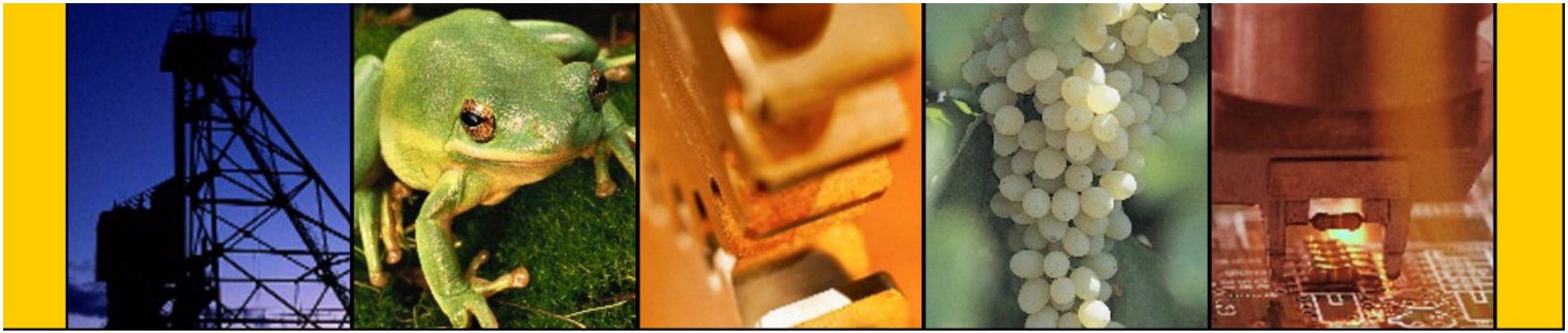
ALS Laboratory Group

ANALYTICAL CHEMISTRY & TESTING SERVICES

Environmental Division



Age dating a heating oil release: investigations into liability ownership following a spill and associated reclamation

D.A. Birkholz, MSc, PhD, P.Chem
M. Flynn – Rochon Engineering

Right solutions….

….Right partner

Background

- Fuel tank, containing heating oil was found to have leaked during investigation.
- Contamination of large amount of area observed
- Following reporting to provincial regulators a costly reclamation ordered
- Current owner of property liable (buyer beware!)
- Owner claimed that he never used the tank

