Forensic Characterization of Gasoline Releases to the Environment

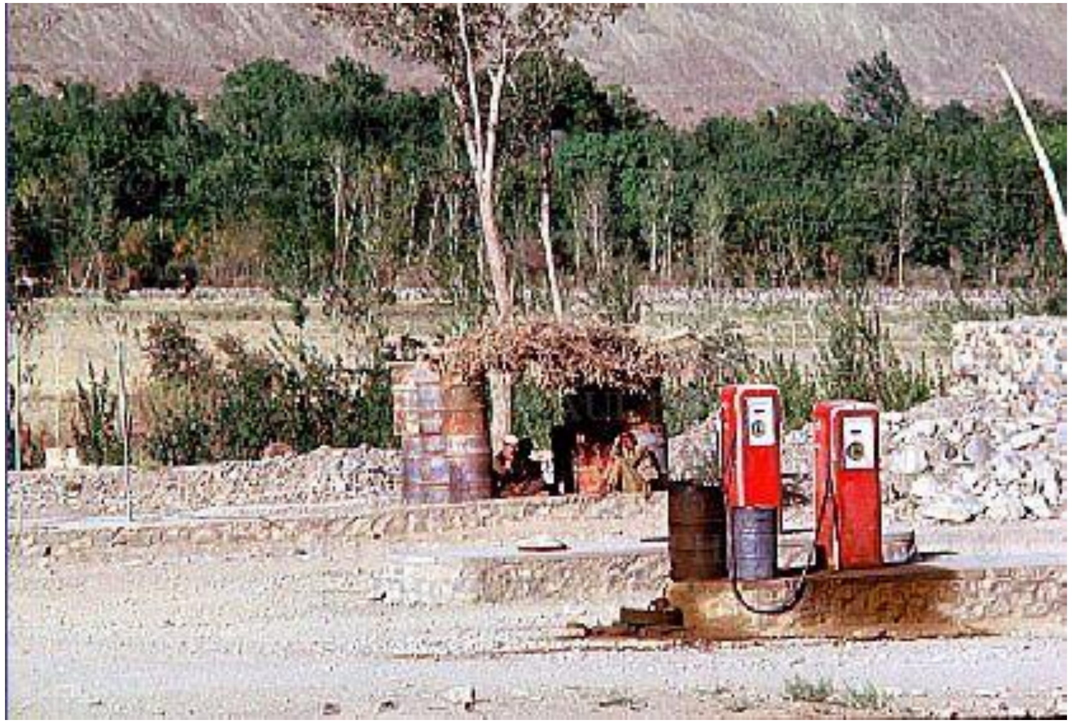
Detlef A. Birkholz[1], Chuck Jochems[2] and Milan Ratitsch[3]

1. D.A. Birkholz, Analytical Consultant, Inc., Edmonton, AB.
2. Hemmera, Burnaby, B.C.
3. Paracel Laboratories, Calgary, AB.

Gasoline

- First recorded use in a four stroke engine, 1876
- Modern gasolines bear little resemblance to earlier gasolines which were straight-run naphtha and batch distilled from crude oil
- Carbon range is n-C_4 – n-C_{13}
- Gasoline reported to contain 361 individual compounds

Analytical Methods



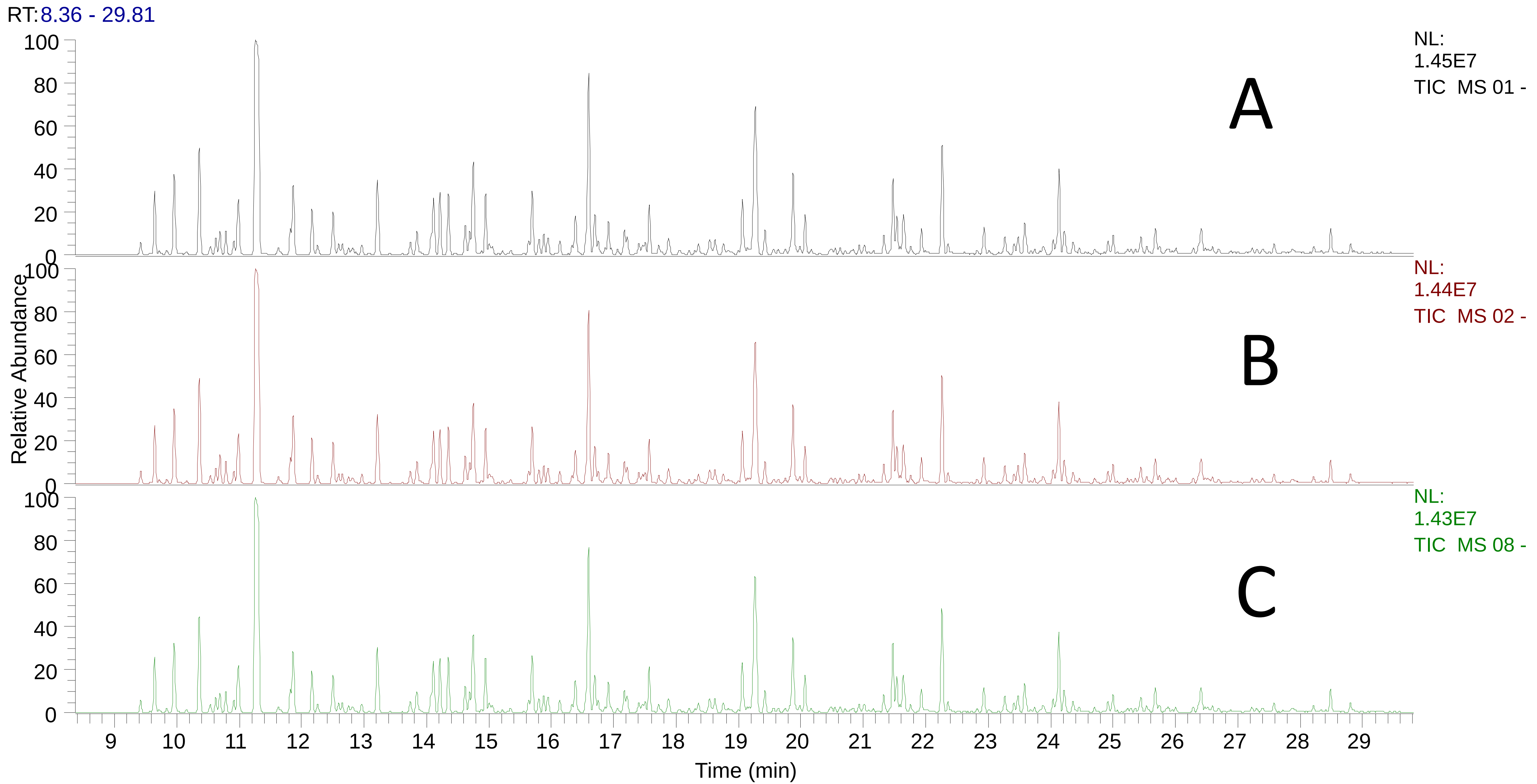
- Most common method of analysis is for PIANO compounds (Paraffin's, Iso-paraffins Aromatics, Naphthenes and Olefins). Industry standard
- Method found favorable for analysis of LNAPLs, soils and water
- High resolution capillary column (PONA 50 – 100 m)
- Based upon chromatographic conditions run times of 67.5 to 140 min
- GC/FID and GC/MS scanning (m/z 35 – 350).
- Based upon EPA methods (8015 and 8270) and ASTM methods (D 6729).
- Still the method of choice based upon most recent book “Oil Spill Environmental Forensics Case Studies” Eds. S.A. Stout and Z. Wang, 2018

