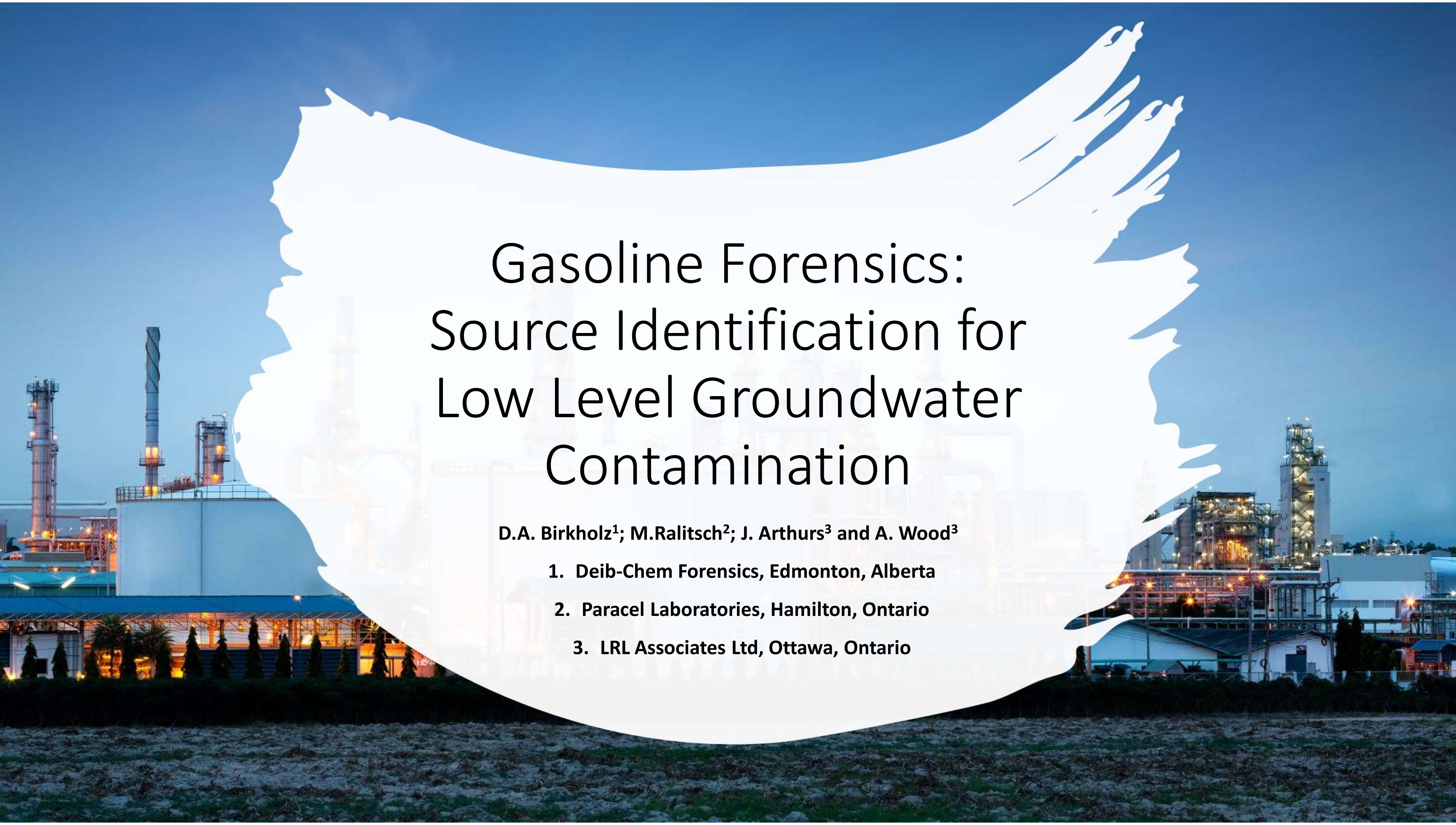

Gasoline Forensics: Source Identification for Low Level Groundwater Contamination

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2. **Paracel Laboratories, Hamilton, Ontario**
3. **LRL Associates Ltd, Ottawa, Ontario**

Part XV.1 Environmental Protection Act - Ontario

Stipulate the maximum levels of total petroleum hydrocarbons (PHC F1-F4) allowed to meet generic site condition standards.

Nine table based on various generic site conditions are provided which may be applied to a Site depending on the drift thickness, proximity to surface water bodies, soil texture, and water usage with the surrounding area (potable or non-potable).

Part XV.1 Environmental Protection Act - Ontario

Depending upon which table is applicable to a subject site, PHC-F1 concentrations between 420 – 750 ug/L and PHC-F2 concentrations of 150 ug/L in groundwater are posted as the criteria.

Exceedance of either of these values generally requires further delineation followed by remediation or risk assessment

Responsible Parties

These low levels provide analytical challenges in determining sources of gasoline (n-C_4 – n-C_{12})

This is particularly true in urban settings where multiple sources of gasoline may exist

Source delineation is critical in determining the responsible parties and assigning liability for remediation. Who is going to pay for cleanup?

How is Gasoline made

- As many as 10 different gasoline components might be blended together to meet finished gasoline specifications

Examples include:

- Straight run gasoline or natural gas condensate
- Reformate
- Alkylate
- Fluid catalytic cracking
- Isomerization of C_5/C_6 normal paraffins
- Butane blending
- Etc.

- Can have simple refineries with few processes and complex refineries with many process

Chromatographic comparisons

- Usually the first step
- BTEX, PHC – F1 – F4 not desirable
- These methods are designed for compliance monitoring, not for forensic investigations.

Information commonly sought

- Composition based on PIANO analysis (paraffins, isoparaffins, aromatics, naphthenes and olefins).
- PIANO tells us a lot about the refinery process (i.e. process forensics)
- Total organic lead concentration
- Identification of lead alkyl types
- Presence of oxygenate additives (MTBE, TAME, ethanol, methanol, etc)
- Bulk carbon and hydrogen isotope analyses
- Some additives have time restrictions and if present can provide insights into likely release dates (e.g. Alkyl lead, MTBE, etc).

Process forensics

- Process forensics focuses on the current and historic engineering practices and how these practices would predictably have affected the chemical composition of the contaminant of interest
- Butane blending – effect on normal-butane and iso-butane abundance
- Isomerate blending – effect on normal pentane and iso-pentane abundance
- Alkylate blending – effect of trimethylpentane distributions
- Naphtha reforming – reformate blending
- Fluidized catalytic cracking
- Octane enhancers – organic lead and oxygenates

Process Forensics

- Alkylation: 2,2,4-trimethylpentane/methylcyclohexane
- Octane index: 2,2,4-trimethylpentane + toluene/(n-C_7 + n-$C_{8)}$
- Butane/isobutane blending: n-C_4/(n-C_4 + i-C_4)
- Isomerate blending: i-C_5/(i-C_5 + n-C_5)
- Reformate blending: toluene/-C_8
- Naphtha Reforming – reformate blending: naphthalene/n-C_{12}
- Fluidized catalytic cracking – presence of pentenes and hexenes
- Catalytic reforming – rich in C_3 and C_4 alkylbenzenes
- Ethanol blending – presence of ethanol

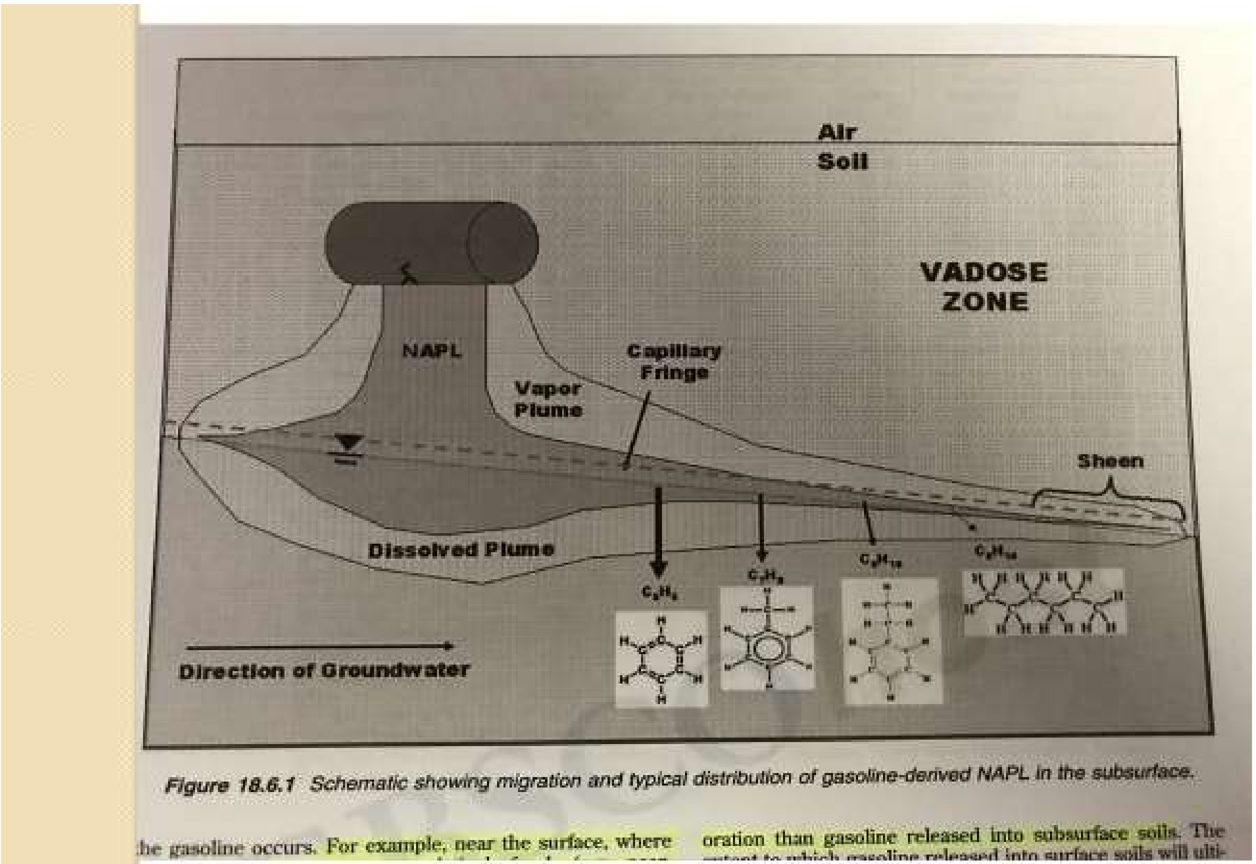
PROCESS FORENSICS

Source	Iso/MCH	Octane index	Butane ratio	Isopentane index	Toluene/ n-C8	Naphth /ISTD	C5 & C6 olefins	C3 and C4 benzenes	Ethanol
A	1.46	2.46	0.84	0.82	3.61	7.37	16.78	52.56	24.34
B	1.4	2.55	0.82	0.79	3.91	7.27	15.29	51.37	22.52
C	1.35	2.44	0.82	0.83	3.62	6.94	14.93	49.00	21.25
D	2.53	3.39	0.86	0.60	5.60	6.32	13.50	58.36	21.40
E	2.60	3.41	0.84	0.61	5.61	6.36	15.79	58.01	22.43
F	2.51	3.16	1.0	0.53	5.07	7.93	11.45	20.40	71.19
G	1.34	2.06	0	0	2.60	15.14	2.82	100.08	0
H	0.17	0.52	0	0	0.75	21.55	0.28	209.29	0
I	0.31	0.52	0.75	0.7	1.02	8.09	5.75	96.08	22.42