Background

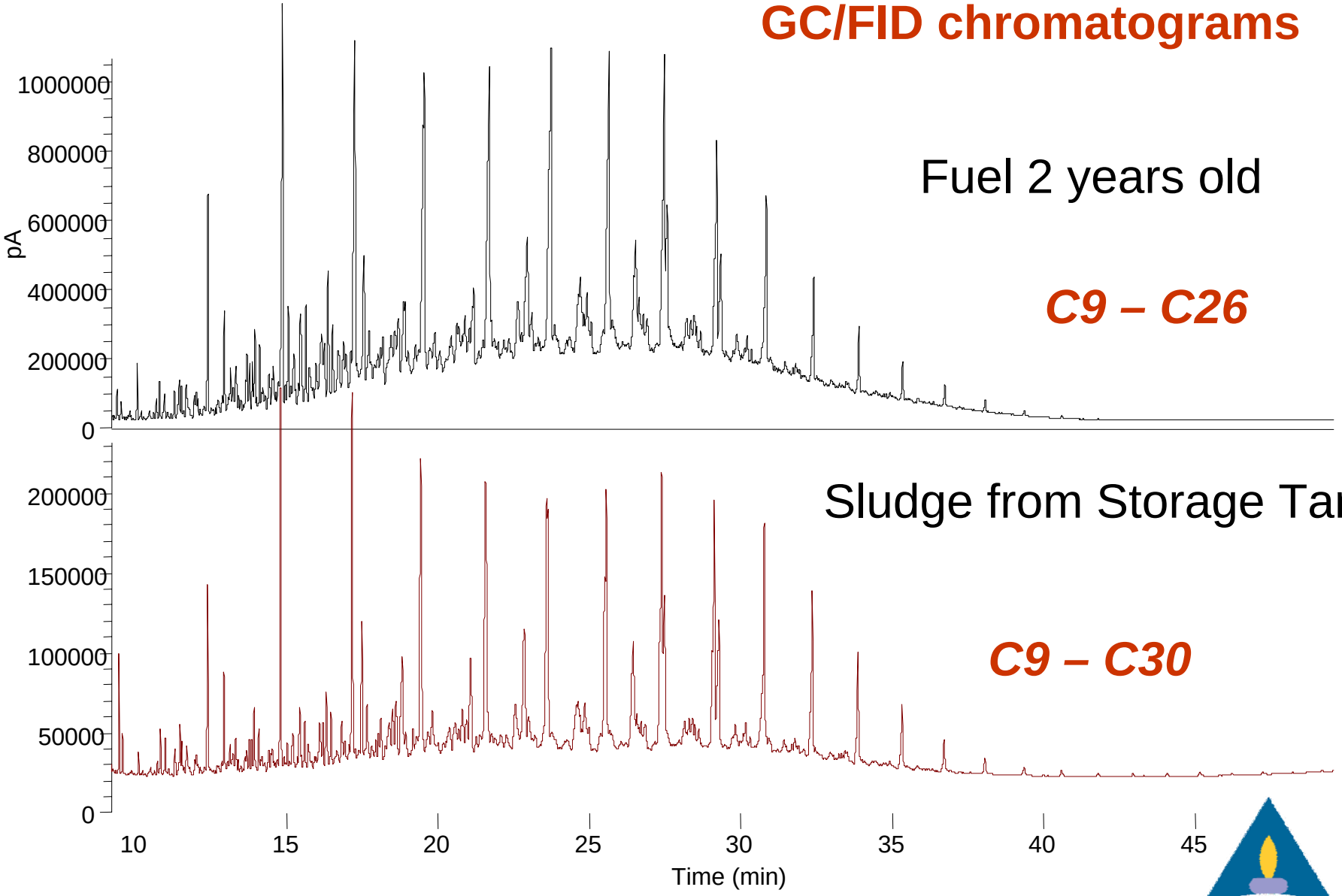
- At issue is the nature and age of oil in the tank
- If it could be proven the oil was at least 10 years old then liability could shift to previous owner. Time of property transfer
- Failing to report a spill may also result in a prosecution and further vindication for the client.
- Phase I audit by consultant suggested the fuel was at least 30 years old.
- ALS commissioned to prove it

Methods

- **Received the following samples:**
- **2 – year old home heating oil (independent source)**
- **Sludge from tank on property (alleged source of spill).**
- **An aliquot of fuel (50 mg) diluted to 10 mL with DCM**
- **An aliquot of sludge (1.0 g) was diluted with 100 mL DCM.**
- **Analyses performed by GC/FID and GC/MS (scanning and SIM)**