Information commonly sought

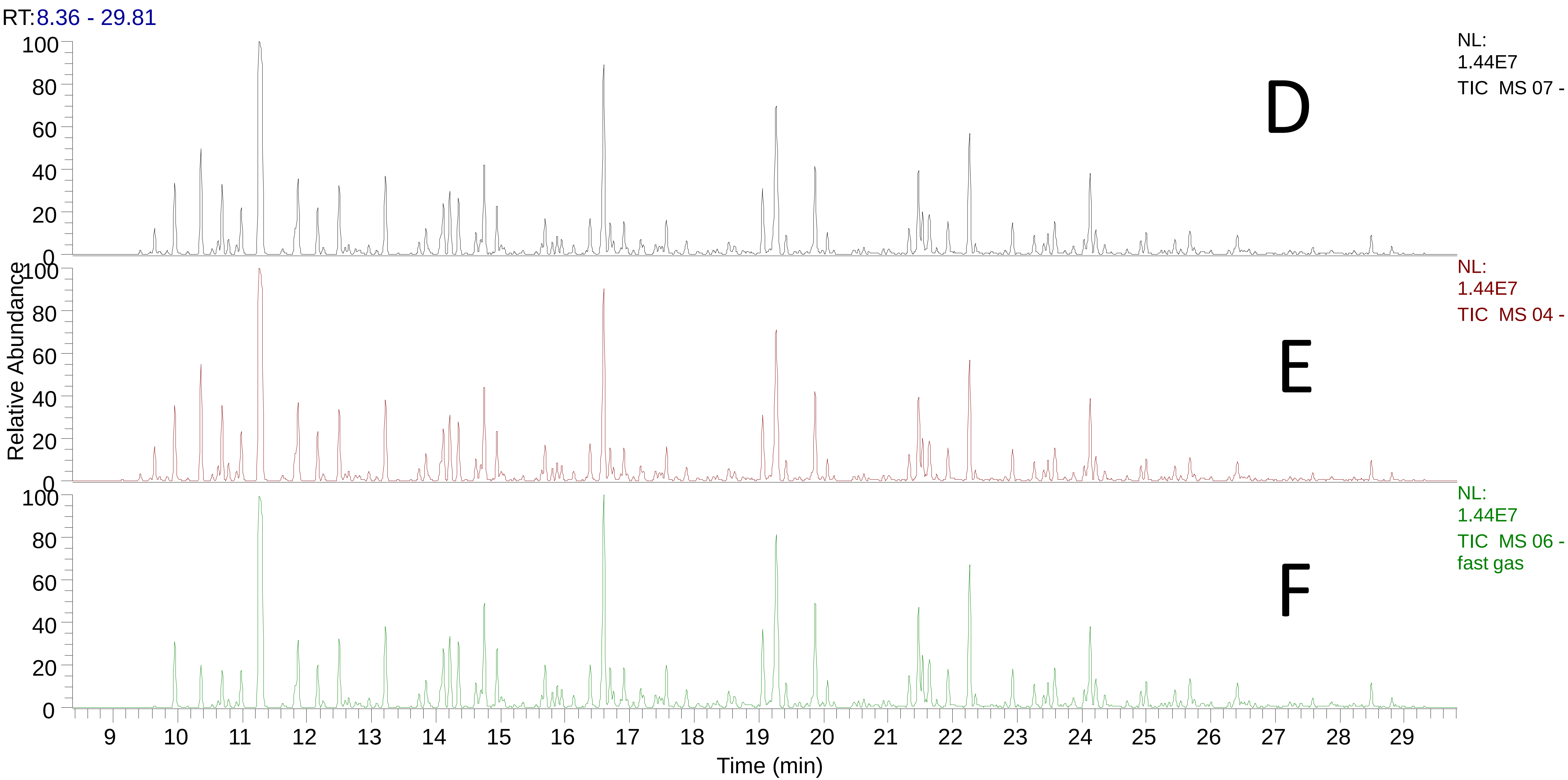
- Composition based on PIANO analysis (paraffin's, isoparaffins, aromatics, naphthenes and olefins).
- PIANO tells us a lot about the refinery process
- Total organic lead concentration
- Identification of lead alkyl types
- Presence of oxygenate additives (MTBE, TAME, ethanol, methanol, etc.)
- Bulk 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.).