PROCESS FORENSICS

- Source A, B, C derived from a common source
- Source D,E – derived from common source
- Source F, G, H, I derived from differing sources

- Data fits with chromatograms of gasoline samples also PCA and cluster analysis



Environmental Forensics, Eds. Morrison and Murphy, 2006, Chpt. 18: Automotive Gasoline

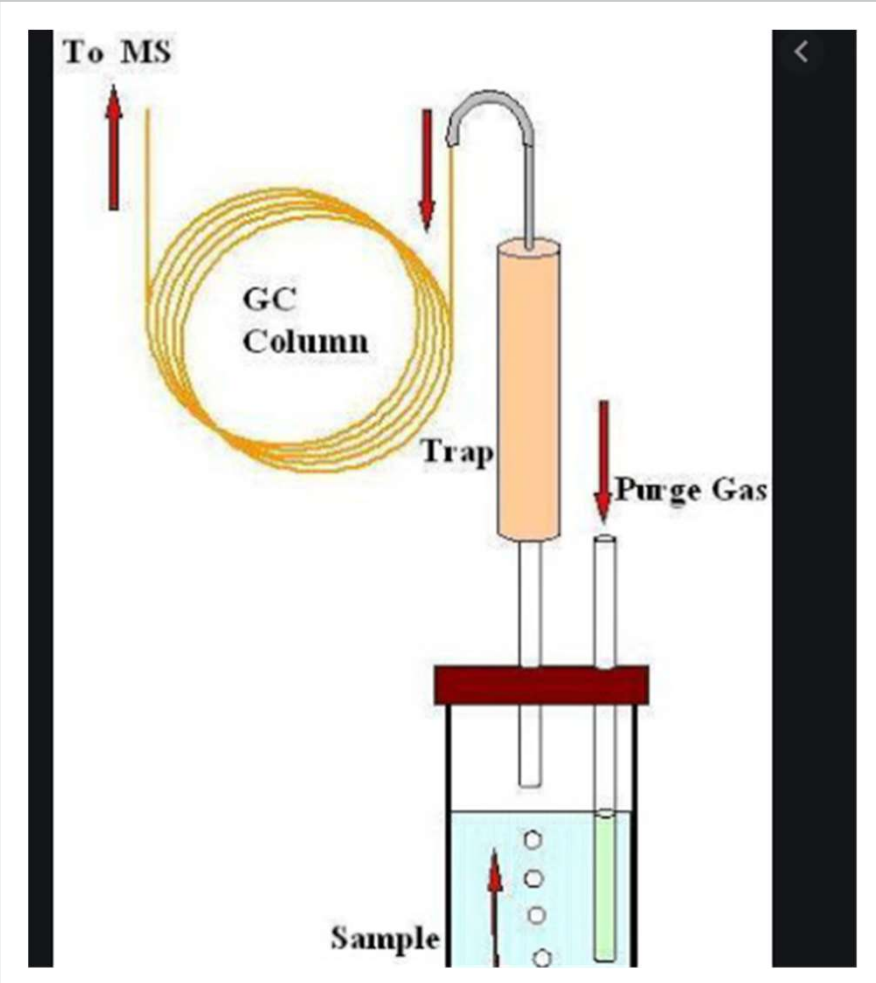
What about weathering

- Evaporation
- Water dissolution
- Biodegradation

Gasoline Analyses

- Several ways to perform forensic analyses of gasoline in water (source/spill investigations)
- If LNAPL is present – direct GC/MS using a PONA column. Used by refineries for product QC. CAN/CGSB-3.0 No. 14.3-2016; ASTM E1618-10
- LNAPL can be analyzed using GC/MS purge and trap; getting concentration right is a challenge
- LNAPL can be analyzed using GC/MS headspace
- If no LNAPL is present, use GC/MS purge and trap
- If no LNAPL is present extract groundwater and employ GC/MS using a PONA column
- Because observed PHC values are low, we proposed concentrating the groundwater samples during collection (multiple composite bailer samples 16 - 20) and extracting the concentrated hydrocarbons using an ETFE net.
- ETFE netting has been reported in the literature for use in collecting gasoline samples but no data
- Propose analyzing the ETFE net using passive headspace because better precision relative to solvent extraction and concentration

LNAPL



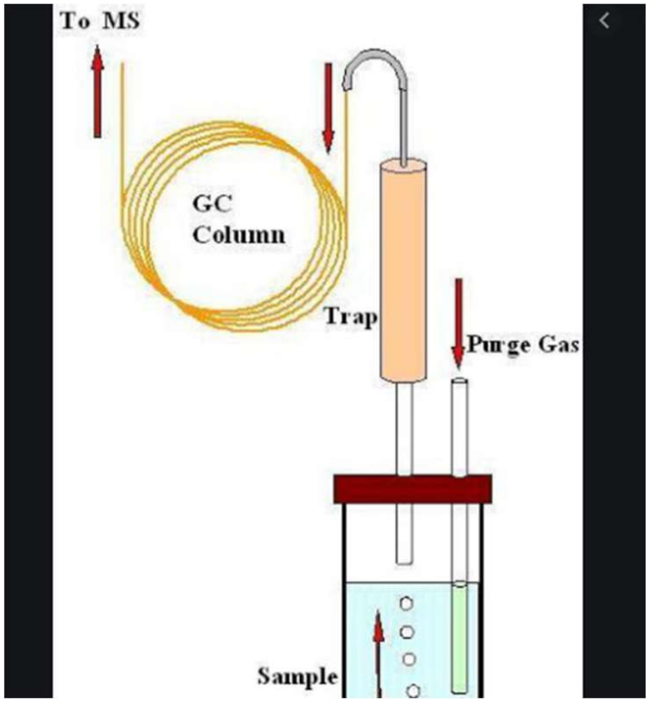
Purge & Trap GC/MS

- Gasoline contains 361 individual compounds (Whittmore, 1979)
- Method 8260 measures 109 compounds
- Method tested using SRMs which reported 23 analytes
- In our experience low concentrations of TPH < 500 ug/L may not provide sufficient chemical details using PIANO methodology or < 100 ug/L BTEX"
- "Values of 6.3 and 160 mg/L contained full suite of detectable PIANO analytes
- " Ref: Uhler, et. al., (2003). Intern. J. Environ. Anal. Chem., 83: 1 – 20
- Ref: Stout, et. al., (2006). Environmental forensics: contaminant specific guide, pp 466 - 527

Purge and Trap – Gasoline Samples

- The accuracy of the modified EPA Method 8260 is demonstrated through the comparison of the published NIST SRM certified and reference values and the concentrations determined by the modified EPA 8260 method
- **23 analytes out of 109 reported**
- ***The RPD between the NIST and modified EPA Method results are shown to be less than 15% for most compounds***.
- RPD not to exceed 25%
- Highest RPDs are evident in compounds present at low concentrations.

We Rejected Purge & Trap



- No data provided on analytes measured at 500 ug/L Using method . What chemicals were detected?
- Experience with purge-and-trap systems has shown that analysis of highly contaminated samples can potentially contaminate the transfer system: after analysis of such a sample, a reagent water blank should be analyzed to confirm that the system is free from interferences and cross-contamination. If the reagent water blank analysis is not free of interferences, the system must be decontaminated by either a bake-out procedure or through more detailed instrument maintenance. Sample analysis should not resume until a reagent water blank demonstrates that the system is free of interferences”
- Need to screen samples before analyses which takes time and is inefficient
- Reference: Douglas et. al., (2007). Chemical Fingerprinting Methods. In:Introduction to Environmental Forensics, Second Edition, Eds. Brian L. Murphy and Robert D. Morrison, Elsevier Academic Press, pp 351 – 352

Alternative Method: ETFE Netting followed by Passive Headspace Analyses

ETFE netting is used to sample petroleum sheens (CEN/TR 15522-1:2012; EN 15522-2:2020) both methods adopted by the Oil Spill International Network of Experts (OSINET). EN 15522-1:2020 deals with light end petroleum hydrocarbons

Has also been recommended for use in gasoline sheen collection (Stout et al., 2016)

Hydrophobic pads to sample ignitable liquids from surface water samples following fire extinguishing (Totten and Willis, 2020).

Passive headspace analysis has been used for fire debris analyses (Stauffer E. et al., 2008) and there have been many peer reviewed publications including an ASTM standard (ASTM E1412-07). Birkholz has a wealth of data looking at precision of ratios, e.g., alkylated benzenes, etc., etc.

We were particularly interested in ratios involving alkylated naphthalenes. Sandcock and Pasquier published three papers involving gasoline (2003, 2004a, 2004b).

