyzed in duplicate. A fresh solution using two vials of crude oil #2 was prepared. A new D6-benzene standard was prepared and added to the crude oil volumetric. This solution was then analyzed in duplicate. Typical chromatographic results are shown in Figure 7. Note the presence of additional C2-alkyl-benzenes.
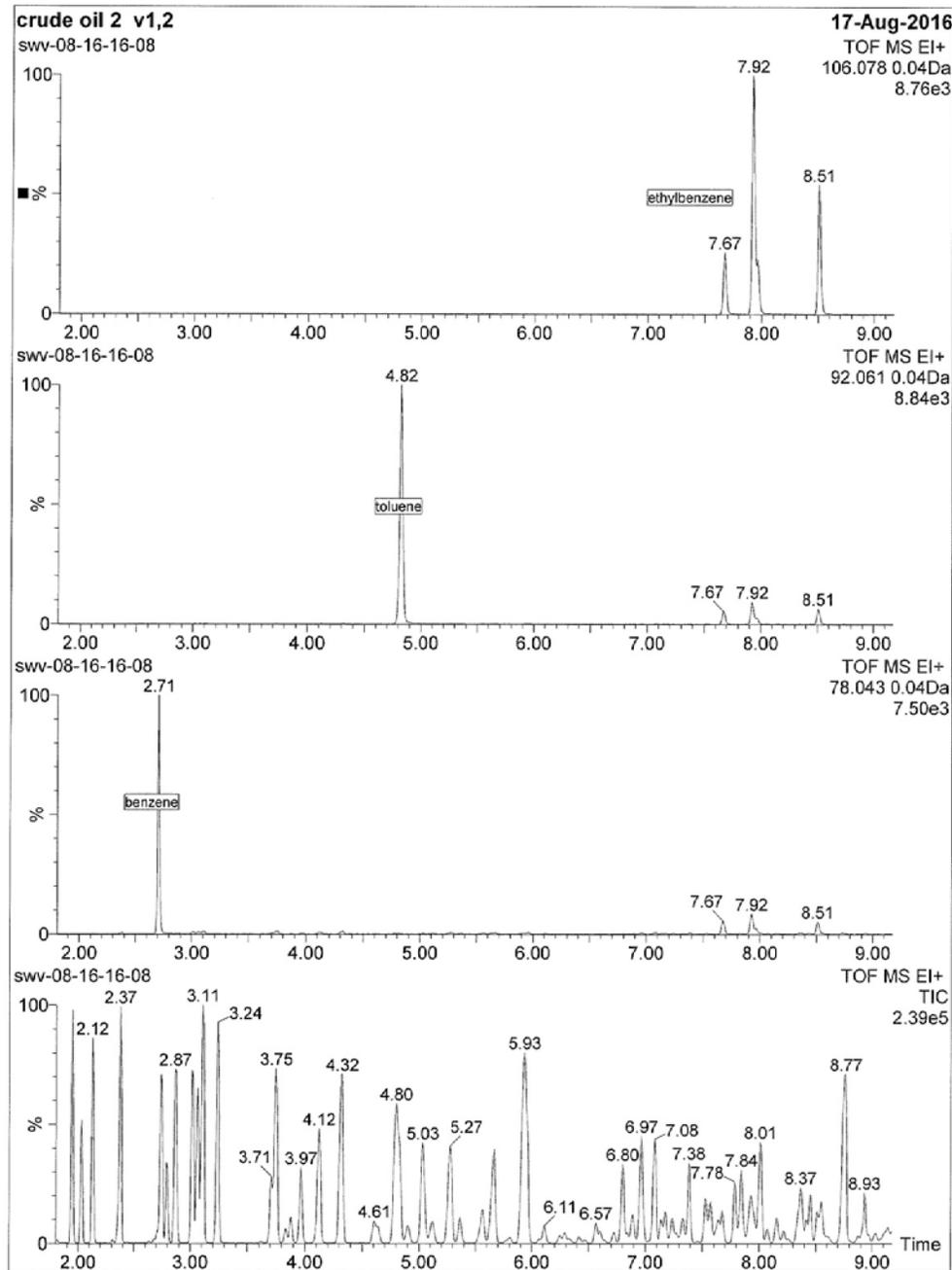
Figure 7. Quantitation chromatographic results, typical (four replicates were performed)

Table 2 Quantitation Calculations

Crude oil #1, vials 2&3, first d6-benzene std

swv-08-16-16-05

	m/z	RT (min)	Pk Ht	Pk Area	Area Ratio	Wt (ppm)	Wt (%)
benzene	78.044	2.700	3149	66.9	2.58	406	0.0406
d6 benzene	84.084	2.675	1225	25.9	1.00		
toluene	92.059	4.809	3874	132.2	5.10	1357	0.1357
ethyl benzene	106.078	7.668	979	31.3	1.21	674	0.0674

swv-08-16-16-06

	m/z	RT (min)	Pk Ht	Pk Area	Area Ratio	Wt (ppm)	Wt (%)
benzene	78.044	2.708	6059	124.6	2.59	408	0.0408
d6 benzene	84.084	2.674	2017	48.1	1.00		
toluene	92.059	4.825	7215	237.7	4.94	1315	0.1315
ethyl benzene	106.078	7.675	1827	54.5	1.13	633	0.0633

Crude oil #2, vials 1&2, new d6-benzene std

swv-08-16-16-07

	m/z	RT (min)	Pk Ht	Pk Area	Area Ratio	Wt (ppm)	Wt (%)
benzene	78.044	2.700	6996	148.5	2.88	454	0.0454
d6 benzene	84.084	2.674	2516	51.5	1.00		
toluene	92.059	4.817	9018	280.9	5.46	1453	0.1453
ethyl benzene	106.078	7.675	2149	68.4	1.33	743	0.0743

swv-08-16-16-08

	m/z	RT (min)	Pk Ht	Pk Area	Area Ratio	Wt (ppm)	Wt (%)
benzene	78.044	2.707	7495	150.1	2.97	467	0.0467
d6 benzene	84.085	2.682	2299	50.6	1.00		
toluene	92.059	4.824	8830	276.5	5.47	1456	0.1456
ethyl benzene	106.079	7.675	2248	67.8	1.34	750	0.0750