RT 9.21 - 49.54

GC/FID chromatograms

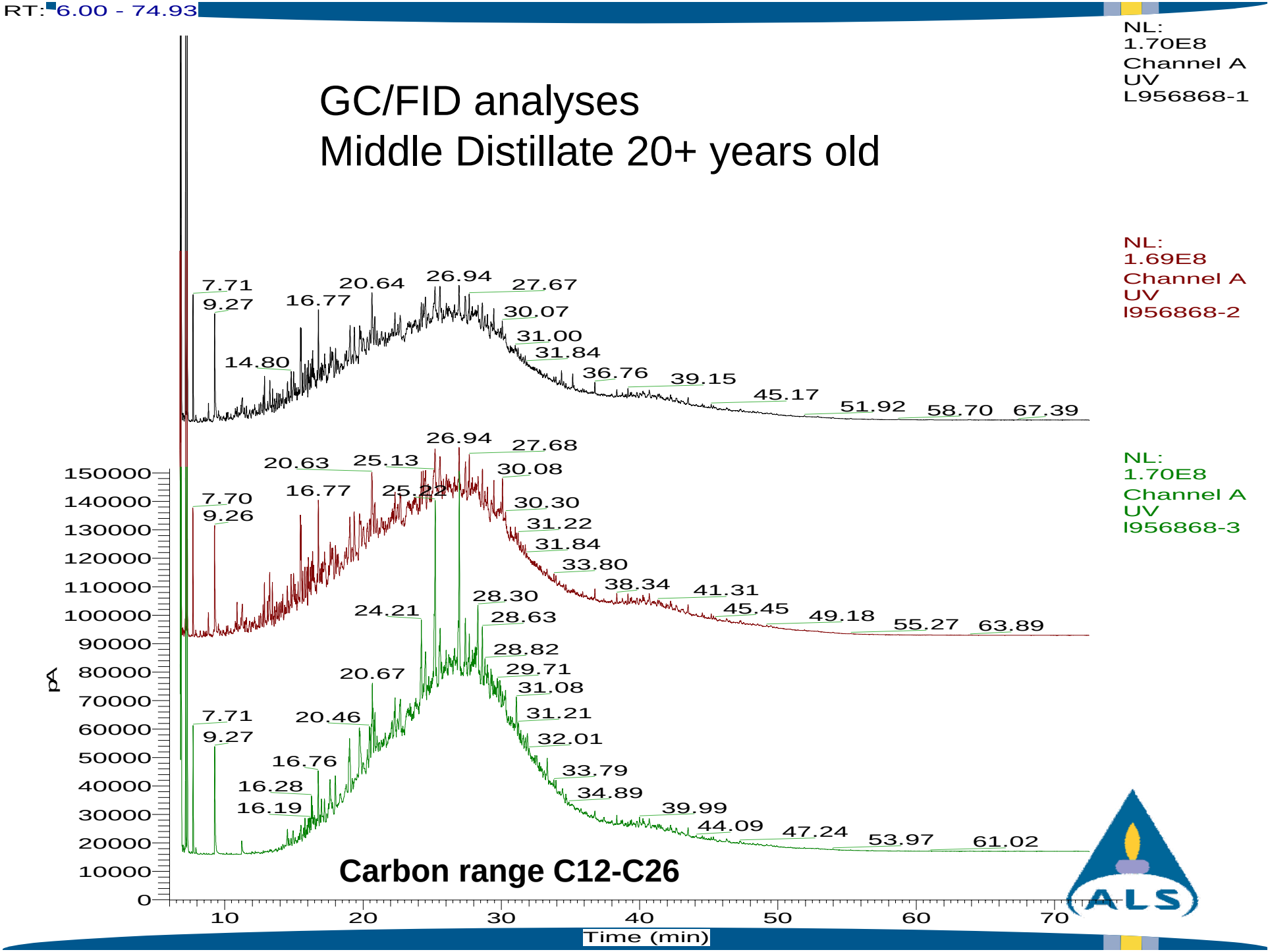


Fuel 2 years old

C9 – C26

Sludge from Storage Tank

C9 – C30


RT: 6.00 - 74.93
NL:
1.70E8
Channel A
UV
L956868-1
NL:
1.69E8
Channel A
UV
I956868-2
NL:
1.70E8
Channel A
UV
I956868-3
GC/FID analyses
Middle Distillate 20+ years old
7.71
9.27
14.80
16.77
20.64
26.94
27.67
30.07
31.00
31.84
36.76
39.15
45.17
51.92
58.70
67.39
7.70
9.26
16.77
20.63
25.13
25.22
26.94
27.68
30.08
30.30
31.22
31.84
33.80
38.34
41.31
45.45
49.18
55.27
63.89
7.71
9.27
16.76
16.28
16.19
20.46
20.67
24.21
28.30
28.63
28.82
29.71
31.08
31.21
32.01
33.79
34.89
39.99
44.09
47.24
53.97
61.02
pA
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10
20
30
40
50
60
70
Time (min)
Carbon range C12-C26
ALS

GC/FID Data

Sample	Pristane/ Phytane	n-C_{17}/pristane	Age (years)
Fresh	1.61 ± 0.19	Ratio based on N.J. 2002-2007	
Moderate	1.73 ± 0.21		
Degraded	1.59 ± 0.23	From Oudijk, 2009	
Very degraded	1.18 ± 0.40		
2-year old fuel	1.42	1.95	3.4 ± 2
Sludge	1.19	1.85	4.3 ± 2
Critical Difference	No Match	Match	

Christensen and Larson Method (1993)

- Applies to middle distillates (heating oil)
- T (years) = -8.4 (n-C_{17}/pristane) + 19.8 (Kaplan 1997)
- Error is ± 2 years (Oudijk, 2009).
- Error is ± 1.5 years under optimal conditions and ± 5 years under the worst case conditions (Hurst and Schmidt (2005)
- Accepted by the courts in New Jersey and Massachusetts
- Is a viable method <u>if it is used within prescribed limitations.</u>
- Cannot be used anywhere and everywhere
- Literature cites many cases where this method does not apply
- Ref: Oudijk et al, 2006; Oudijk, 2009

Age of Product

- Need more than just Christensen and Larsen method to determine age.
- Considering possible litigation, it would be risky to just use this method
- Another approach follows the depletion of select chemical classes as a function of soil type
- This approach provides a weight of evidence approach and age range.
- Ref: Oudijk (2009).