Because we had two well established methods under ISO Guide ISO/IEC 17025 all we had to do was a validation study

Gasoline Samples Employed in Method Validation Obtained from Hamilton, ON

Triplicate analyses of neat samples PROCESS FORENSICS

	Esso	Costco	Pionner	Comment
		Premium		
toluene/n-C8	19.62 ± 2.11	33.38 ± 3.12	9.55 ± 1.34	Amount of reformate blended
1M3PB/1M4PB	2.00 ± 0.02	1.80 ± 0.04	1.85 ± 0.06	Reforming conditions
1M2EB/1M3EB	2.27 ± 0.05	1.98 ± 0.03	2.08 ± 0.08	Reforming conditions
224-TMP/MCH	8.12 ± 0.56	11.72 ± 1.19	2.83 ± 0.06	Amount of alkylate blended
isopentane/pentane	0.76 ± 0.05	1.59 ± 0.24	0.92 ± 0.13	Amount of isomerate blended
KI = 2MH + 23 DMP/3MH + 24 DMP	0.93 ± 0.01	0.87 ± 0.01	1.01 ± 0.01	Amount of straight run gasoline
2-MN/1-MN	1.93 ± 0.06	2.00 ± 0.08	2.17 ± 0.06	Reforming conditions
pentenes/pentane	13.65 ± 2.03	8.31 ± 0.73	9.54 ± 0.45	Amount of FCC gasoline
octane index	10.96 ± 0.93	15.50 ± 0.90	4.92 ± 0.20	Index relates to octane rating

Process

- 1.0 mL gasoline added to 500 mL distilled water
- Gasoline and water mixed
- Mixture extracted with ETFE netting
- Netting stored in a jar for several days
- After addition of surrogates placed in a 1 quart can
- Carbon strip added
- Heated at 80^{o}C overnight
- Carbon strip retrieved added to vial containing CS_2 + ISTD
- Analyzed by GC/MS scanning using PONA column (GC/MS SIM may be required in some instances)

ETFE Netting followed by Passive Headspace Analysis

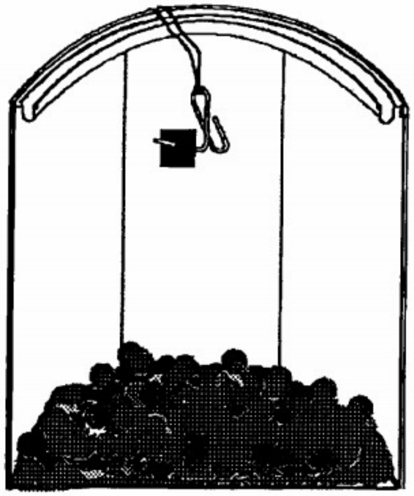
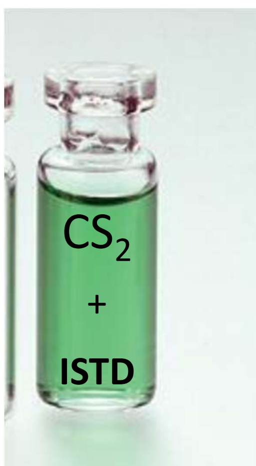
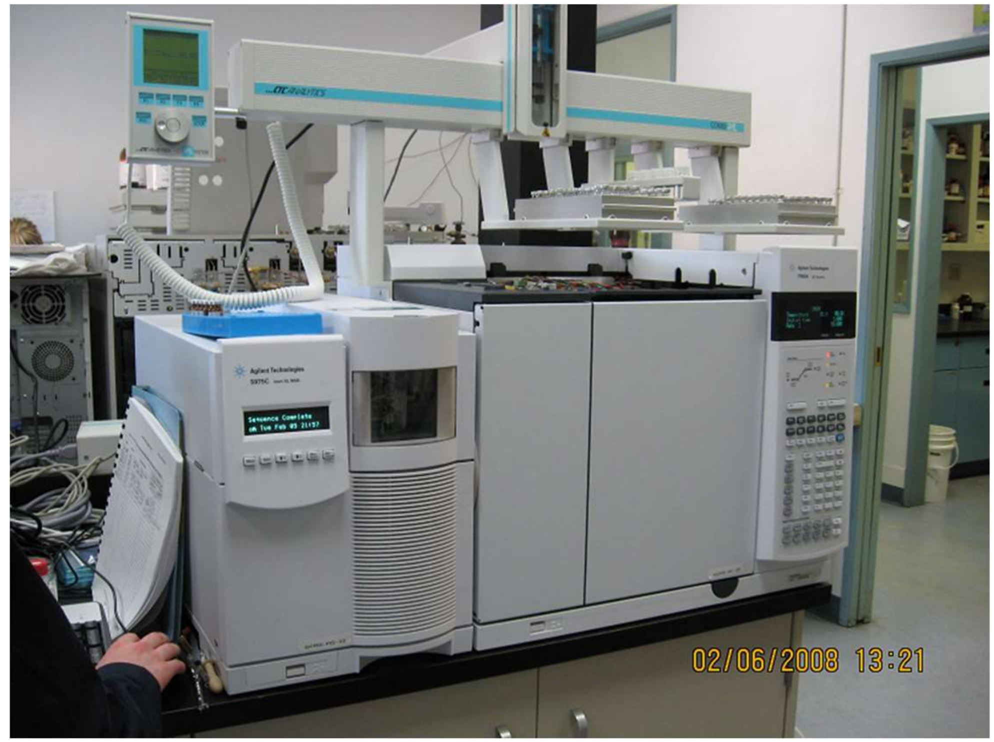
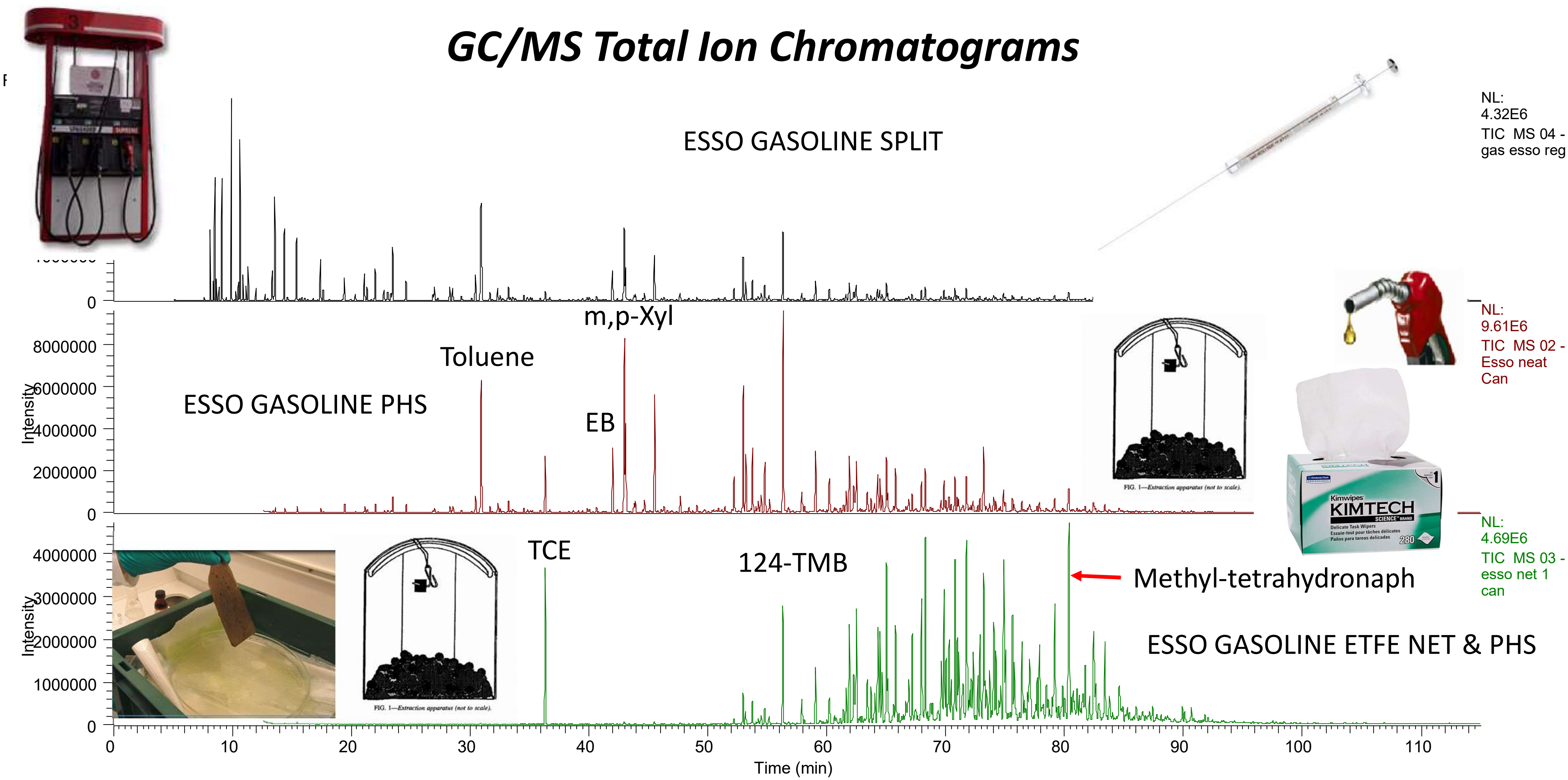


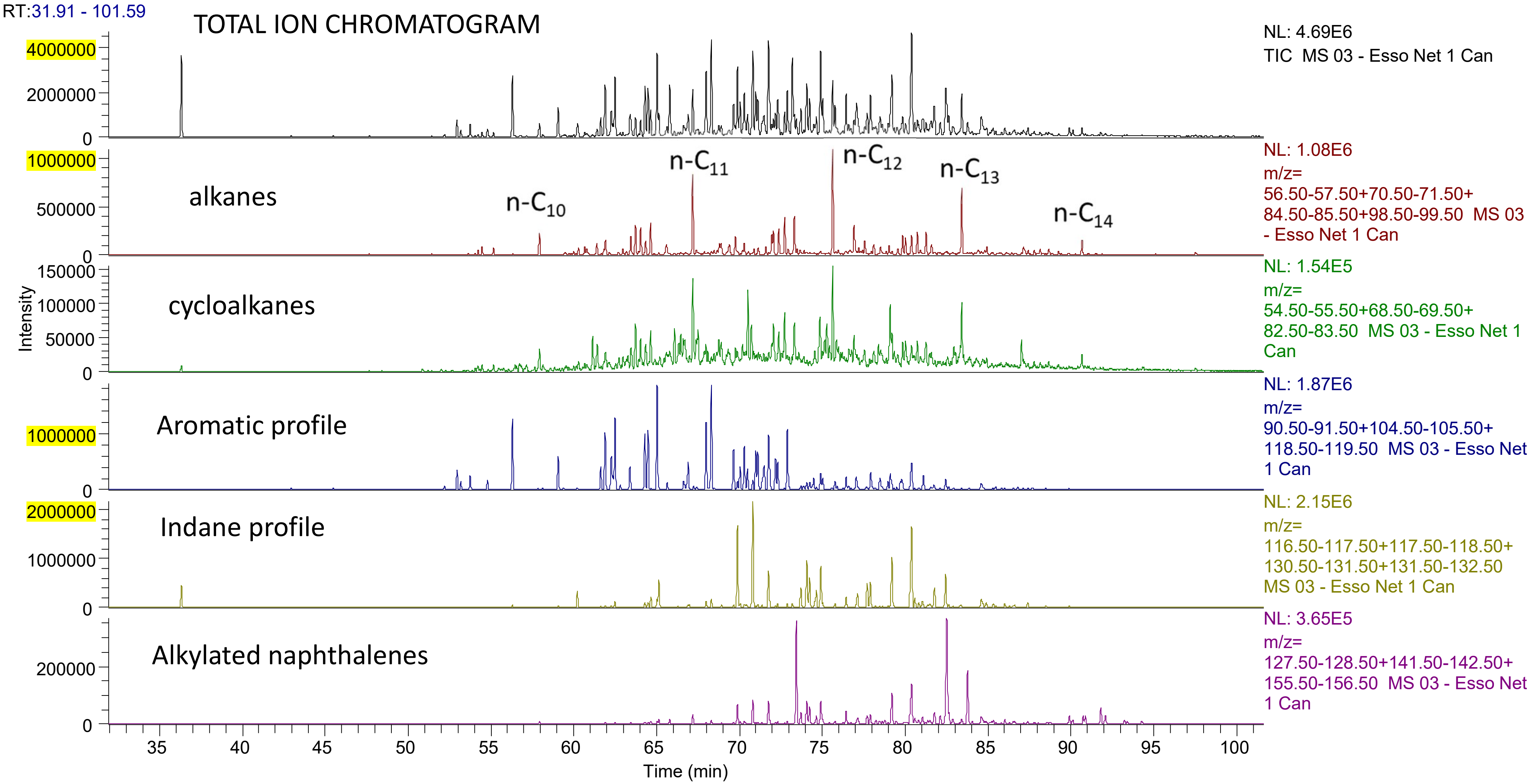
FIG. 1—*Extraction apparatus (not to scale).*