NOTE: d6-benzene internal standard added: 151 ppm by weight

	RRf (avg)
Benzene	0.959
D6 benzene	1.000
Toluene	0.567
Ethyl benzene	0.270

Quantification Results (average of four runs)

	Wt (ppm)	Stdev	Wt (%)	Stdev
Benzene	434	32	**0.043**	0.003
Toluene	1395	71	**0.140**	0.007
Ethyl benzene	700	56	**0.070**	0.006

Data Analysis to Identify Unsaturated Compounds – August 19 and 21

Data file _swv-08-01-16-04_ acquired on August 1 was re-examined to determine the presence of unsaturated compounds where rings+double bonds is four or greater. Because the data was acquired with accurate mass precision, two approacheds were used to find unsaturated compounds. First, alkyl-benzenes were located by searching for the predicted or observed masses of the molecular ions. RDB=4 for this class of compounds. Results are summarrized in Table 3 below, and shown in Figures 8 and 9.

TABLE 3 Presence of Alkyl-Benzenes

Sum of sat. alkyl groups	Formula	Mol.Wt Target Ion	Notes	# of compounds
C=0	C6H6	78..043	benzene	1
C=1	C7H8	92.061	toluene	1
C=2	C8H10	106.076	Figure 8	4
C=3	C9H12	120.091	Figure 8	8
C=4	C10H14	134.111	Figure 8	~17
C=5	C11H16	148.127	Figure 8	~29
C=6	C12H18	162.143	Figure 9	~26
C=7	C13H20	176.157	Figure 9	~39
C=8	C14H22	190.174	Figure 9	~30
C=9	C15H24	204.188	Figure 9	~13

Note: Quantitation was only performed for benzene, toluene, and ethyl-benzene. Approximate amounts of the other alkyl benzenes with respect to ethyl benzene could be determined from the areas of the single-ion chromatograms, but this would only be a rough approximation.

Note: The presence of unsaturated alkyl-benzenes where RDB=5 was also observed. A systematic approach to find these compounds using accurate target ions for RDB=5 and RDB=6 could be performed with this data.
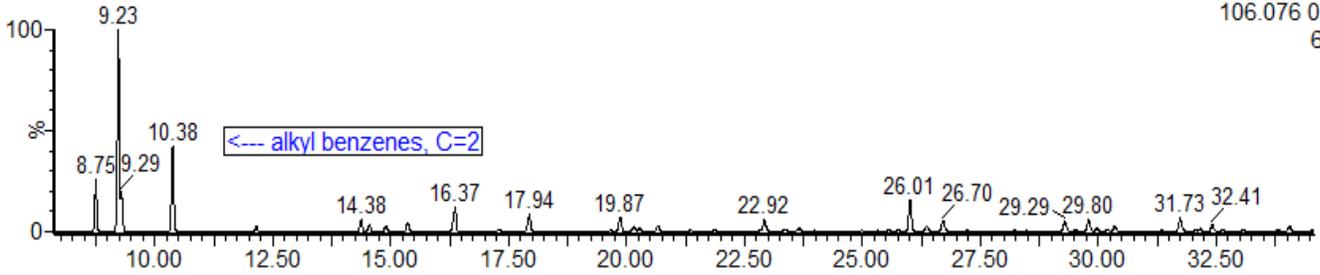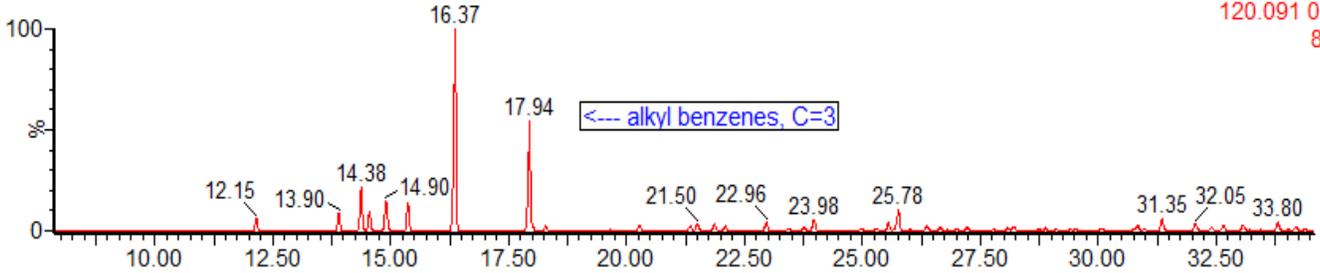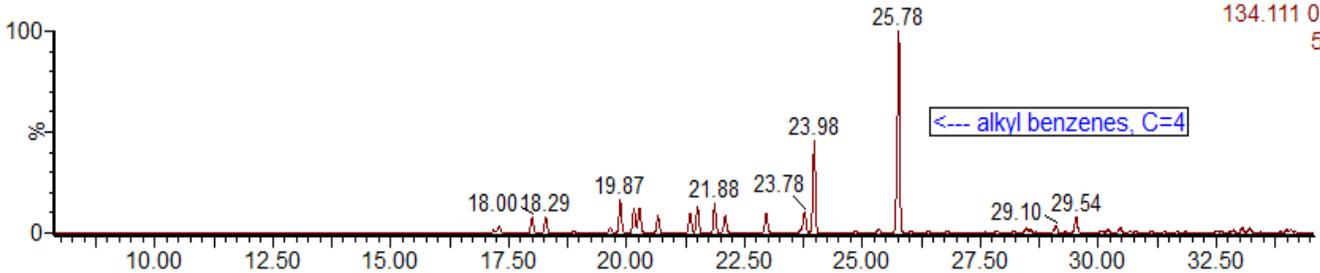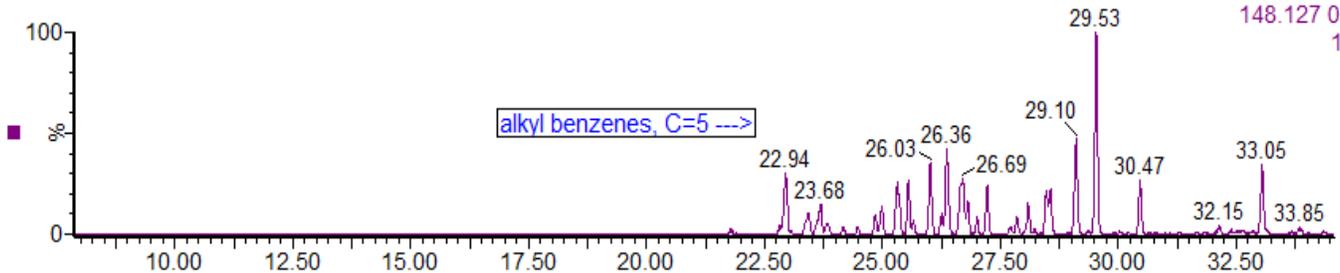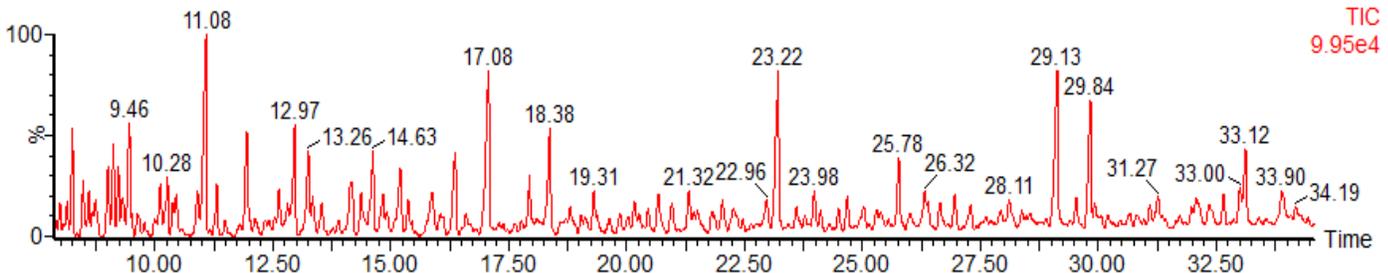
Figure 8 Alkyl benzene profiles, C=2,3,4,5