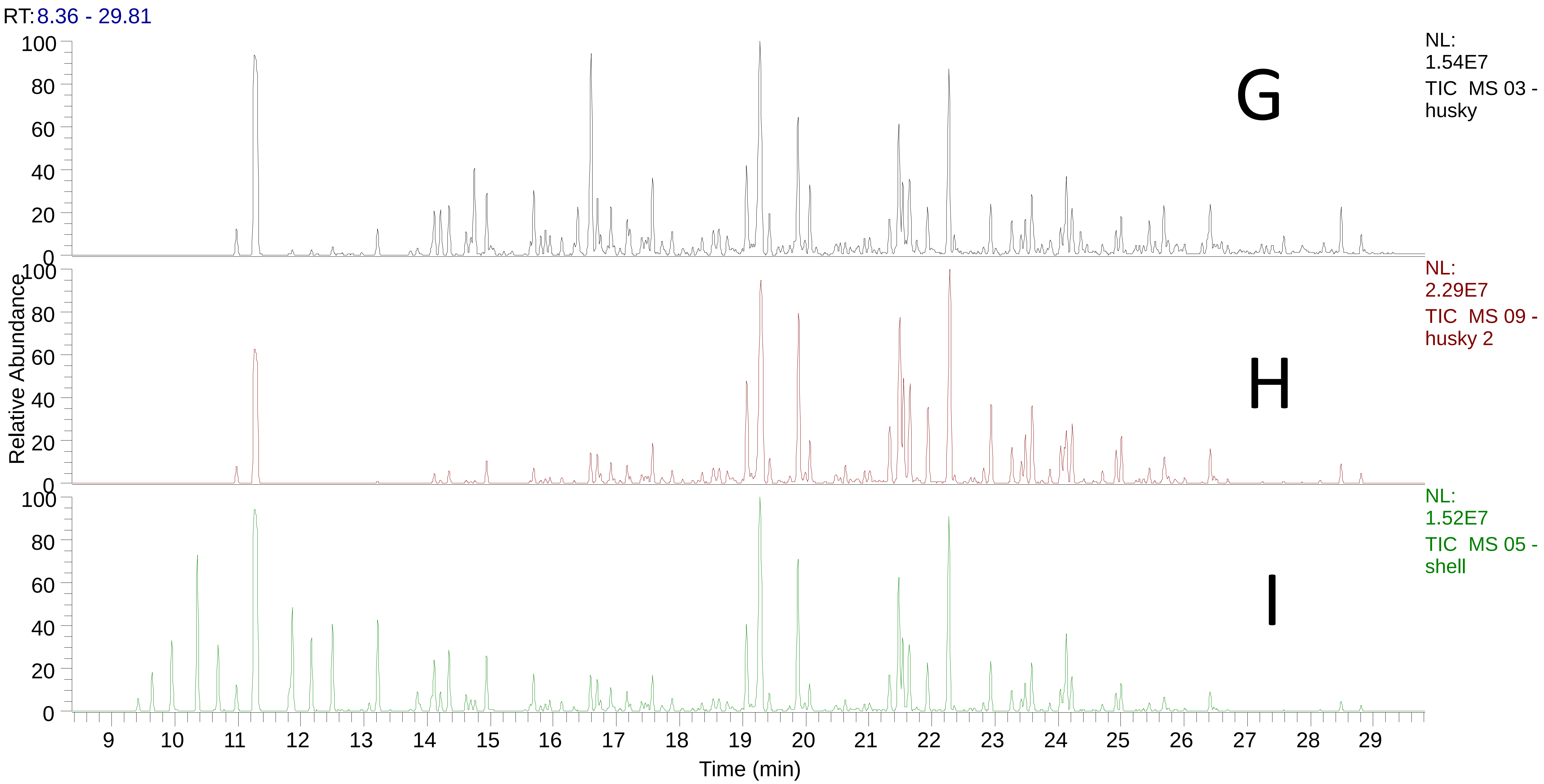
Chromatographic comparisons

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



RT: 8.36 - 29.81
NL: 1.45E7
TIC MS 01 -
A
NL: 1.44E7
TIC MS 02 -
B
NL: 1.43E7
TIC MS 08 -
C
Relative Abundance
0
20
40
60
80
100
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Time (min)

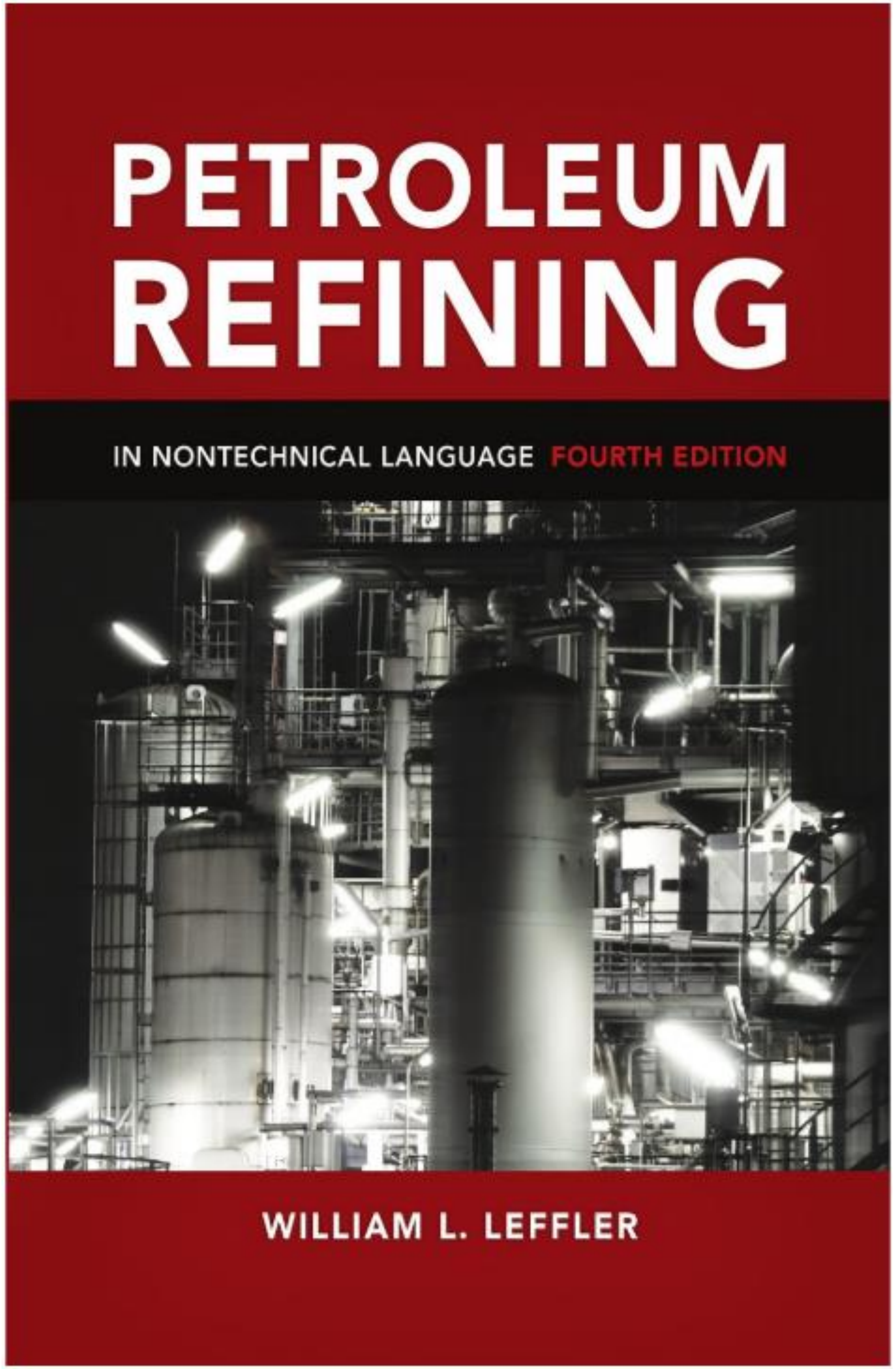

RT: 8.36 - 29.81
NL: 1.44E7
TIC MS 07 -
D
NL: 1.44E7
TIC MS 04 -
E
NL: 1.44E7
TIC MS 06 - fast gas
F
Relative Abundance
0
20
40
60
80
100
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Time (min)



RT: 8.36 - 29.81
NL: 1.54E7
TIC MS 03 - husky
G
NL: 2.29E7
TIC MS 09 - husky 2
H
NL: 1.52E7
TIC MS 05 - shell
I
Relative Abundance
0
20
40
60
80
100
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Time (min)

Application of Process Forensics in Gasoline Chemical Fingerprinting

- Finished automotive gasoline produced by any given refiner has always been blended from multiple gasoline component streams coming out of various process units within a refinery.
- Some refineries are simple and blend in few components, and some are complex and blend in many components.
- As many as 10 different gasoline components might be blended together to meet finished gasoline specifications (Stout et al., 2001)
- Because of this fact, the blending of gasoline at a modern refinery can impart a significant amount of character and diagnostic information to finished gasoline produced.
- Understanding these processes and their implications on the chemical character of the gasoline can be valuable to the forensic investigation of fugitive gasoline.