GC/MS Total Ion Chromatograms





RT:31.91 - 101.59
TOTAL ION CHROMATOGRAM
NL: 4.69E6
TIC MS 03 - Esso Net 1 Can
4000000
2000000
0
alkanes
n-C10
n-C11
n-C12
n-C13
n-C14
NL: 1.08E6
m/z= 56.50-57.50+70.50-71.50+ 84.50-85.50+98.50-99.50 MS 03 - Esso Net 1 Can
1000000
500000
0
cycloalkanes
NL: 1.54E5
m/z= 54.50-55.50+68.50-69.50+ 82.50-83.50 MS 03 - Esso Net 1 Can
150000
100000
50000
0
Intensity
Aromatic profile
NL: 1.87E6
m/z= 90.50-91.50+104.50-105.50+ 118.50-119.50 MS 03 - Esso Net 1 Can
1000000
0
Indane profile
NL: 2.15E6
m/z= 116.50-117.50+117.50-118.50+ 130.50-131.50+131.50-132.50 MS 03 - Esso Net 1 Can
2000000
1000000
0
Alkylated naphthalenes
NL: 3.65E5
m/z= 127.50-128.50+141.50-142.50+ 155.50-156.50 MS 03 - Esso Net 1 Can
200000
0
35 40 45 50 55 60 65 70 75 80 85 90 95 100
Time (min)

ALKYLATED INDANS

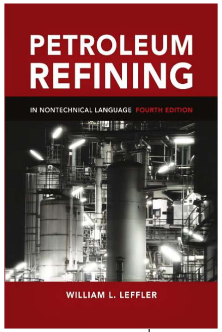
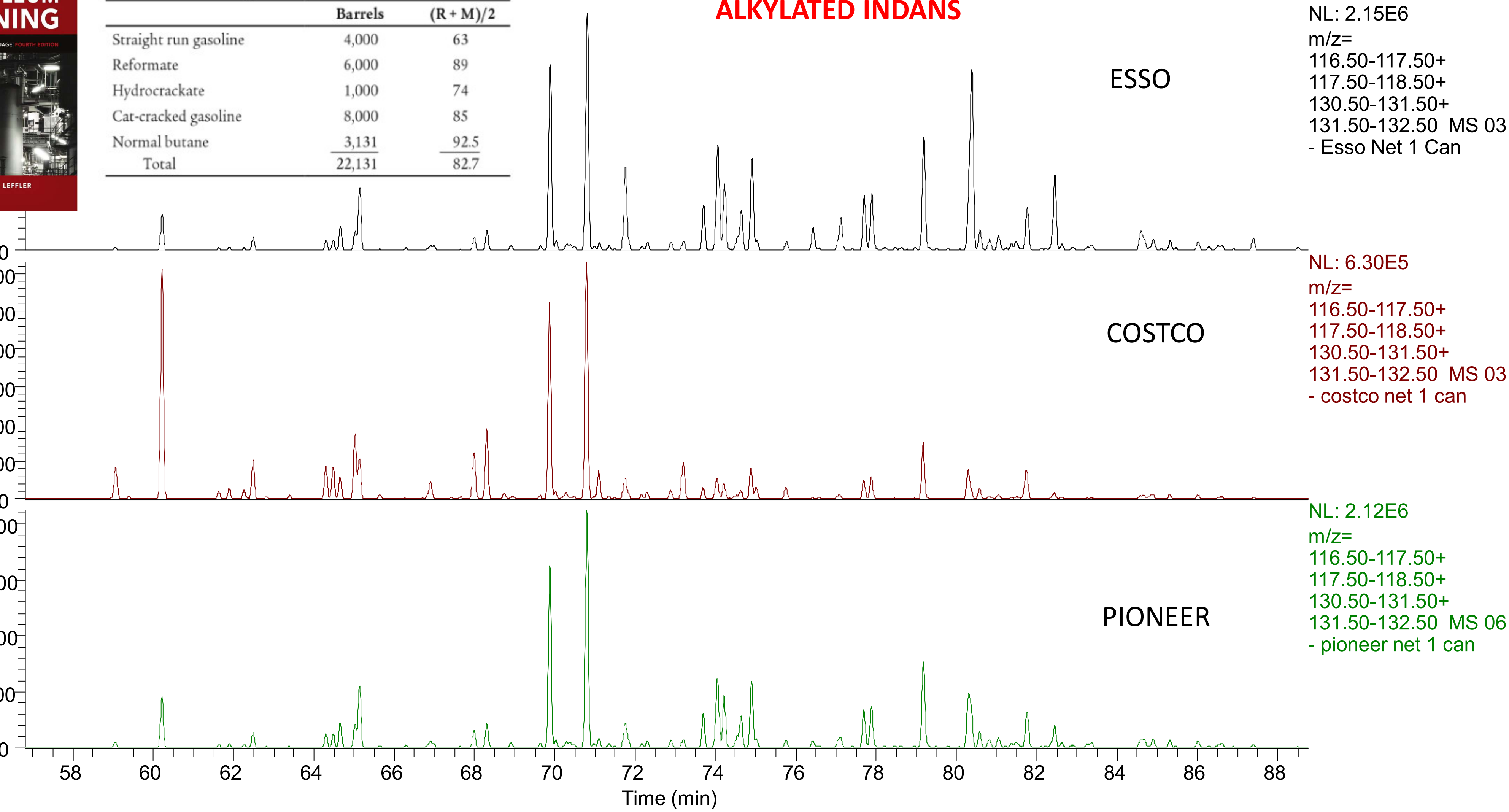


Table 14–3. Blending for octane number

	Barrels	(R + M)/2
Straight run gasoline	4,000	63
Reformate	6,000	89
Hydrocrackate	1,000	74
Cat-cracked gasoline	8,000	85
Normal butane	3,131	92.5
Total	22,131	82.7



DOES OSINET PROCESS ETFE NETTING USING PASSIVE HEADSPACE ANALYSES

- No, they rinse with solvent (DCM) and concentrate
- Why did you not follow the OSINET process?
- Why did you opt for Passive Headspace Analyses?