Stages in Biodegradation of Heating Oil

Stage	Description
1	Abundant n-alkanes
2	Light end n-alkanes removed
3	Middle range n-alkanes, benzene, toluene removed
4	More than 90% of n-alkanes removed
5	Alkylcyclohexanes and alkylbenzenes removed
6	Isoprenoids, C1-naphthalanes, benzothiophene and alkylbenzothiophenes removed, C2-naphthalenes selectively reduced
7	Phenanthrenes, dibenzothiophenes, and other PAHs reduced

Reference: Oudijk (2009)

Kaplan Stages and Weathering Potential Age Ranges in Years for Release of Heating Oil

Kaplan Stage	Weathering Regime	Moderate Soil – Age Range
1	Abundant n-alkanes	0 - 4
2	Light n-akanes removed, benzene & toluene removed	4-8
3	Middle range n-alkanes removed, ethylbenzene and xylenes removed	8-12
4	More than 50% n-alkanes removed	12 - 16
5	More than 90% n-alkanes removed, alkylbenzenes and alkylcyclohexanes begin to degrade	16 - 20
6	All n-alkanes removed, alkylbenzenes and alkylcyclohexanes removed by 50%	20 – 24
7	Isoprenoid removal significant	> 24

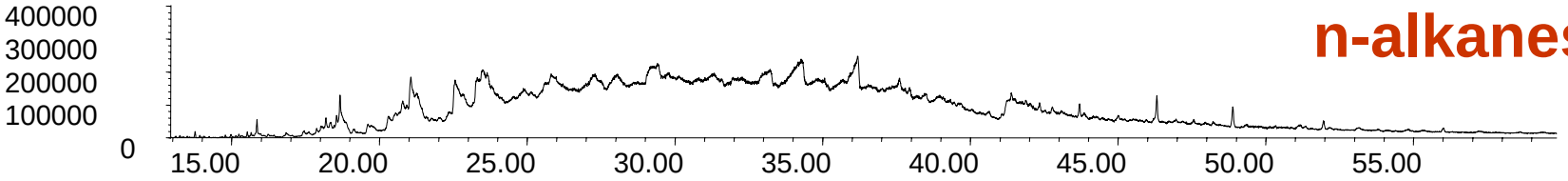
Age of sludge

- If greater than 10 years old we should observe the following
- 50-90% depletion of n-alkanes
- Significant depletion of alkylbenzenes and alkylcyclohexanes

- Reference: Oudijk (2009)