TH 2A
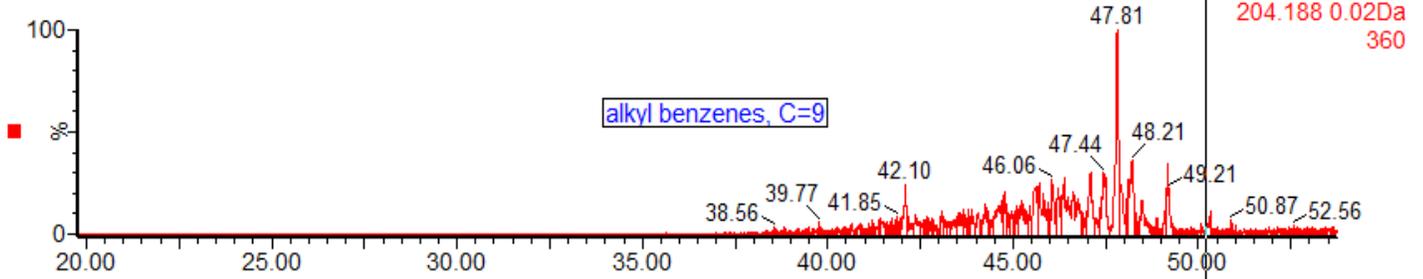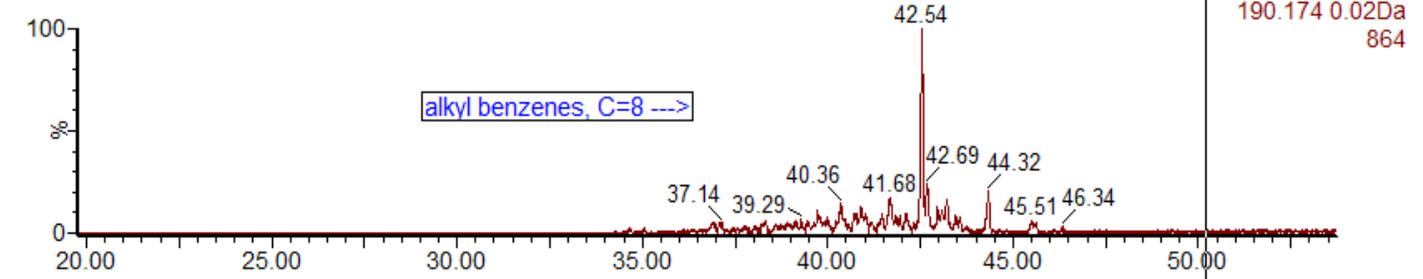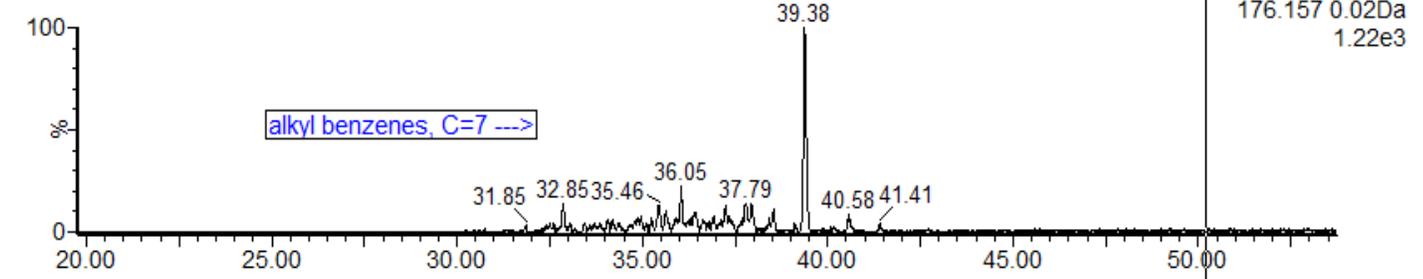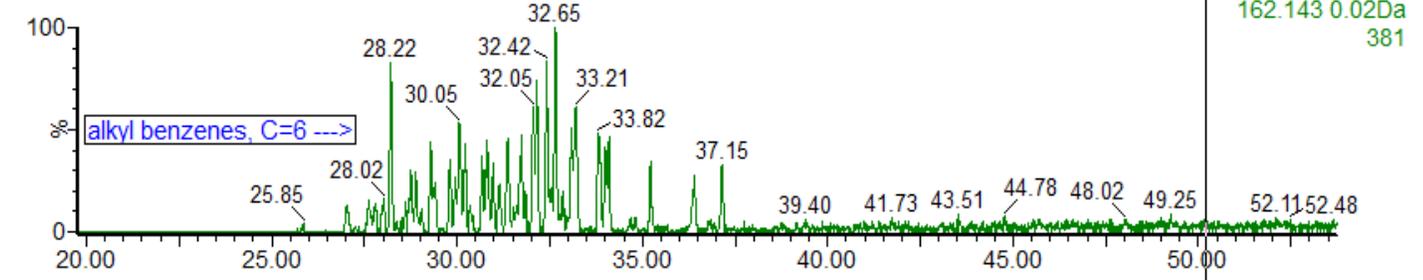
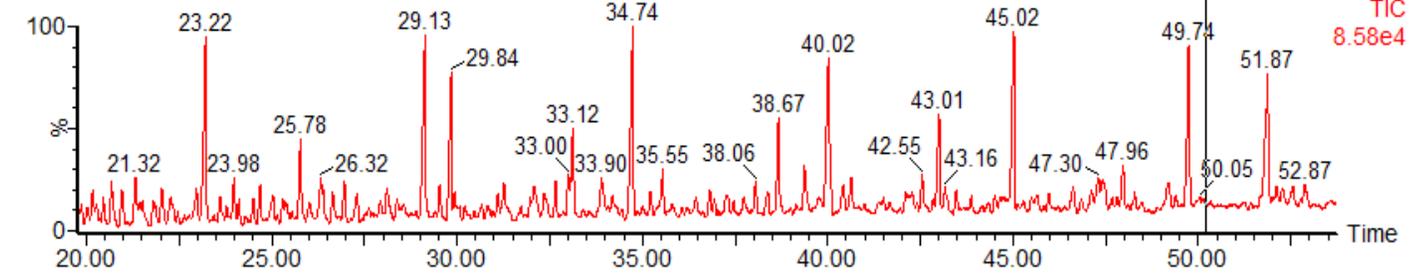Figure 9 Alkyl benzene profiles, C= 6, 7, 8, 9