Reason we processed ETFE nets using PHS

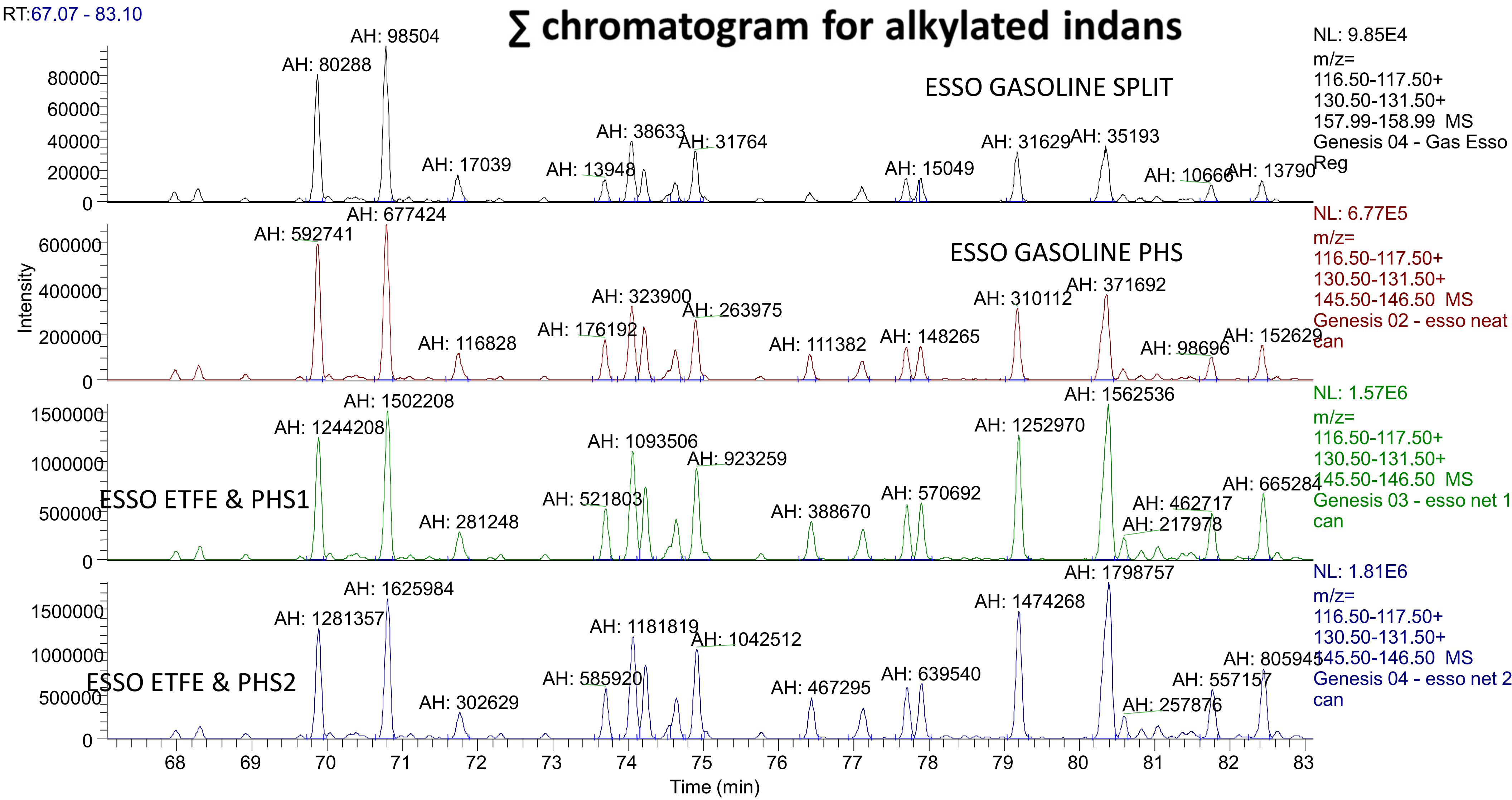
	Relative Percent Difference Duplicate Analyses								
	ESSO	ESSO	Costco	Costco	Pioneer	Pioneer	Esso	Costco	Pioneer
	ETFE	ETFE & Can	ETFE	ETFE & Can	ETFE	ETFE & Can	mean	mean	mean
EB/MPX	#DIV/0!	200.00	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!			
135TMB/124TMB	59.46	16.22	30.00	18.18	34.78	**0.00**	0.19	0.22	0.20
1M3PB/1M4PB	**0.54**	**1.05**	**4.71**	**0.58**	27.21	**0.57**	1.90	1.72	1.75
1M2EB/1M3EB	26.92	16.22	11.76	6.90	23.08	6.25	0.55	0.58	0.64
1M3EB/1M4EB	**1.34**	**2.14**	**0.49**	**4.40**	24.86	**4.67**	2.34	2.04	2.14
1M2EB/1M4EB	27.83	18.60	13.22	10.97	47.42	**1.47**	1.29	1.19	1.36
1M2EB/123TMB	109.86	18.18	34.67	20.95	153.13	10.81	0.33	0.52	0.37
123-TMB/124TMB	48.98	6.74	**0.00**	**0.00**	154.29	**4.76**	0.44	0.40	0.42
1M2EB/124-TMB	66.67	6.90	31.58	19.05	5.13	6.45	0.15	0.21	0.16
1M3EB/124-TMB	90.32	26.42	22.22	27.78	15.79	4.08	0.27	0.36	0.24

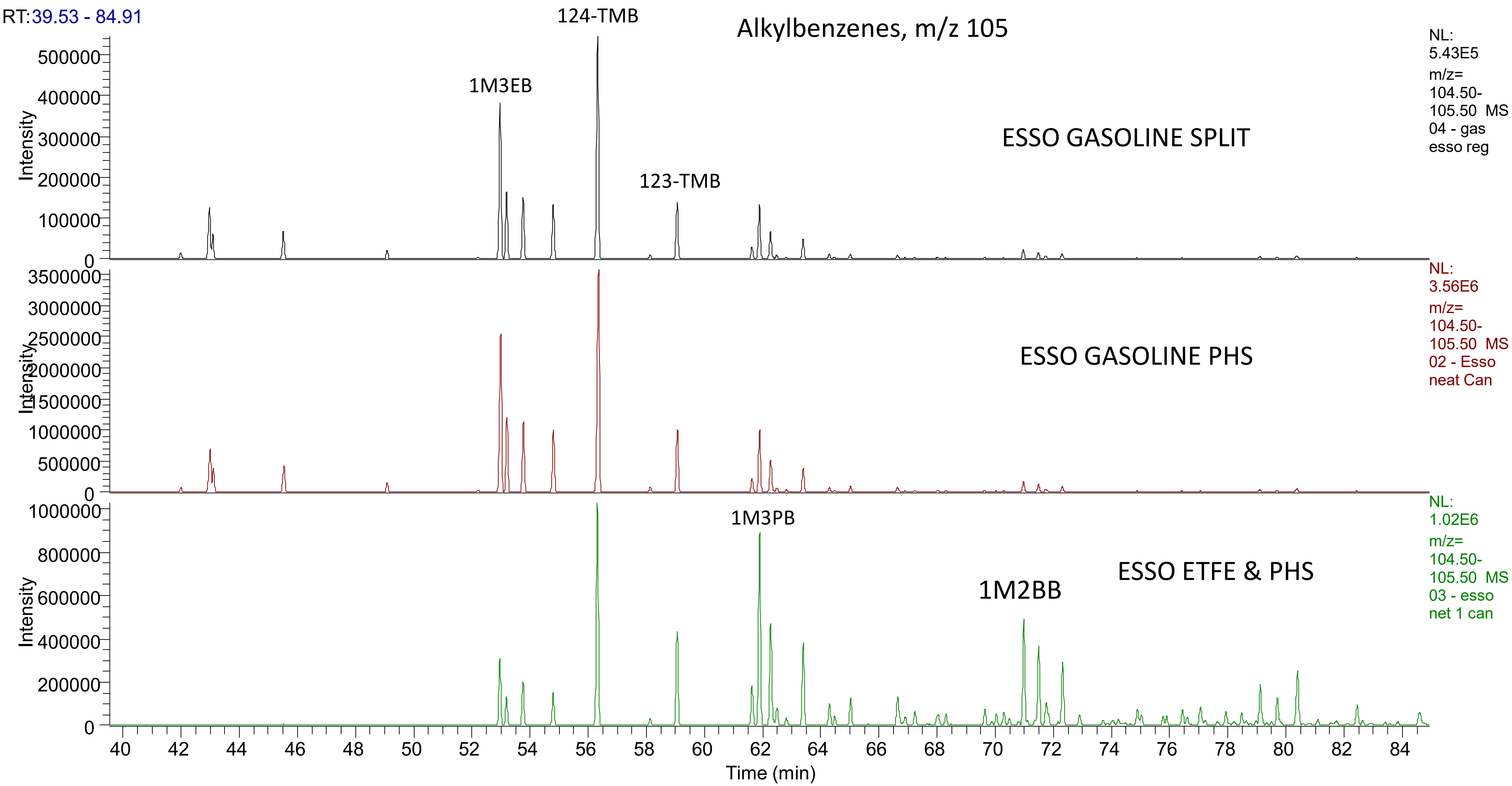
C_3-BENZENES, M/Z 105

Reason we processed ETFE nets using PHS

	Relative Percent Difference Duplicate Analyses								
	ESSO	ESSO	Costco	Costco	Pioneer	Pioneer	Esso	Costco	Pioneer
	ETFE	ETFE & Can	ETFE	ETFE & Can	ETFE	ETFE & Can	mean	mean	mean
123TMB/124TMB	51.92	**2.22**	10.40	9.79	25.49	14.21	0.90	0.72	0.91
124TMB/123TMB	52.43	**2.69**	10.34	8.57	26.00	14.55	1.11	1.40	1.10
14M2EB/12M4EB	4.17	5.71	10.31	3.92	36.52	7.14	0.53	0.51	0.56
1245/1235	1.57	**0.00**	9.38	**3.08**	14.97	**0.00**	0.64	0.65	0.67

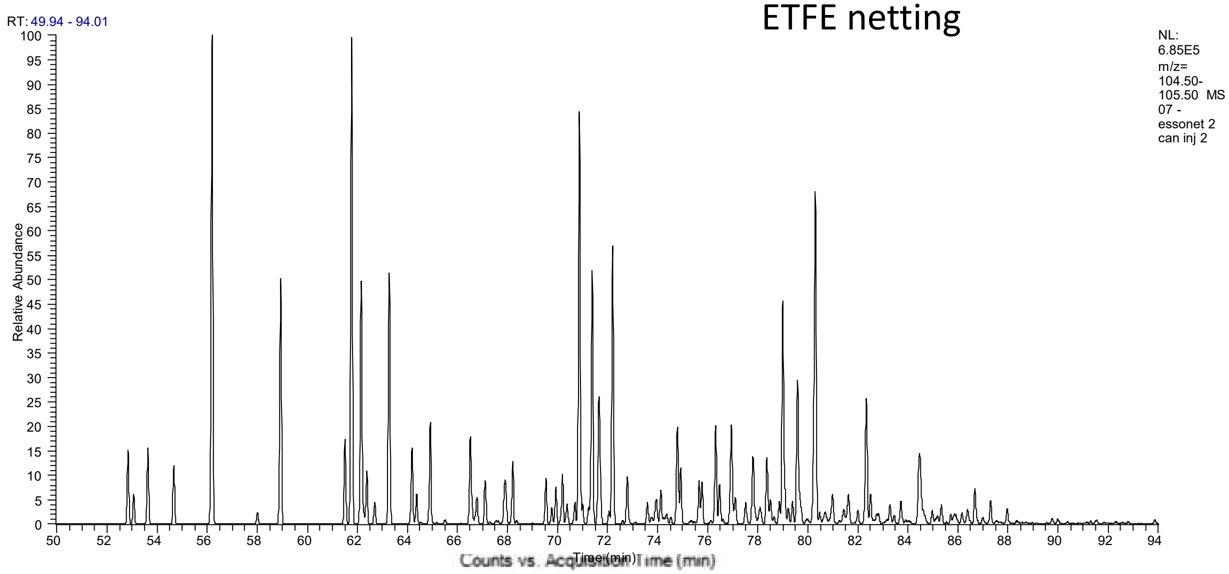
∑ chromatogram for alkylated indans



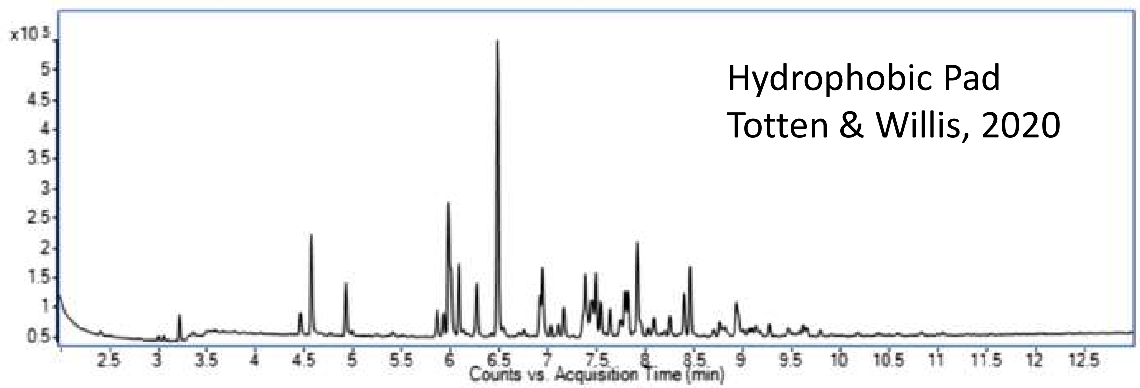


RT:39.53 - 84.91
Alkylbenzenes, m/z 105
124-TMB
1M3EB
123-TMB
ESSO GASOLINE SPLIT
NL:
5.43E5
m/z=
104.50-
105.50 MS
04 - gas
esso reg
ESSO GASOLINE PHS
NL:
3.56E6
m/z=
104.50-
105.50 MS
02 - Esso
neat Can
1M3PB
1M2BB
ESSO ETFE & PHS
NL:
1.02E6
m/z=
104.50-
105.50 MS
03 - esso
net 1 can
Intensity
Time (min)