Abundance

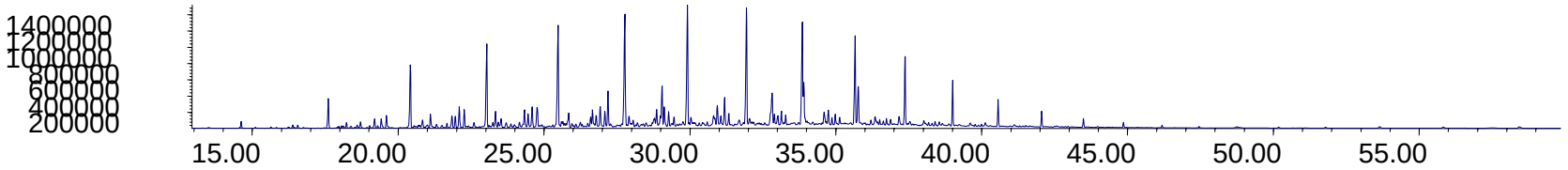
Ion 85.00 20+ year middle distillate



n-alkanes

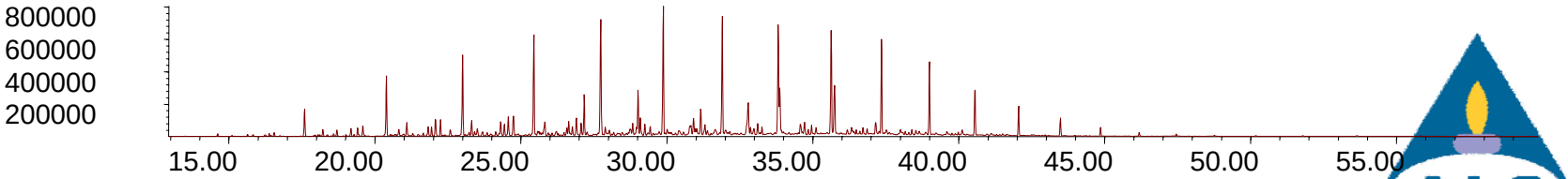
Time-->
Abundance

Ion 85.00 2-year old heating oil



Time-->
Abundance

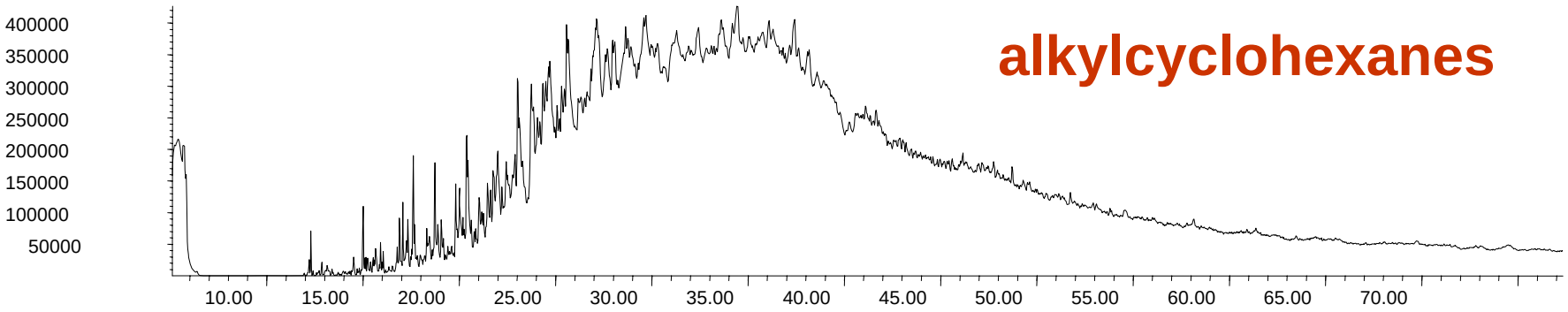
Ion 85.00 sludge



Time-->

Abundance

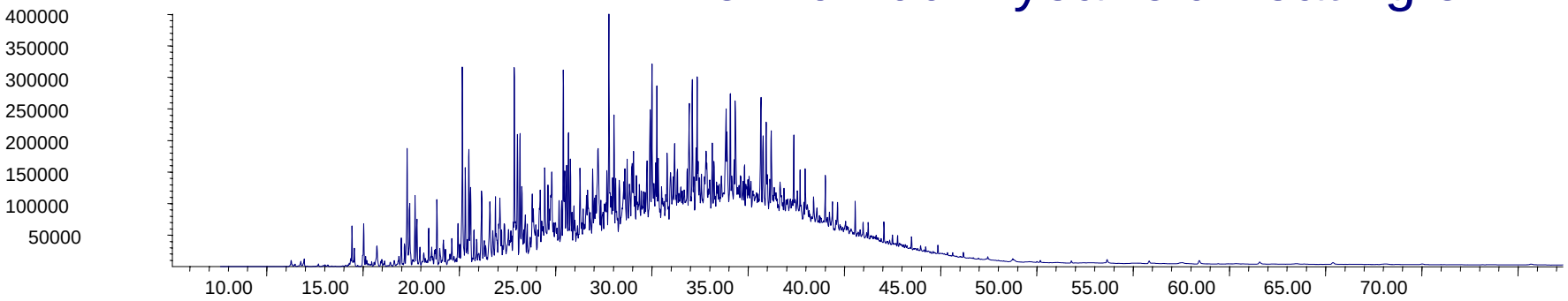
Ion 97.00 20+ year old middle distillate