Another approach to finding unsaturated compounds in the crude oil sample involved using "mass defect filters" to create mass-defect chromatograms. The approach used above to locate specific alkyl-benzenes requires a knowledge of their molecular weights and also relies on the molecular ion being significant in the spectrum. The approach can be used (although not as selectively) with less precise quadrupole mass spec data. Mass defect filters rely only on the fact that as a hydrocarbon becomes more unsaturated (RDB increases) the mass defect of the accurate mass from the integer mass, while still positive, becomes less as the degree of unsaturation increases. If the compound contains O, N, or other heteroatoms such as P, S or Cl, the mass defect will also be less than for saturated alkanes. Mass defect filters can only be used with precise mass spec data.

The mass defect filters used to extract data were:

Filter Name	Mass Range	Mass Defect Range
A	100 – 450	0.02 - 0.04
B	100 - 450	0.04 – 0.06
C	100 – 450	0.06 – 0.08
D	130 – 450	0.08 - 0.10
E	140 – 450	0.10 – 0.12
F	160 – 450	0.12 – 0.14
G	180 – 450	0.14 – 0.16
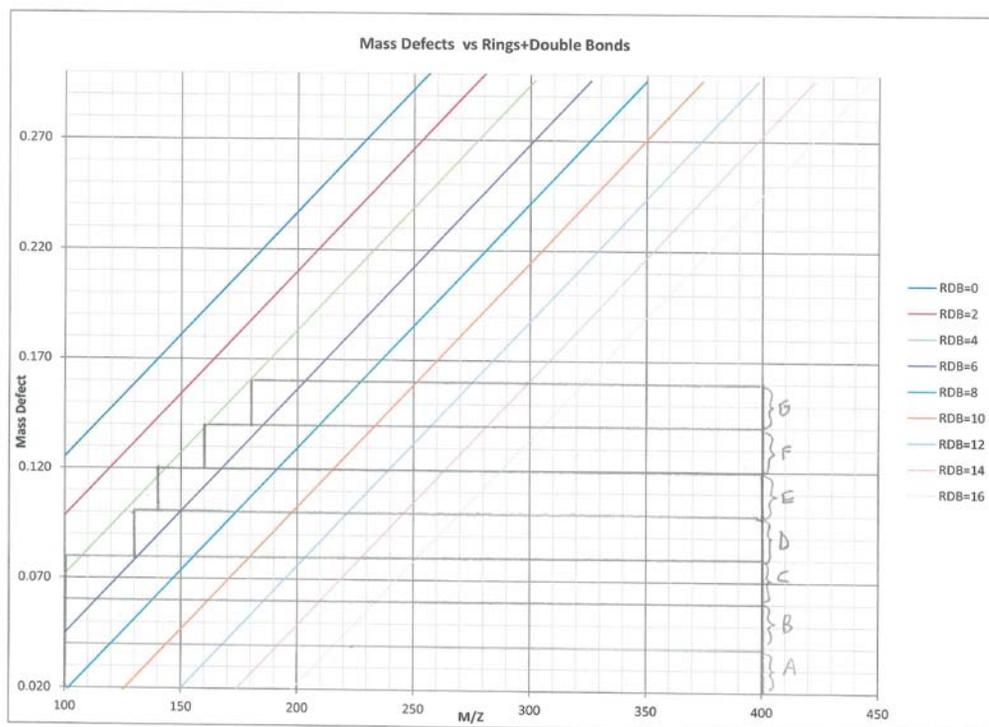
Figure 10 Mass Defect algorithms used