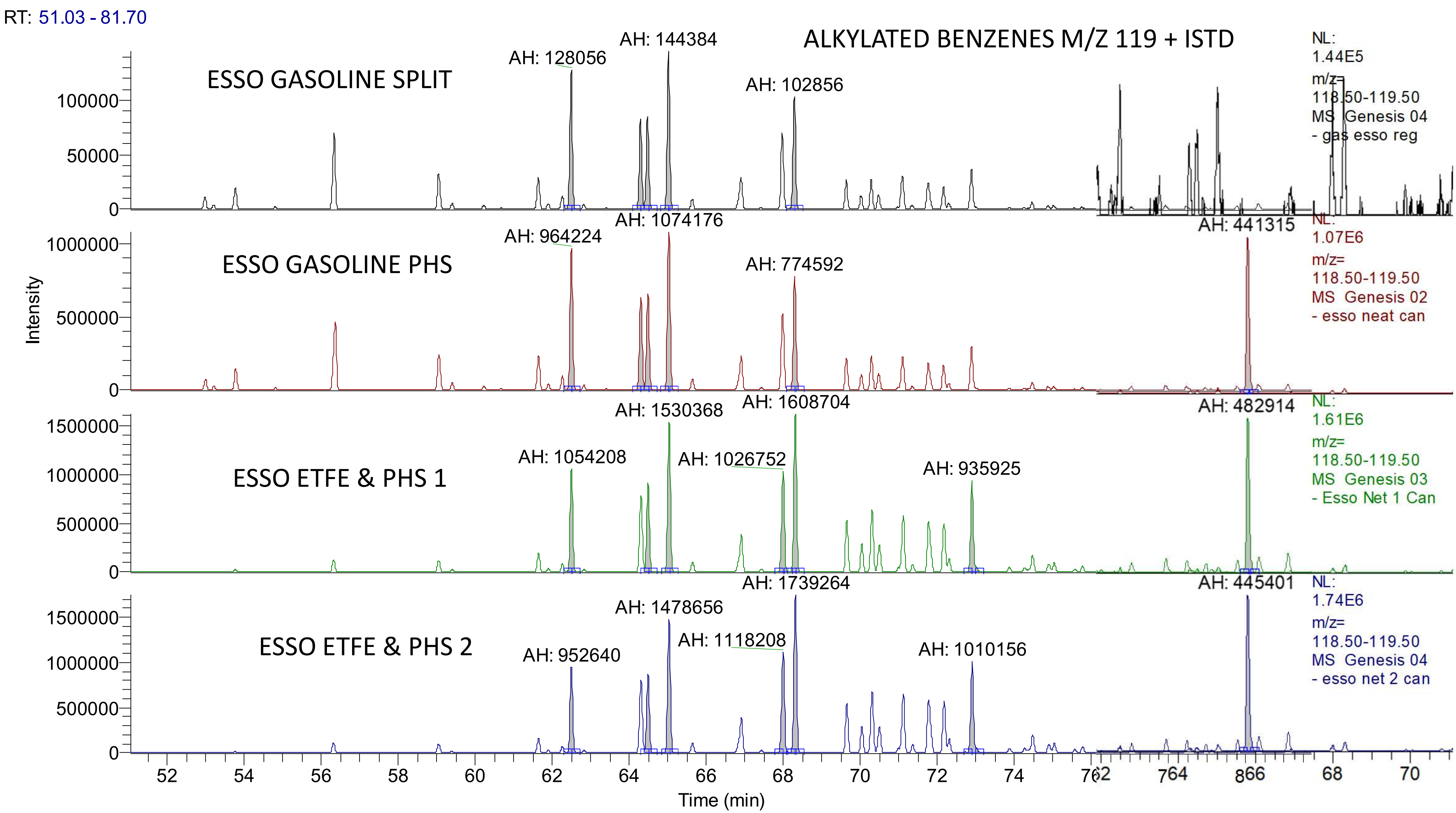
ETFE netting



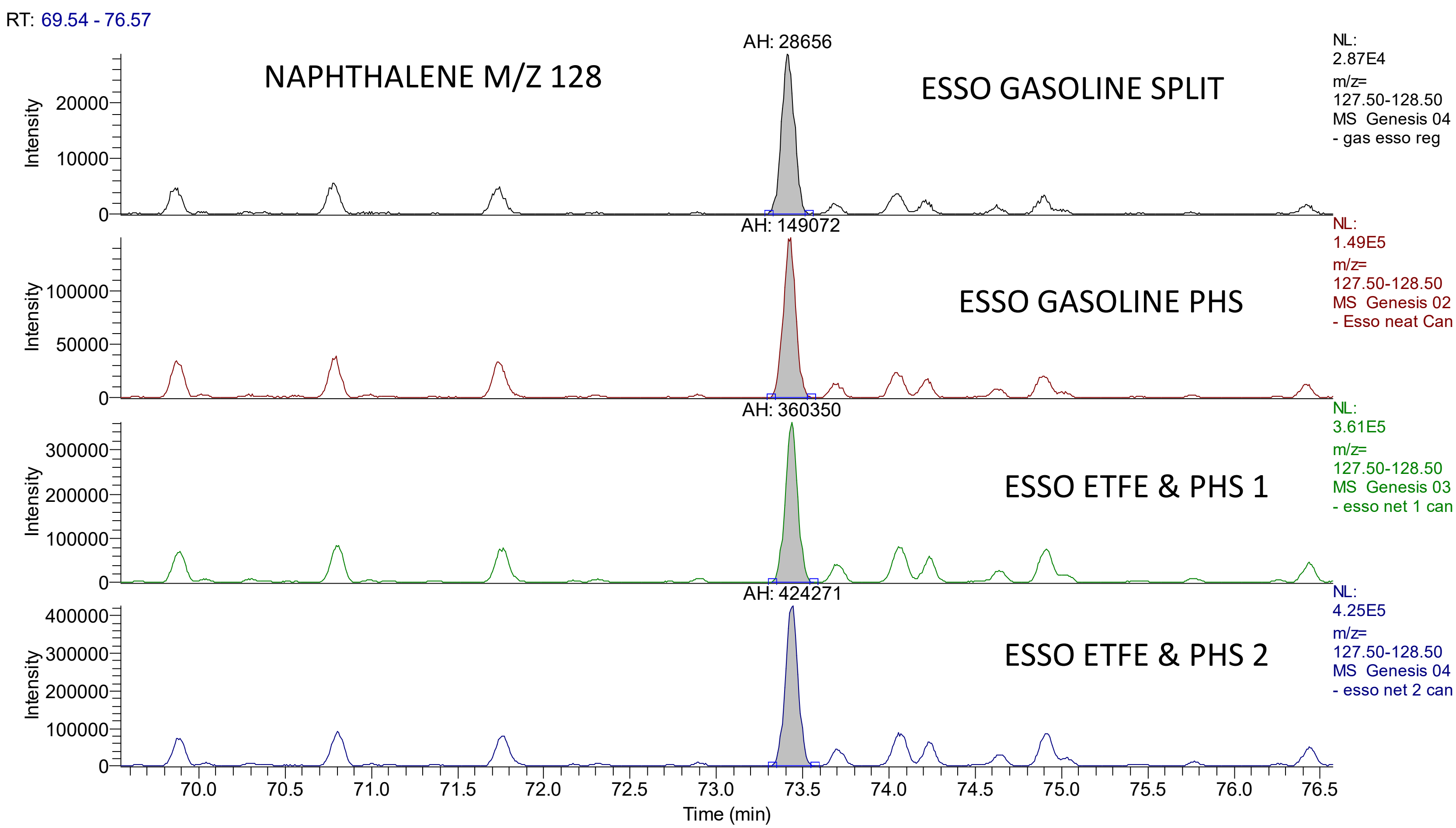
d.