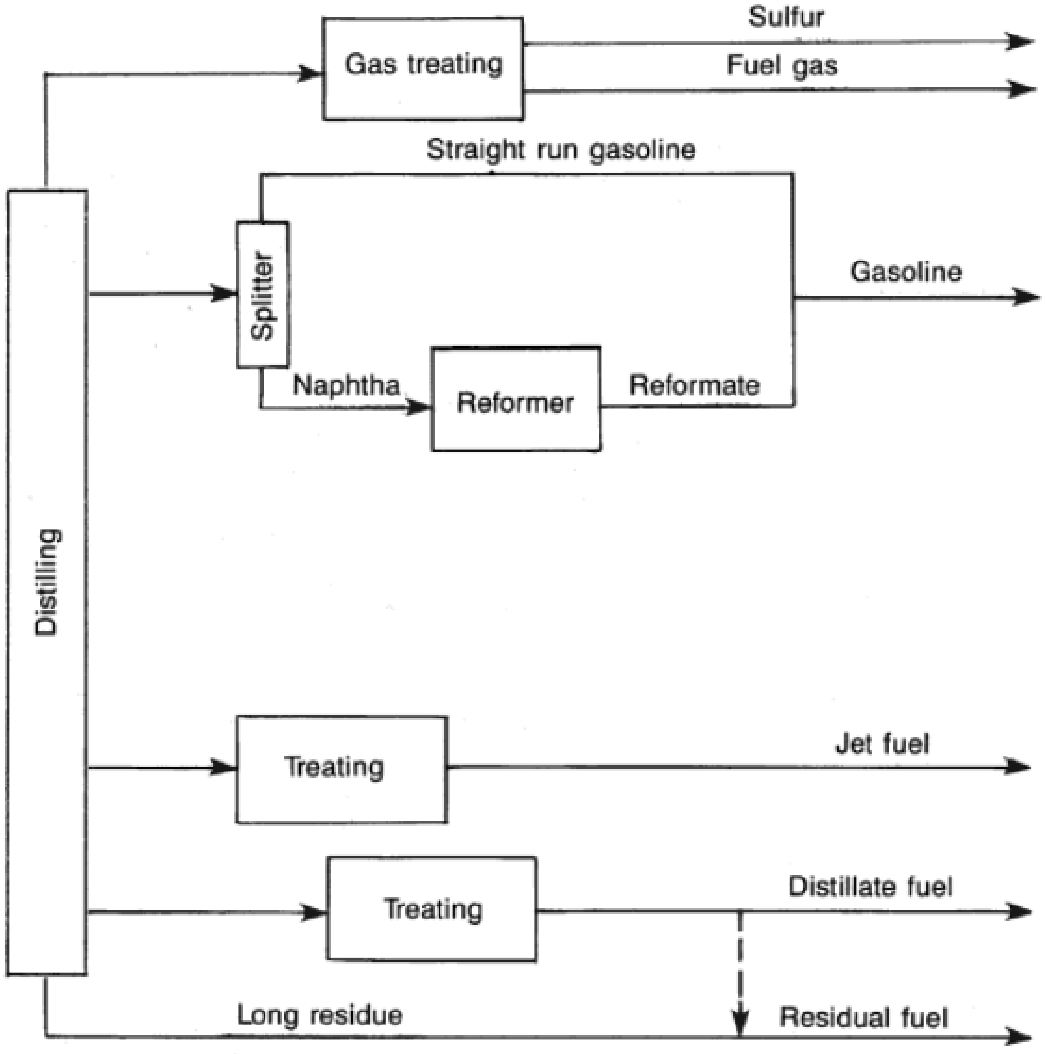


Fig. 20–1. Simple or hydroskimming refinery

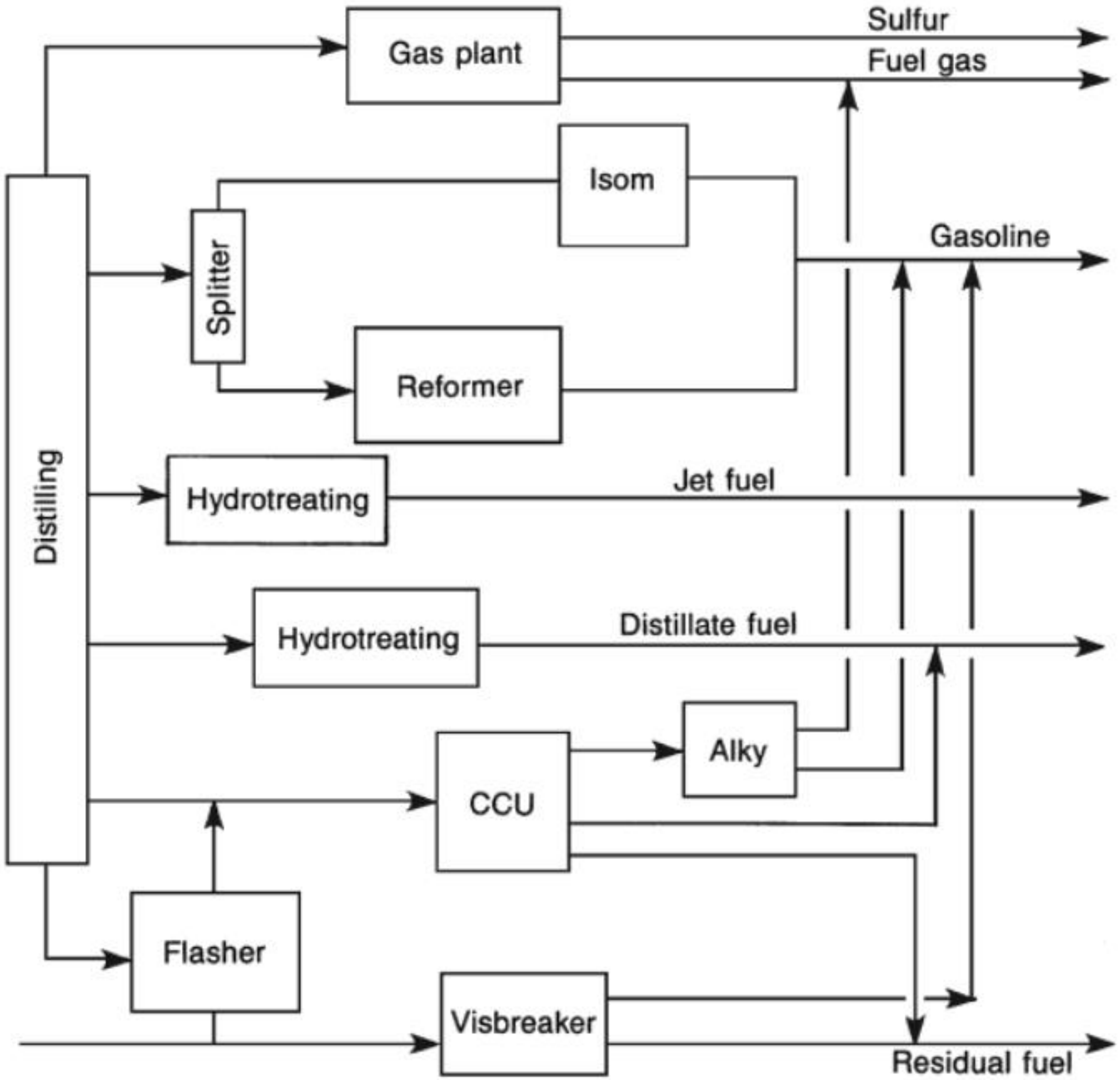


Fig. 20–2. Complex or gasoline refinery

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 isopentane 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/methyl cyclohexane
- 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/n-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 alkyl benzenes
- 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