Using mass defect chromatograms, poly-unsaturated compounds with various molecular weights were extracted as examples. At m/z values of 156.092, 160.129, 170.111, 184.127, 188.160, and 210.144. These are shown in Figures 11-16. Representative spectra and library match results are also shown.
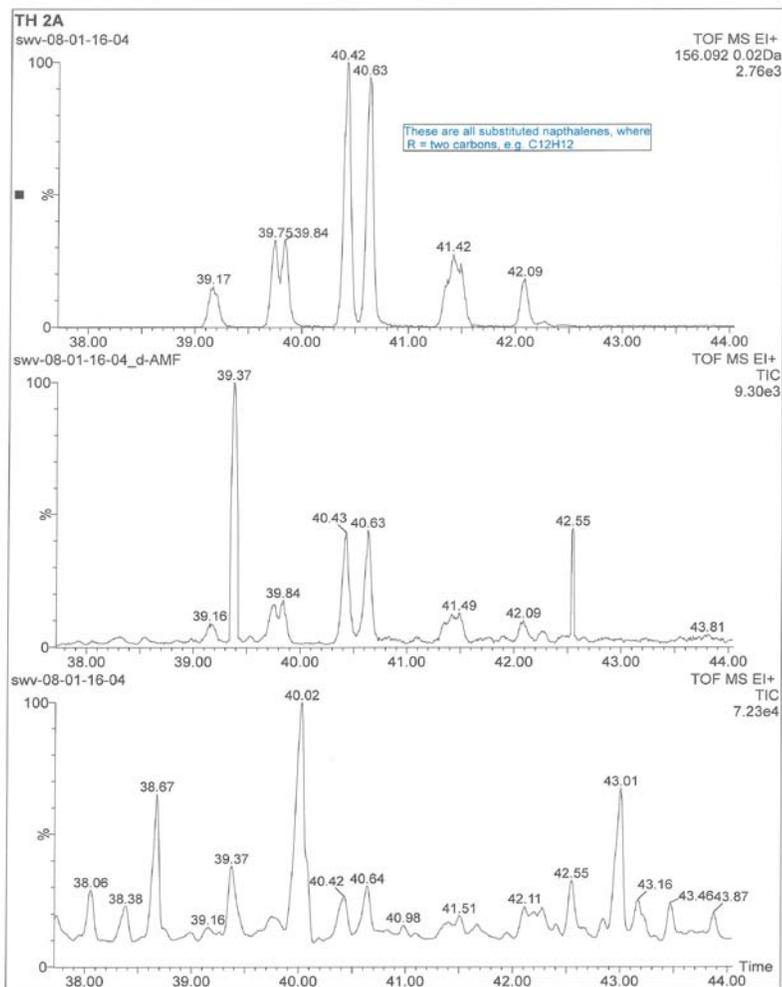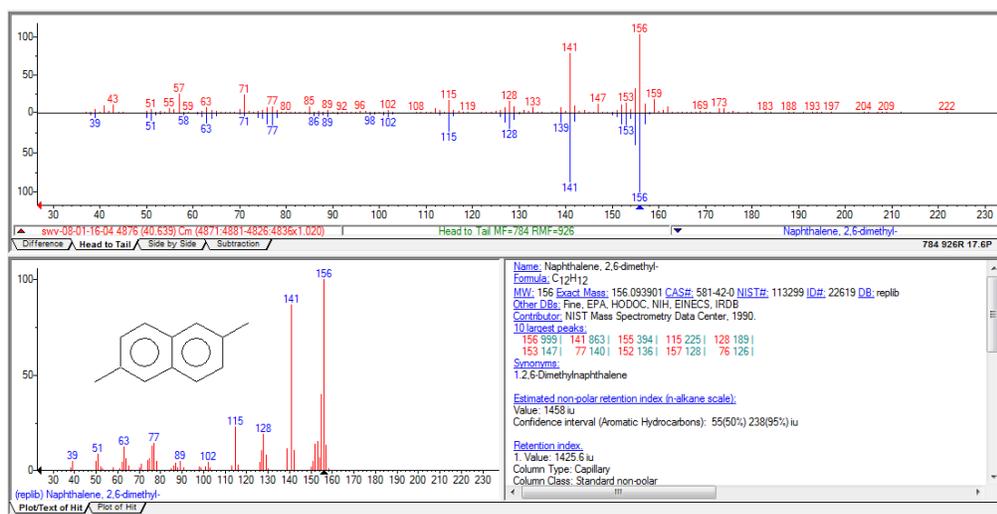
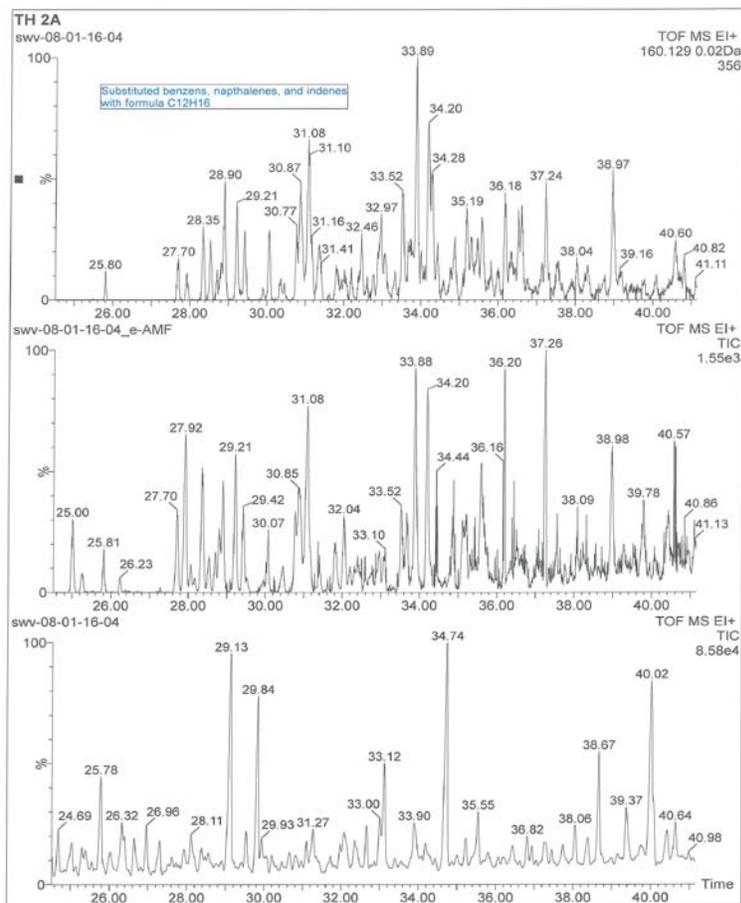*Figure 11 M/Z 156.092. These appear to be substituted naphthalenes, where R = 2 carbons*