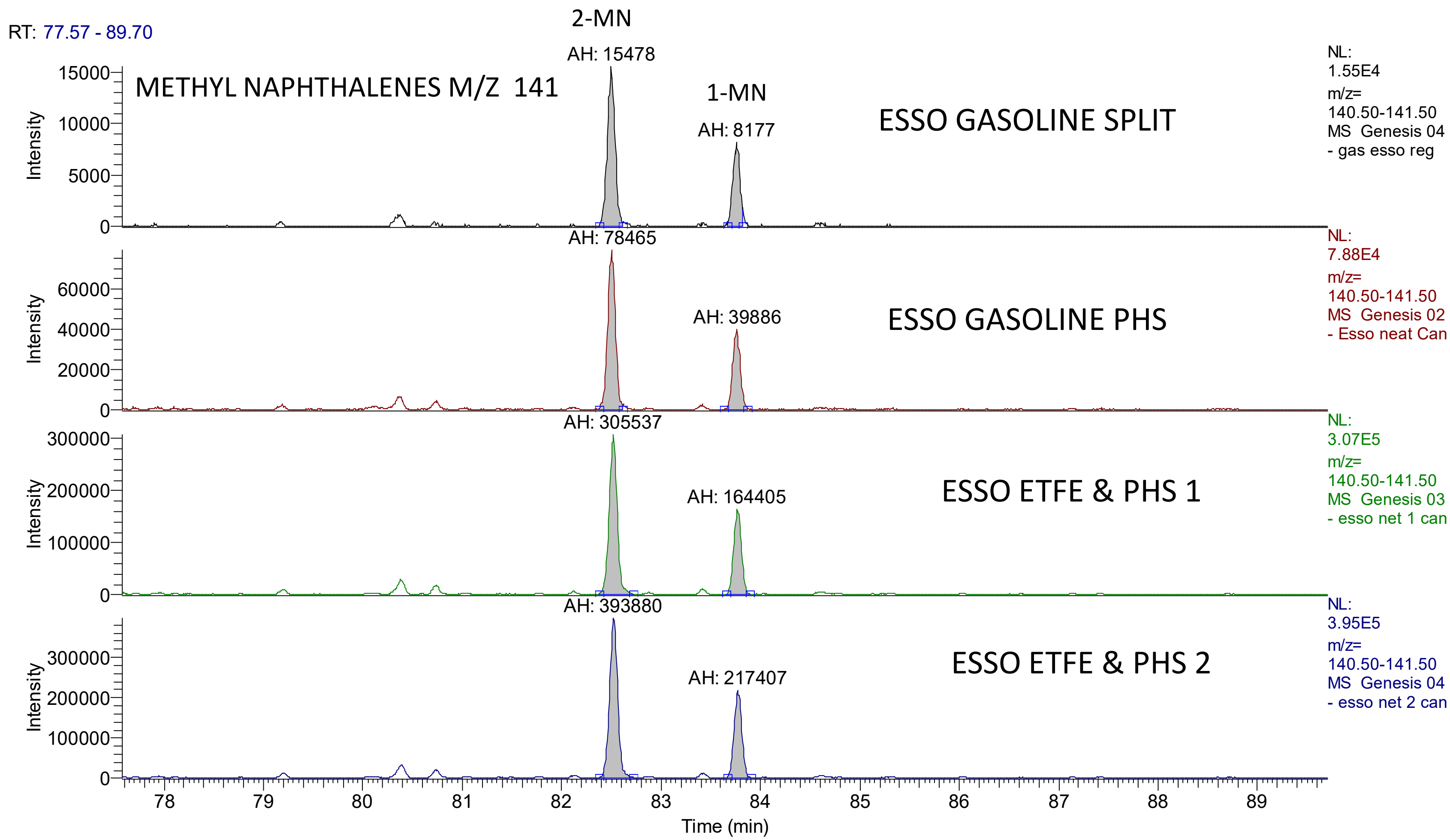
Hydrophobic Pad
Totten & Willis, 2020

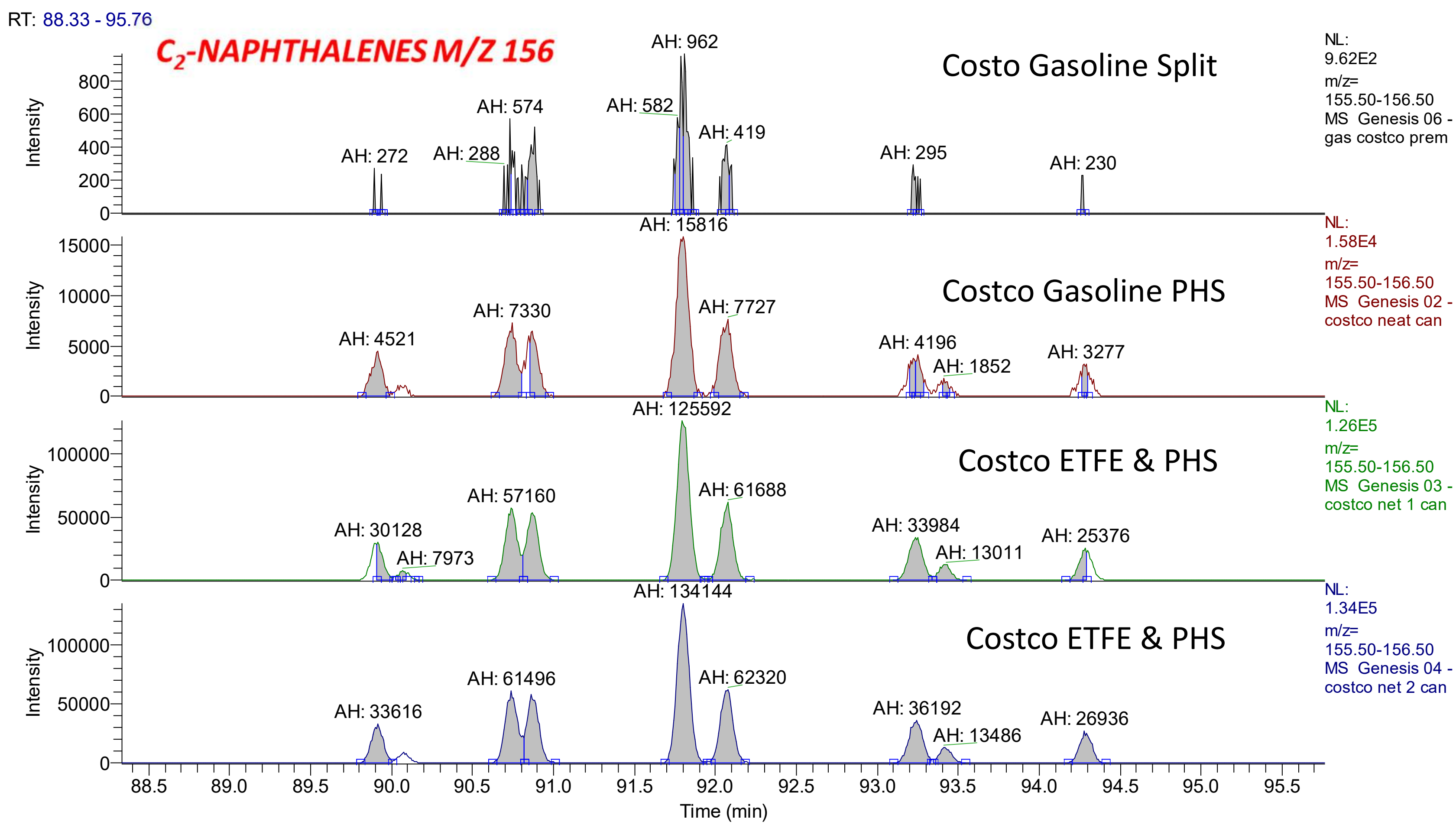


RT: 51.03 - 81.70
ALKYLATED BENZENES M/Z 119 + ISTD
ESSO GASOLINE SPLIT
AH: 128056
AH: 144384
AH: 102856
NL: 1.44E5
m/z= 118.50-119.50
MS Genesis 04 - gas esso reg
ESSO GASOLINE PHS
AH: 964224
AH: 1074176
AH: 774592
AH: 441315
NL: 1.07E6
m/z= 118.50-119.50
MS Genesis 02 - esso neat can
ESSO ETFE & PHS 1
AH: 1054208
AH: 1530368
AH: 1026752
AH: 1608704
AH: 935925
AH: 482914
NL: 1.61E6
m/z= 118.50-119.50
MS Genesis 03 - Esso Net 1 Can
ESSO ETFE & PHS 2
AH: 952640
AH: 1478656
AH: 1118208
AH: 1739264
AH: 1010156
AH: 445401
NL: 1.74E6
m/z= 118.50-119.50
MS Genesis 04 - esso net 2 can
Intensity
Time (min)

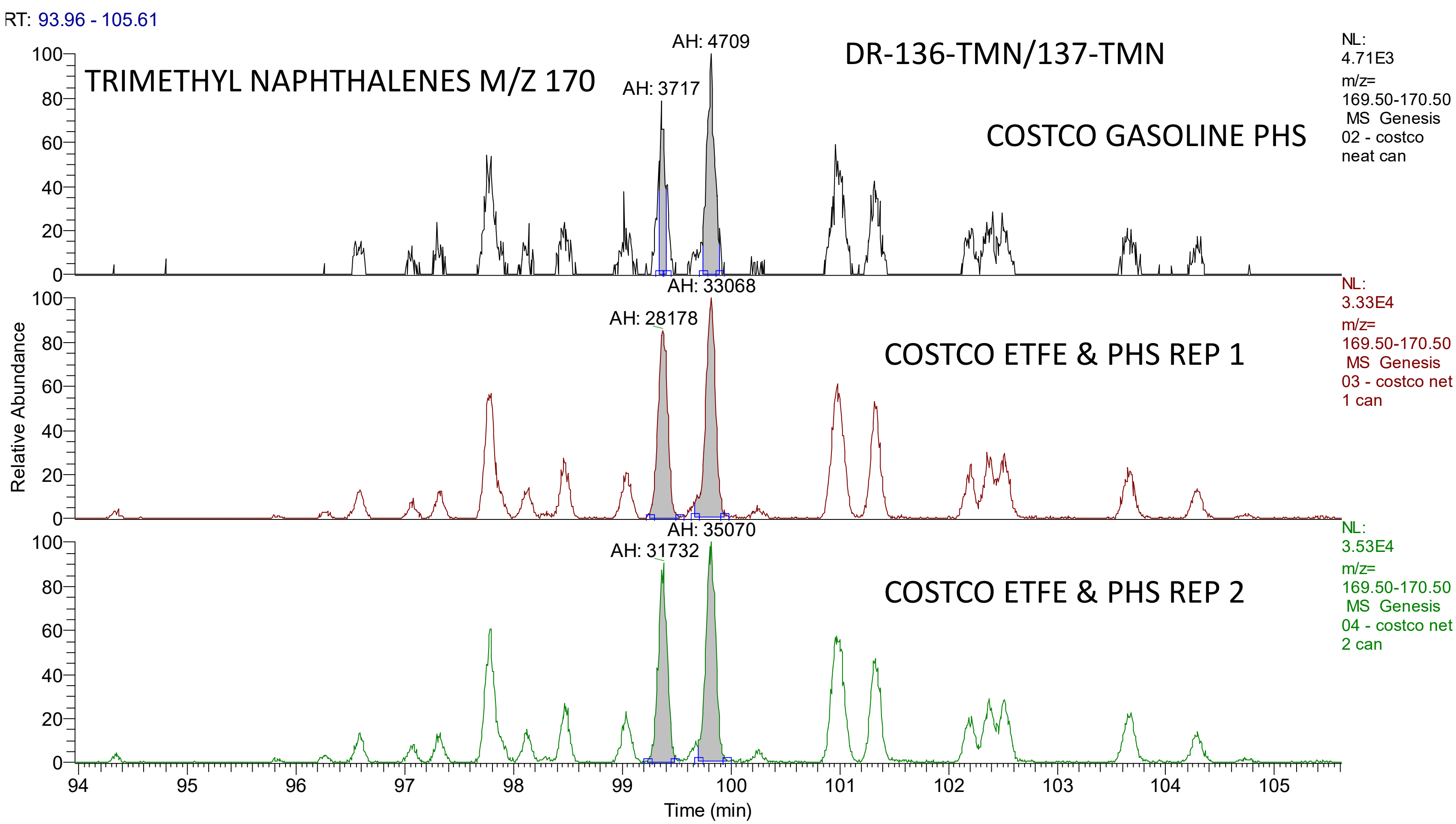


RT: 69.54 - 76.57
NAPHTHALENE M/Z 128
ESSO GASOLINE SPLIT
AH: 28656
NL: 2.87E4 m/z= 127.50-128.50 MS Genesis 04 - gas esso reg
ESSO GASOLINE PHS
AH: 149072
NL: 1.49E5 m/z= 127.50-128.50 MS Genesis 02 - Esso neat Can
ESSO ETFE & PHS 1
AH: 360350
NL: 3.61E5 m/z= 127.50-128.50 MS Genesis 03 - esso net 1 can
ESSO ETFE & PHS 2
AH: 424271
NL: 4.25E5 m/z= 127.50-128.50 MS Genesis 04 - esso net 2 can
Intensity
Time (min)