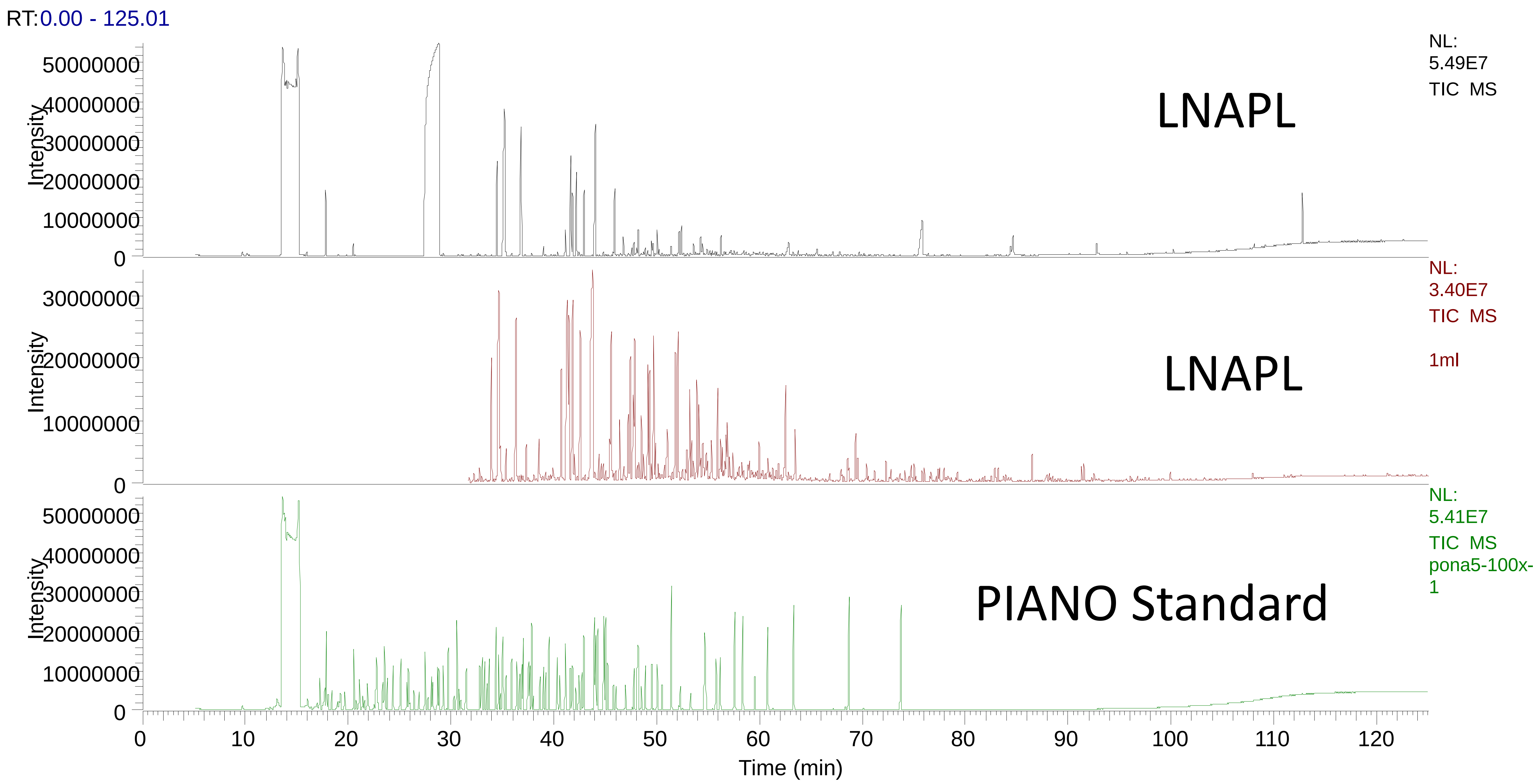
PROCESS FORENSICS

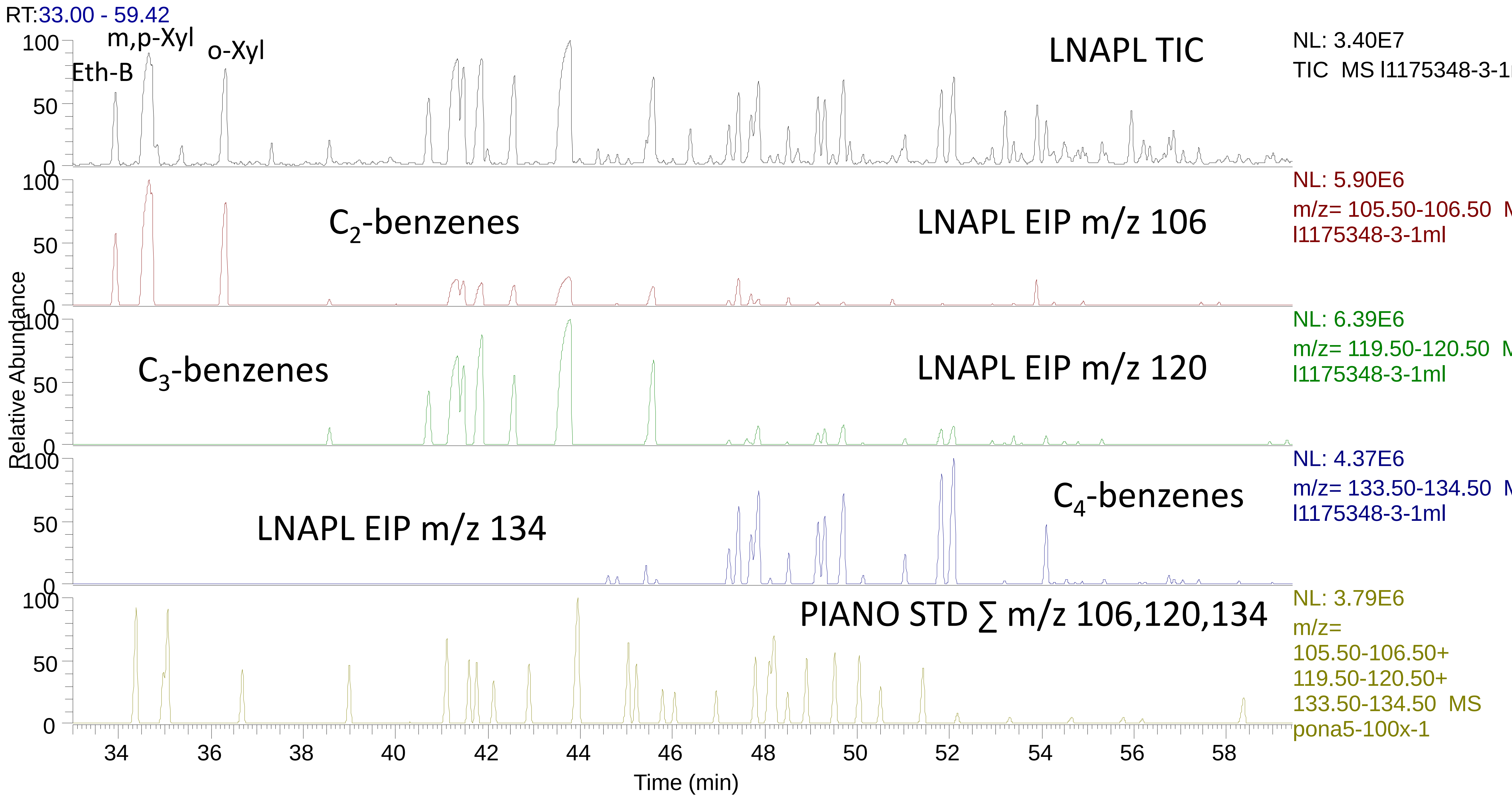
- Source A, B, C derived from a common source
- Source D,E – derived from common source
- Source F, G, H, I derived from differing sources

- Data fits with chromatograms of gasoline samples, i.e. process forensics supports the chromatographic data.

REALITY CHECK

- Forensic analyses of gasoline rarely performed
- Usually associated with property development on a contaminated site
- Phase I audit may reveal several past service stations and sources of contamination
- Done to determine parties responsible in order delineate liability
- Usually done long after operations ceased.
- Source likely not possible to collect
- Best you can hope for is LNAPL and compare with samples taken on the site to determine if one or more sources