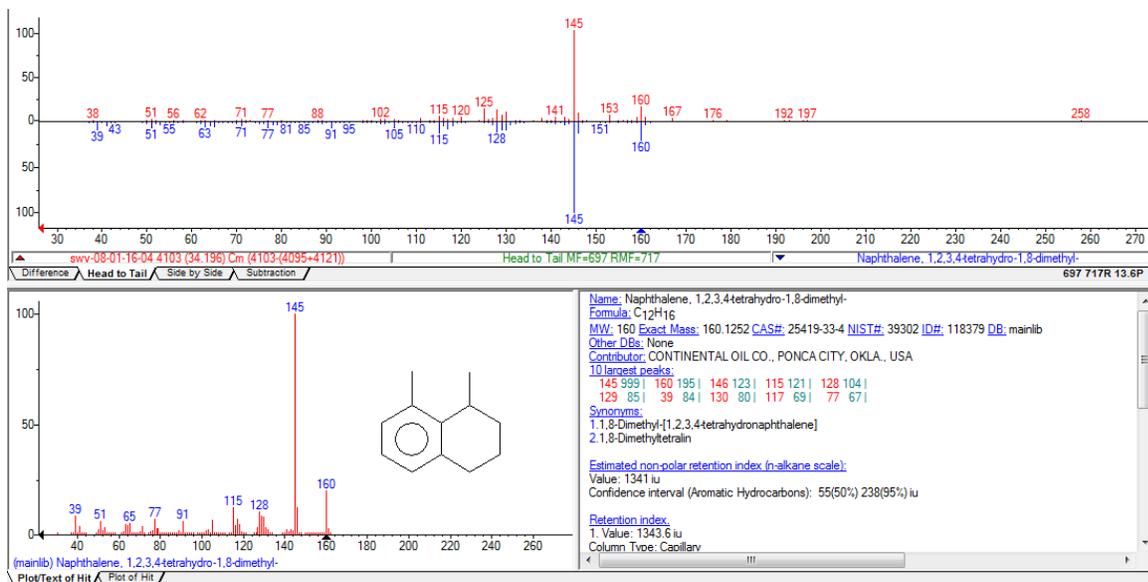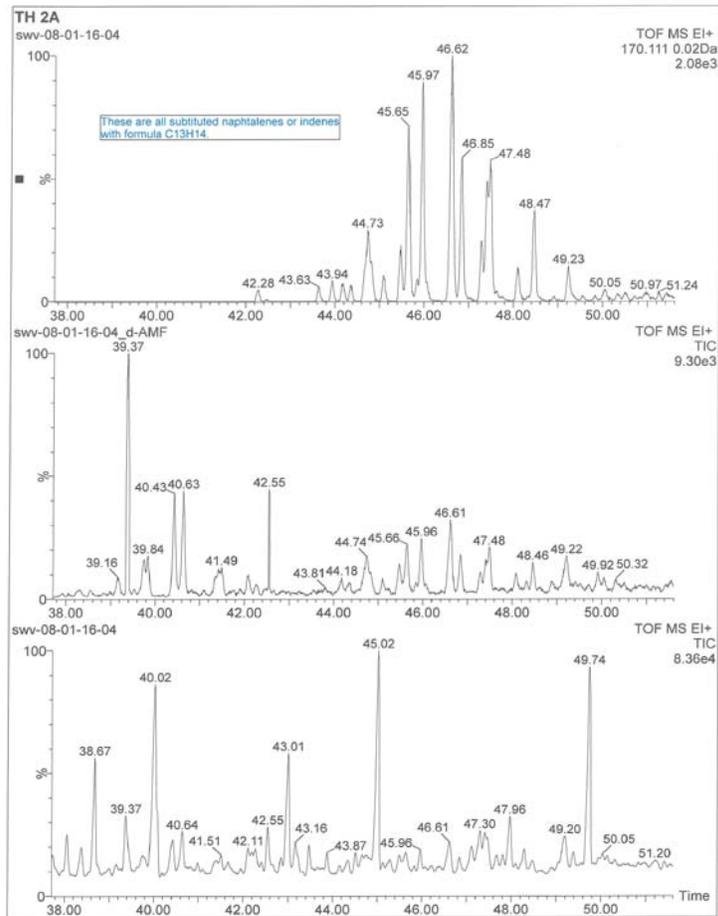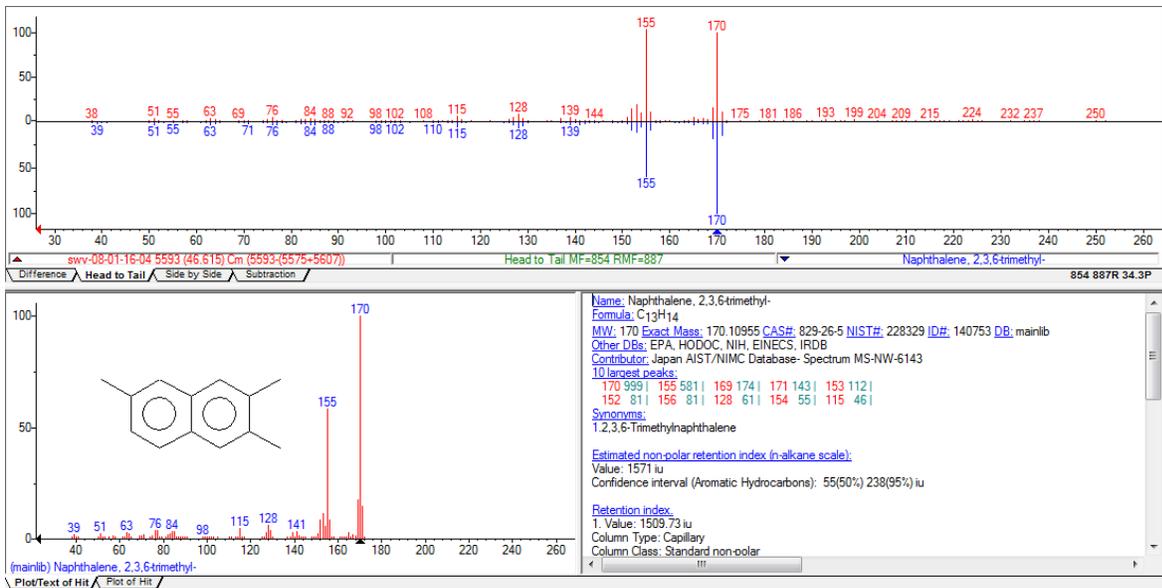*Figure 12 M/Z 160.129.   These appear to be C12H16 substituted benzenes, naphthalenes and indenes*