RT: 77.57 - 89.70
METHYL NAPHTHALENES M/Z 141
2-MN
1-MN
AH: 15478
AH: 8177
ESSO GASOLINE SPLIT
NL: 1.55E4 m/z= 140.50-141.50 MS Genesis 04 - gas esso reg
AH: 78465
AH: 39886
ESSO GASOLINE PHS
NL: 7.88E4 m/z= 140.50-141.50 MS Genesis 02 - Esso neat Can
AH: 305537
AH: 164405
ESSO ETFE & PHS 1
NL: 3.07E5 m/z= 140.50-141.50 MS Genesis 03 - esso net 1 can
AH: 393880
AH: 217407
ESSO ETFE & PHS 2
NL: 3.95E5 m/z= 140.50-141.50 MS Genesis 04 - esso net 2 can
Intensity
Time (min)



RT: 88.33 - 95.76
C2-NAPHTHALENES M/Z 156
Costo Gasoline Split
NL: 9.62E2 m/z= 155.50-156.50 MS Genesis 06 - gas costco prem
AH: 272
AH: 288
AH: 574
AH: 582
AH: 962
AH: 419
AH: 295
AH: 230
Costco Gasoline PHS
NL: 1.58E4 m/z= 155.50-156.50 MS Genesis 02 - costco neat can
AH: 4521
AH: 7330
AH: 15816
AH: 7727
AH: 4196
AH: 1852
AH: 3277
Costco ETFE & PHS
NL: 1.26E5 m/z= 155.50-156.50 MS Genesis 03 - costco net 1 can
AH: 30128
AH: 7973
AH: 57160
AH: 125592
AH: 61688
AH: 33984
AH: 13011
AH: 25376
Costco ETFE & PHS
NL: 1.34E5 m/z= 155.50-156.50 MS Genesis 04 - costco net 2 can
AH: 33616
AH: 61496
AH: 134144
AH: 62320
AH: 36192
AH: 13486
AH: 26936
Intensity
Time (min)


RT: 93.96 - 105.61
TRIMETHYL NAPHTHALENES M/Z 170
DR-136-TMN/137-TMN
AH: 4709
AH: 3717
COSTCO GASOLINE PHS
NL: 4.71E3 m/z= 169.50-170.50 MS Genesis 02 - costco neat can
AH: 33068
AH: 28178
COSTCO ETFE & PHS REP 1
NL: 3.33E4 m/z= 169.50-170.50 MS Genesis 03 - costco net 1 can
AH: 35070
AH: 31732
COSTCO ETFE & PHS REP 2
NL: 3.53E4 m/z= 169.50-170.50 MS Genesis 04 - costco net 2 can
Relative Abundance
Time (min)

	ESSO NEAT			COSTCO NEAT			PIONEER NEAT		
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
2-MN/1-MN	1.90	0.09	4.74	2.00	0.08	4.13	2.17	0.06	2.53
2-EN/26 + 27-DMN	0.33	0.02	5.52	0.40		0 RPD	0.39		2.6 RPD
16-DMN/13 + 17-DMN	0.46	0.01	1.37	0.47		0 RPD	0.44		2.3 RPD
DR-B/2-EN	0.78	0.10	12.54	0.26		3.9 RPD	0.93		6.45
NAPH/DODECANE	0.71	0.09	12.98	NA	NA	NA	6.75	0.55	8.12
	ESSO NEAT PHS			COSTO NEAT PHS			PIONEER NEAT PHS		
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
2-MN/1-MN	2.02	0.07	3.63	1.95	0.03	1.42	2.18	0.07	3.00
2-EN/26 + 27-DMN	0.48	0.08	16.66	0.56	0.04	7.46	0.56	0.01	2.04
16-DMN/13 + 17-DMN	0.50	0.04	8.28	0.42	0.02	5.23	0.48	0.00	0.43
DR-B/2-EN	0.76	0.06	8.35	0.92	0.03	2.88	0.25	0.01	4.38
NAPH/DODECANE	0.34	0.07	19.60	22.11	2.73	12.34	3.59	0.15	4.29
137-TMN/136-TMN	1.08	0.12	11.14	0.84	0.09	10.73	0.85	0.03	3.52
	ESSO ETFE PHS			COSTCO ETFE PHS			PIONEER ETFE PHS		
2-MN/1-MN	1.81	0.07	3.61	1.86	0.03	1.78	2.00	0.04	2.15
2-EN/26 + 27-DMN	0.46	0.03	6.74	0.51	0.01	2.47	0.50	0.00	0.26
16-DMN/13 + 17-DMN	0.47	0.03	6.13	0.43	0.01	2.30	0.48	0.01	3.02
DR-B/2-EN	0.81	0.03	4.05	0.87	0.02	1.90	0.24	0.01	3.97
NAPH/DODECANE	0.26	0.04	14.48	15.63	3.23	20.69	2.28	0.47	20.50
137-TMN/136-TMN	0.90	0.05	5.19	0.88	0.04	4.12	0.94	0.01	0.99

	ETFE Nets Followed by PHS (n = 6)								
		ESSO			COSTCO			PIONEER	
m/z 105	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
135TMB/124TMB	0.18	0.02	12.45	0.19	0.03	17.95	0.18	0.02	12.09
1M3PB/1M4PB	***1.92***	0.05	2.64	***1.75***	0.04	2.46	***1.79***	0.05	2.66
1M2EB/1M3EB	0.67	0.12	17.68	0.58	0.02	3.97	0.62	0.03	4.75
1M3EB/1M4EB	***2.38***	0.08	3.17	***2.05***	0.05	2.25	***2.16***	0.09	4.01
1M2EB/1M4EB	***1.61***	0.32	19.78	***1.18***	0.06	4.80	***1.34***	0.05	3.51
1M2EB/123TMB	***0.29***	0.06	19.69	***0.45***	0.09	20.36	***0.33***	0.06	16.69
123-TMB/124TMB	***0.48***	0.03	7.18	***0.39***	0.05	13.01	***0.41***	0.04	9.03
1M2EB/124-TMB	0.14	0.02	14.46	0.17	0.04	21.09	0.13	0.02	15.07
1M3EB/124-TMB	0.21	0.06	30.10	0.30	0.07	21.59	0.22	0.03	12.11
		ESSO			COSTCO			PIONEER	
m/z 119	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
123TMB/124TMB	***0.86***	0.06	6.70	***0.69***	0.11	15.86	***0.87***	0.16	18.02
124TMB/123TMB	***1.16***	0.08	7.08	***1.47***	0.26	17.58	***1.18***	0.23	19.05
14M2EB/12M4EB	0.54	0.08	15.17	0.49	0.03	5.54	0.49	0.06	11.70
1245/1235	0.60	0.09	15.38	0.63	0.03	4.91	0.63	0.04	5.66
		ESSO			COSTCO			PIONEER	
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
DR-naphthalene/dodecane	***0.26***	0.04	14.48	***15.63***	3.23	20.69	***2.28***	0.47	20.50
		ESSO			COSTCO			PIONEER	
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
DR-2MN/1-MN	***1.81***	0.07	3.61	***1.86***	0.03	1.78	***2.00***	0.04	2.15
		ESSO			COSTCO			PIONEER	
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
2-EN/26 + 27-DMN	0.46	0.03	6.74	0.51	0.01	2.47	0.50	0.00	0.26
16-DMN/13 + 17-DMN	0.47	0.03	6.13	0.43	0.01	2.30	0.48	0.01	3.02
DR-B/2-EN	***0.81***	0.03	4.05	***0.87***	0.02	1.90	***0.24***	0.01	3.97
		ESSO			COSTCO			PIONEER	
137-TMN/136-TMN	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
	0.90	0.05	5.19	0.88	0.04	4.12	0.94	0.01	0.99
Average RSD%			11.14			9.72			8.70

USEABLE SOURCE APPORTIONMENT RATIOS ETFE & PHS

MASS/CHARGE (M/Z)	RATIO
105	1M3PB/1M4PB
105	1M3EB/1M4EB
105	123-TMB/124-TMB
119	1245-TeMB/1235-TeMB
128,57	NAPHTHALENE/UNDECANE
141	2-MN/1-MN
156	2-EN/26+27-DMN
156	16-DMN/13+17-DMN
154,156	B/2-EN
170	137-TMN/136-TMN
117,131	2-ME-INDAN/1-ME-INDAN

Quality Control

	Naphthalene-d8
	Percent Recovery
Costco - Neat PHS	118
Costco - ETFE & PHS Rep 1	108
Costco -ETFE & PHS Rep 2	105
Pioneer - Neat PHS	103
Pioneer -ETFE & PHS Rep 1	96
Pioneer - ETFE & PHS Rep 2	104
Esso - Neat PHS	88
Esso - ETFE & PHS Rep 1	90
Esso - ETFE & PHS Rep 2	88

CONCLUSIONS

- Extraction of water samples containing low levels of gasoline can be performed using ETFE netting
- The gasoline is extracted and concentrated using passive headspace analysis
- Analyses are performed using GC/MS (scanning or SIM) using a 100 m PONA column
- RSDs and RPDs consistent with an alternative method namely purge & trap GC/MS
- The netting actually concentrates some analytes from water, namely alkylated benzenes, alkylated naphthalenes, alkylated indans, etc.
- This results in greater signal to noise response and increases precision

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