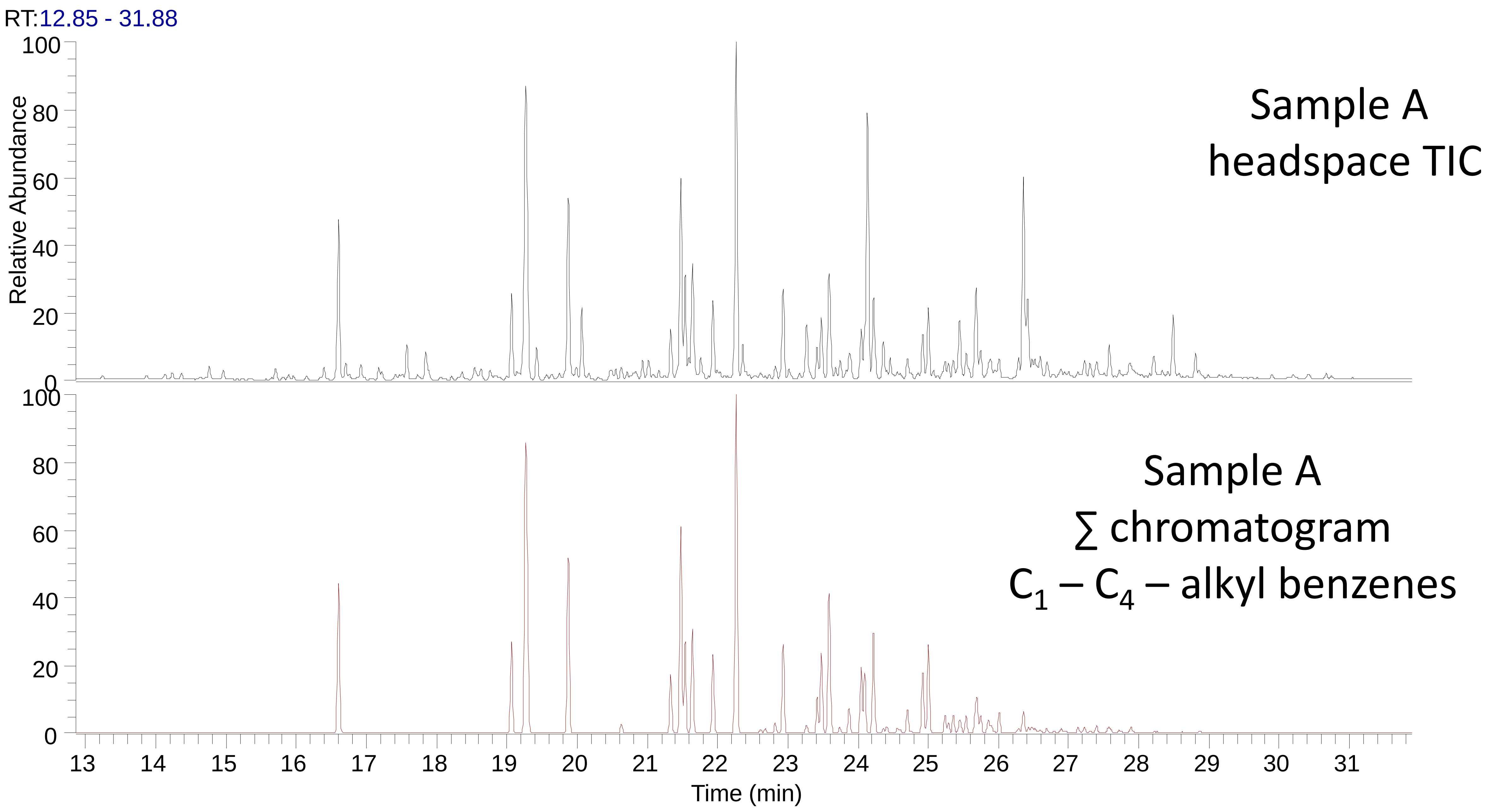

RT:0.00 - 125.01
NL:
5.49E7
TIC MS
LNAPL
NL:
3.40E7
TIC MS
1ml
LNAPL
NL:
5.41E7
TIC MS
pona5-100x-
1
PIANO Standard
Intensity
Time (min)



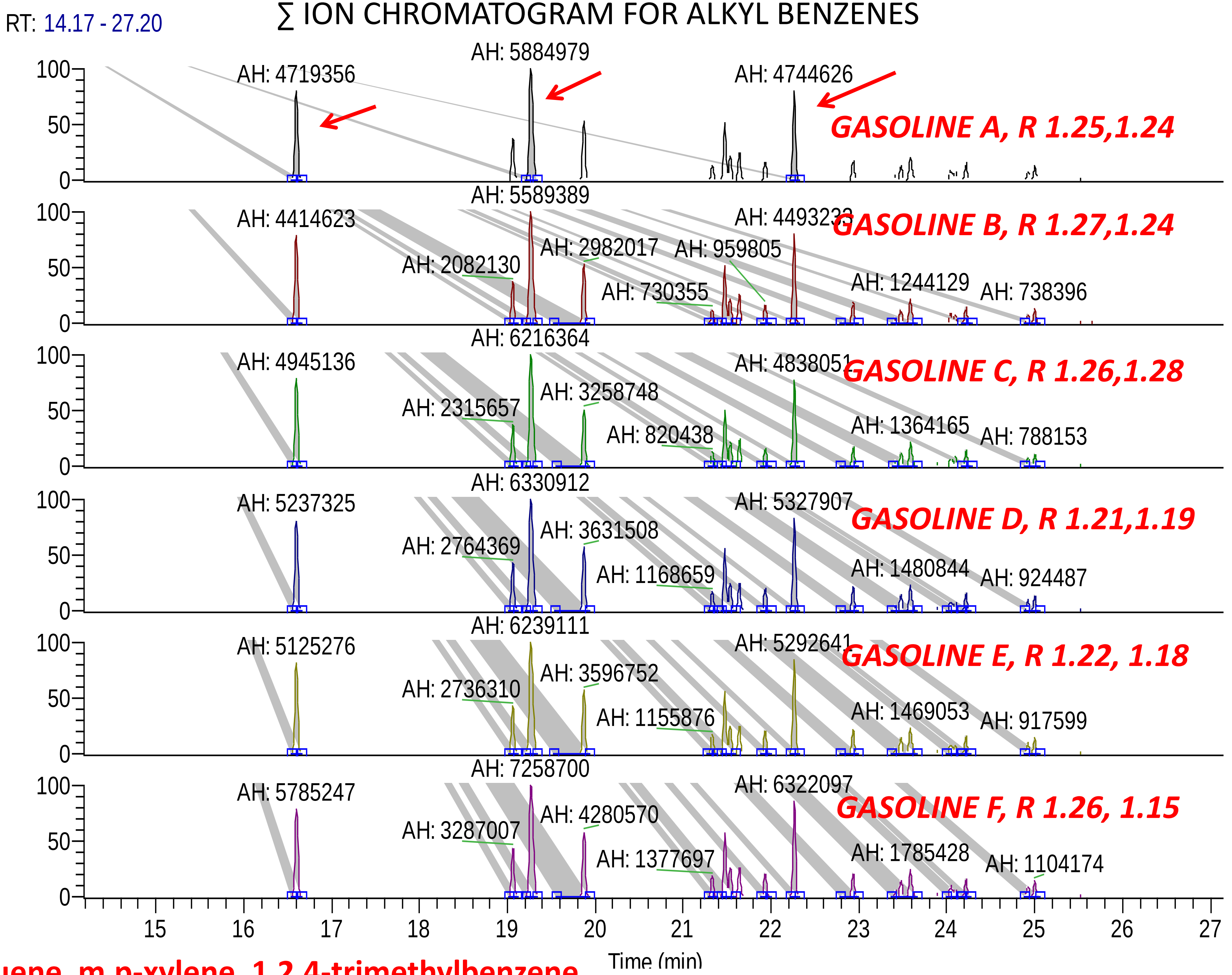
RT:33.00 - 59.42
m,p-Xyl
o-Xyl
Eth-B
LNAPL TIC
NL: 3.40E7
TIC MS l1175348-3-1
C$_2$-benzenes
LNAPL EIP m/z 106
NL: 5.90E6
m/z= 105.50-106.50
l1175348-3-1ml
C$_3$-benzenes
LNAPL EIP m/z 120
NL: 6.39E6
m/z= 119.50-120.50
l1175348-3-1ml
C$_4$-benzenes
LNAPL EIP m/z 134
NL: 4.37E6
m/z= 133.50-134.50
l1175348-3-1ml
PIANO STD ∑ m/z 106,120,134
NL: 3.79E6
m/z=
105.50-106.50+
119.50-120.50+
133.50-134.50 MS
pona5-100x-1
Relative Abundance
Time (min)

Catalytic Reforming

- All regulatory era refineries employ some form of cracking gasoline
- Catalytic reporting (reformates) are major blending stocks for most automotive gasolines
- There are often multiple catalytic reforming units operating at a modern refinery under slightly different conditions, thereby producing reformates with slightly different conditions.
- The higher boiling aromatic components within reformate, e.g. C_3 and C_4 – alkyl benzenes and alkylated naphthalenes are relatively stable and can provide some basis to distinguish gasolines.