Figure 13 M/Z 170.111. These appear to be C13H14 substituted naphthalenes and indenes
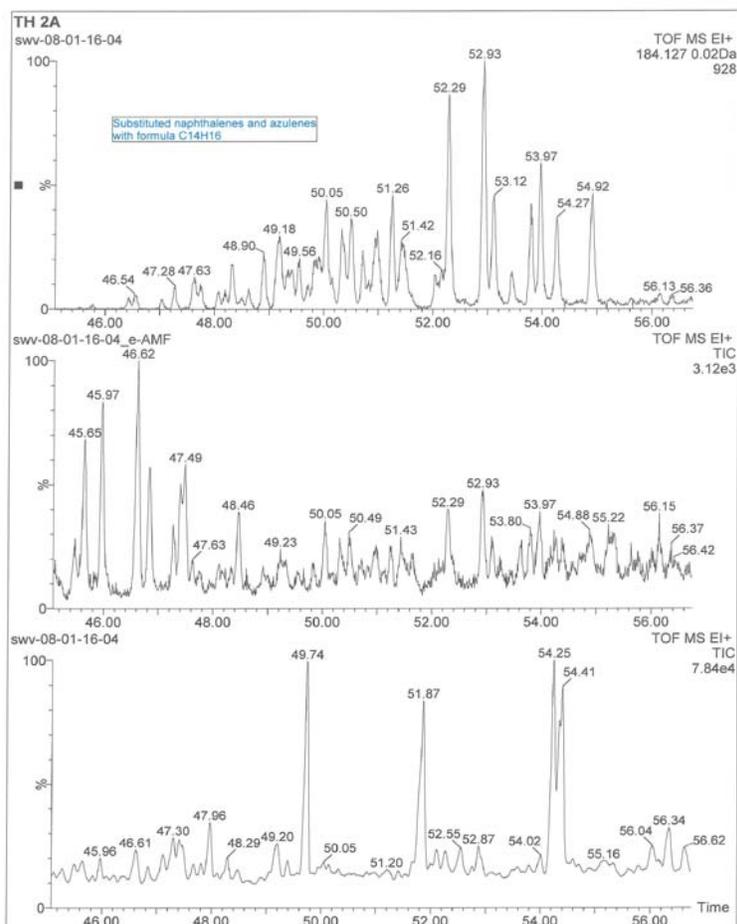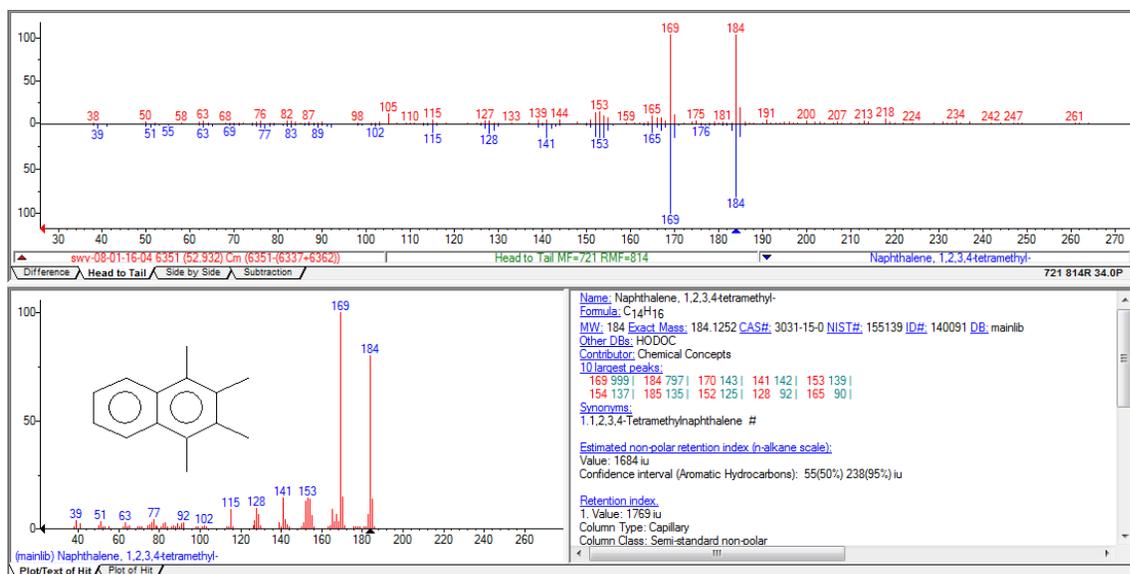
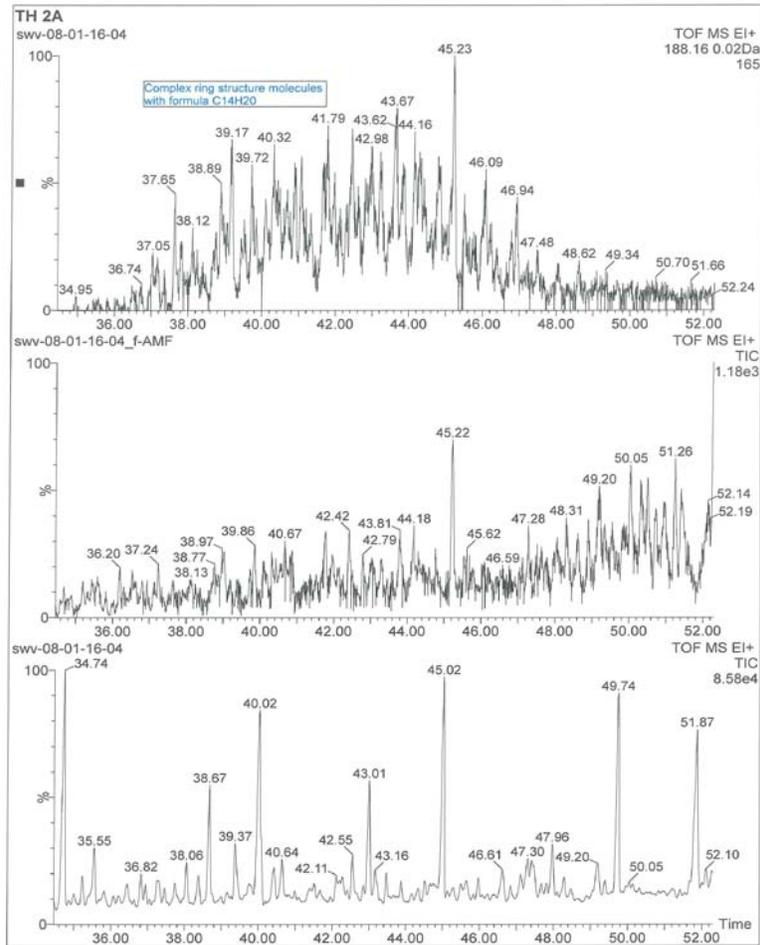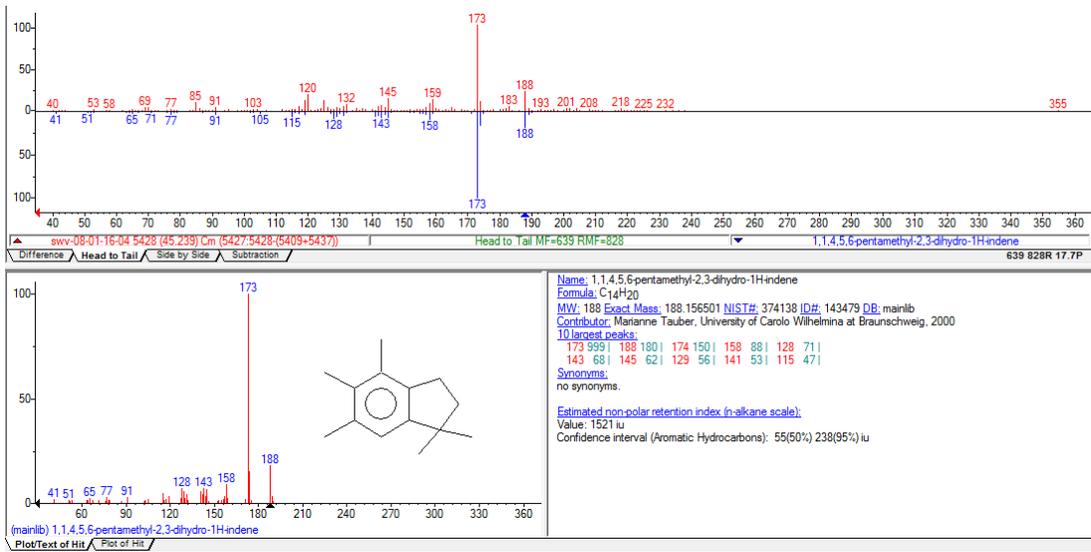*Figure 14 M/Z 184.127. These appear to be C14H16 substituted naphthalenes and azulenes*

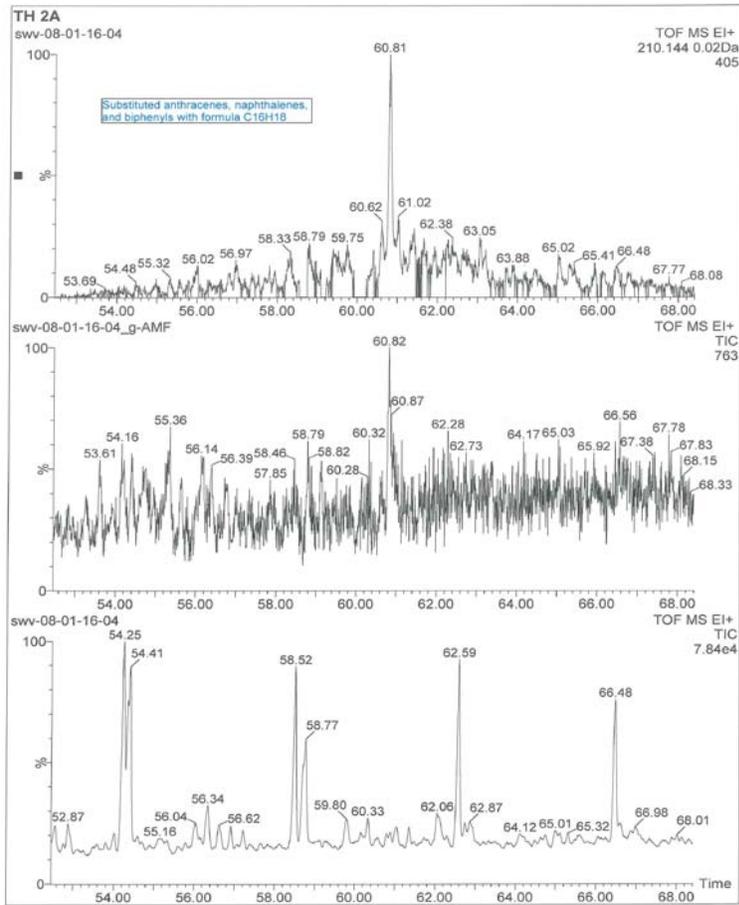*Figure 15 M/Z 188.160. C14H20 complex ring structure compounds*

Figure 16 M/Z 210.144. Appear to be C16H18 anthracenes, naphthalenes, and biphenyls