RT:12.85 - 31.88
Relative Abundance
100
80
60
40
20
0
Sample A
headspace TIC
100
80
60
40
20
0
Sample A
∑ chromatogram
C1 – C4 – alkyl benzenes
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
Time (min)

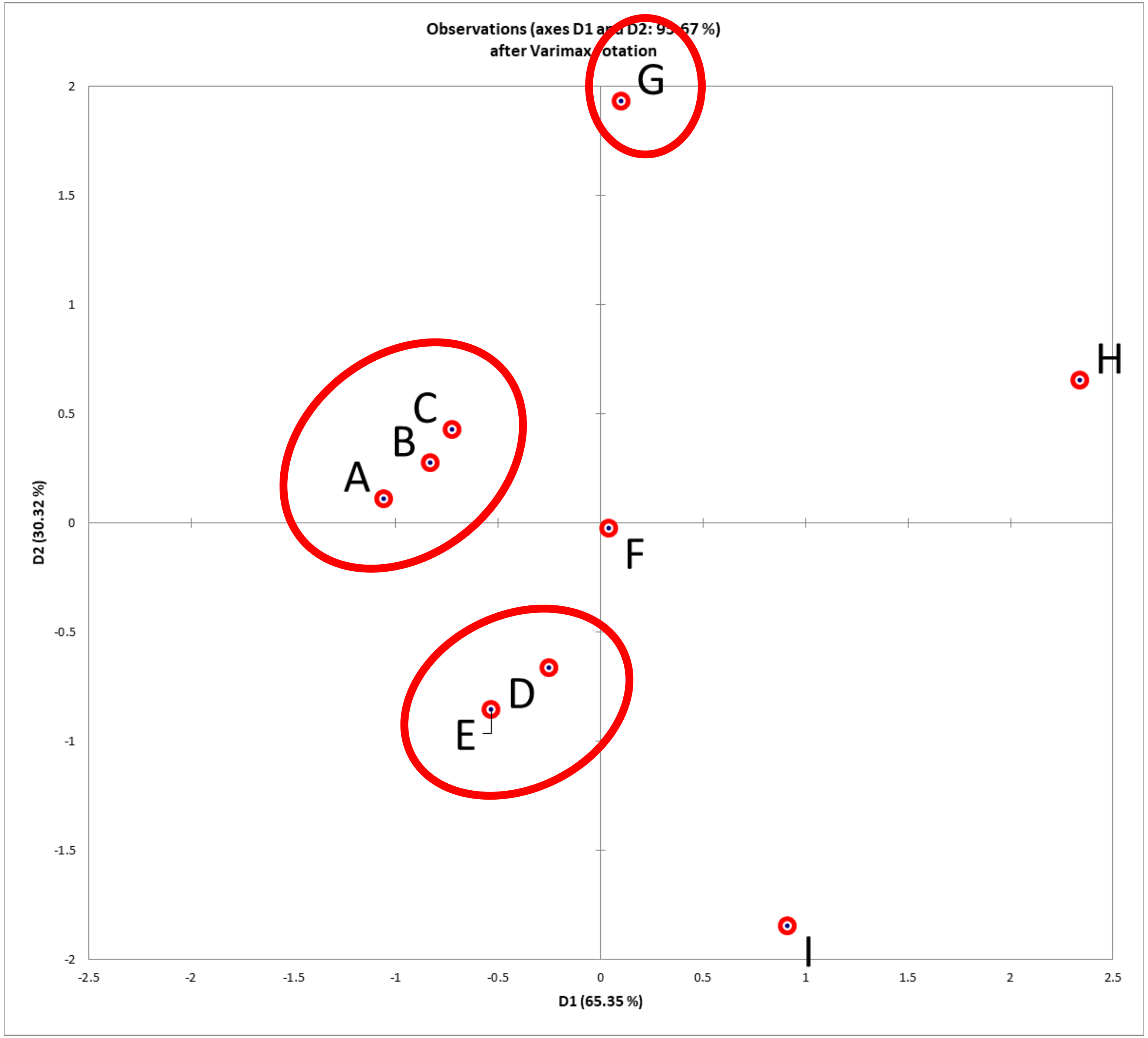
∑ ION CHROMATOGRAM FOR ALKYL BENZENES



Toluene, m,p-xylene, 1,2,4-trimethylbenzene

Methods

- Collected data for 34 alkyl benzenes obtained via headspace for A - I
- Data transformed (Aitchison)
- PCA generated (Varimax rotation)
- AHC analysis using factor scores and Mahalanobis distance
- Software: XLSTAT


Observations (axes D1 and D2: 95.67 %)
after Varimax rotation
D1 (65.35 %)
D2 (30.32 %)
A
B
C
D
E
F
G
H
I
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2

Dissimilarity: Mahalanobis distance						
Class	1	2	3	4	5	6
Objects	3	1	2	1	1	1
Sum of we	3	1	2	1	1	1
Within-cla	0.100	0.000	0.085	0.000	0.000	0.000
Minimum	0.086	0.000	0.206	0.000	0.000	0.000
Average d	0.235	0.000	0.206	0.000	0.000	0.000
Maximum	0.330	0.000	0.206	0.000	0.000	0.000
	A	G	E	I	F	H
	B		D			
	C					

Conclusions

- Determining how a gasoline is made (refinery process) provides invaluable information when delineating sources of fugitive gasoline emissions.
- This is particularly useful when you are able obtain LNAPL samples or even tank samples.
- More often than not, LNAPL samples are not available. Sheens on top of groundwater and/or contaminated soil are all that you have to work with.
- Many of the PIANO analytes, used to delineate process design are gone due to weathering (evaporation, water washing, and biodegradation).

Conclusions

- Alkylated benzenes, are abundant, even after extreme weathering.
- Combinations of straight run gasoline (distillation) and reformate can result in various formations of alkyl benzenes.
- Alkyl benzene distribution may be useful to the forensic chemist in delineating sources of fugitive emissions.
- We have shown that chromatograms of fuel and process forensics have identified similarities and differences from nine gasoline samples.
- Data obtained using headspace analysis, followed by chemometric analysis of the alkyl benzene data provided similar conclusions to that obtained using process forensics and chromatography.

Conclusion

- For contaminated sites which have undergone extreme weathering and for which samples to work with are limited (no or little LNAPL, possible sheens on groundwater or only soil contamination) collection of data using alkybenzenes may be of value in delineating sources of fugitive gasolines.
- Alkylated benzene data as well as alkylated naphthalene data is currently used in arson investing(2003ations. Many of the samples collected are highly weathered (Fire Debris Analysis, Eds. Stauffer, Dolan and Newman, Academic Press, 2008); Sandercock and Pasquier (2003), Forensic Science International, 134: 1-10.

Many outstanding forensic experts contributed to this book

Butterworth-Heinemann is an imprint of Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States


Thank you

Contact Information

- **D.A. Birkholz, Analytical Consultant, Inc.**
  Phone: (587) 597-5197
  Email: birkholz@ualberta.ca
- **<u>In Calgary call</u>**: **Paracel Laboratoreis**:
  c/o Dr. Milan Ralitsch
- 1423 – 45 Avenue N.E., Unit F
  Calgary, AB T2E 2P3
  Phone: (403) 776-4443
  Email: MRalitsch@paracellabs.com