alkylcyclohexanes

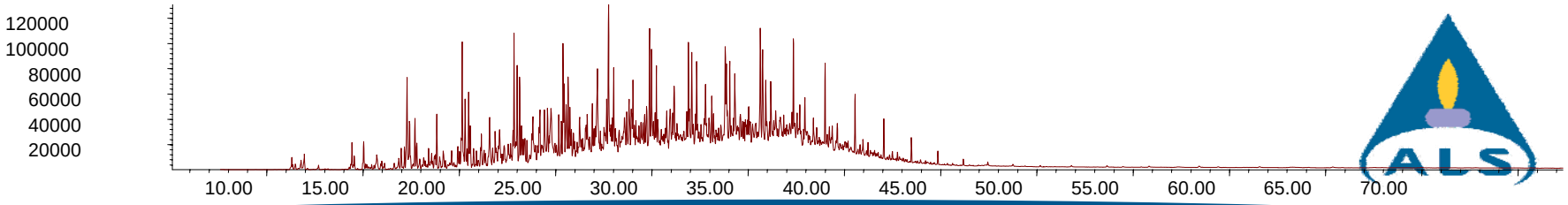
Time-->
Abundance

Ion 97.00 2-year old heating oil

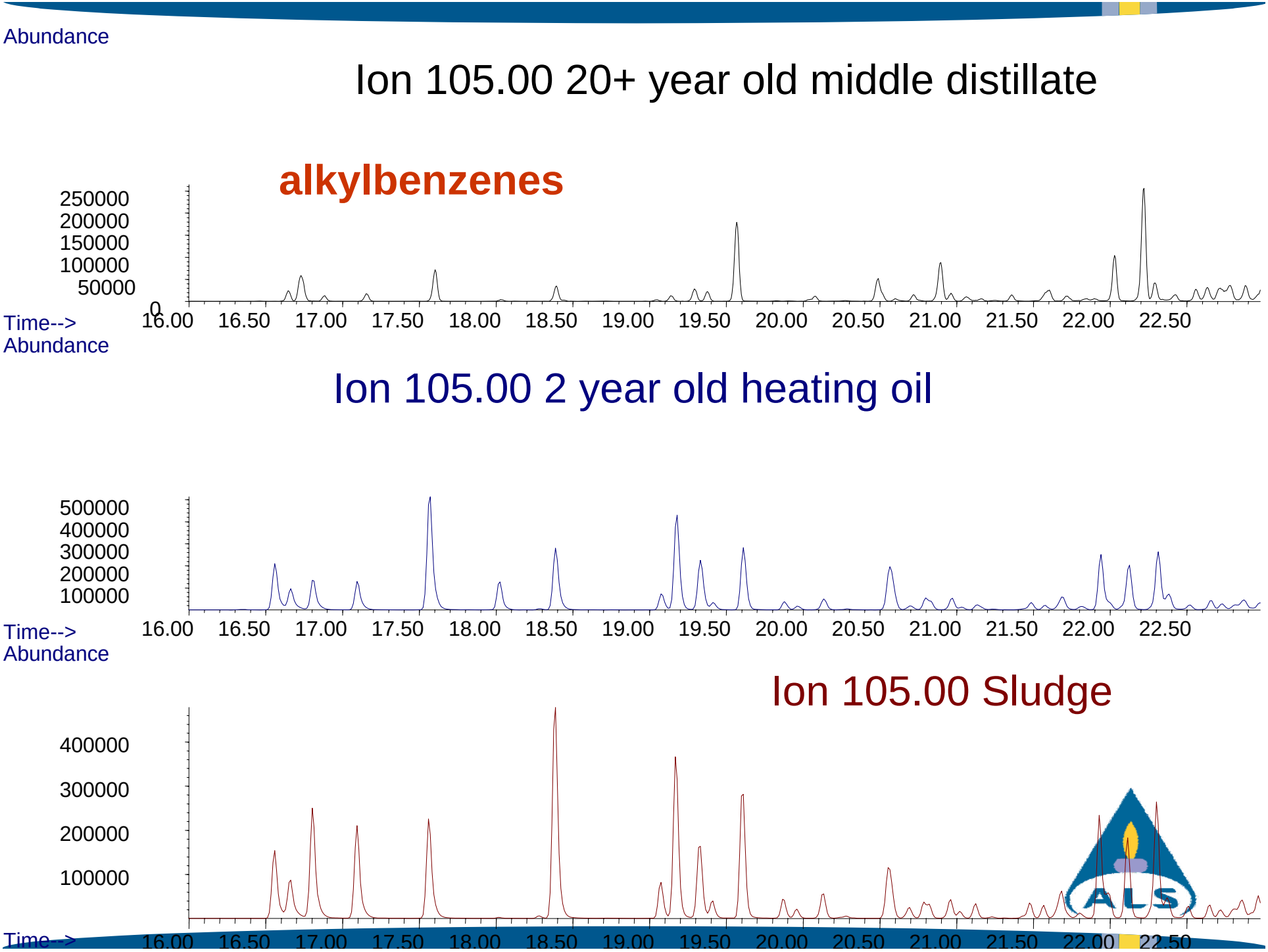


Time-->
Abundance

Ion 97.00 sludge



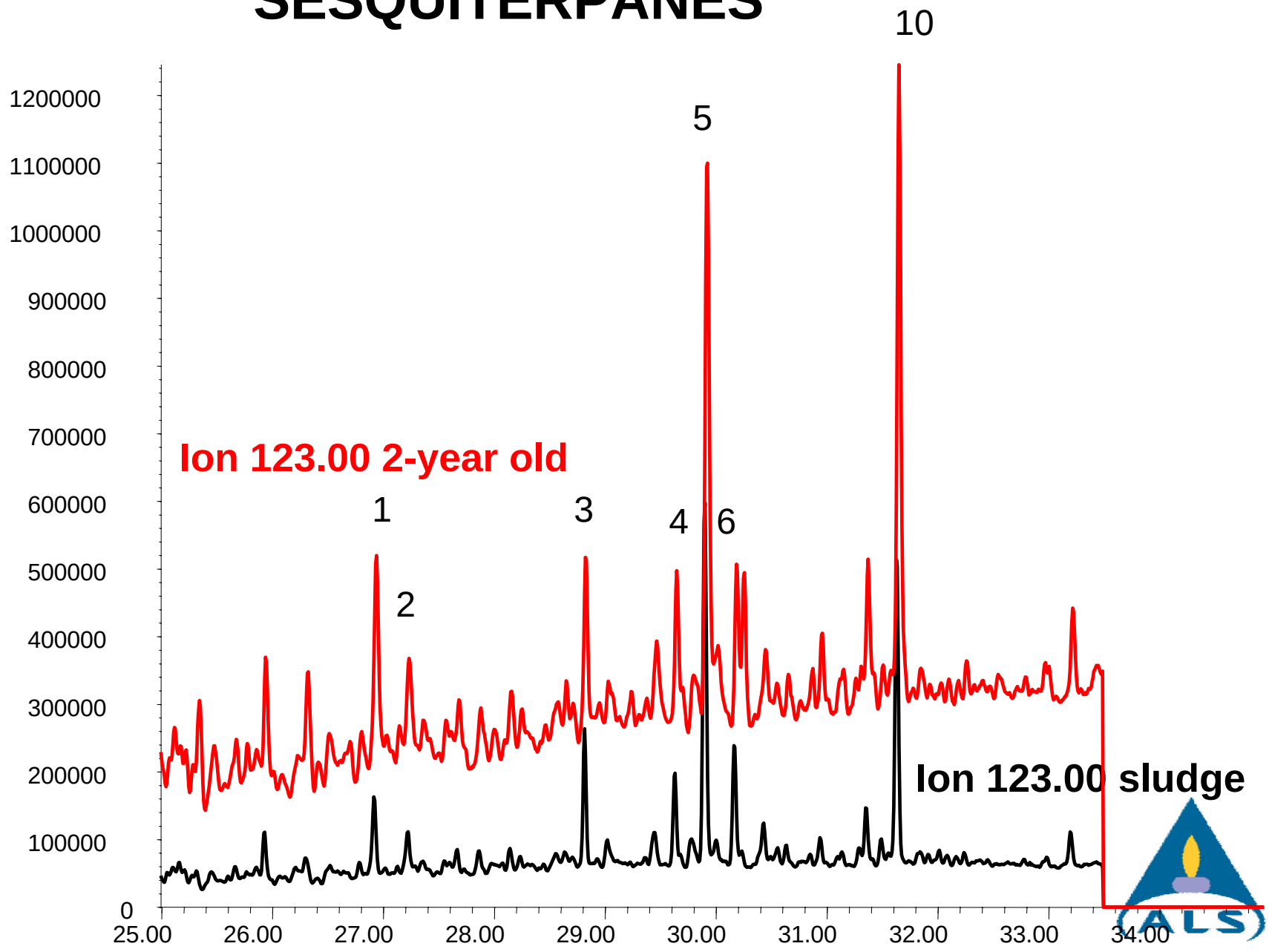
Time-->

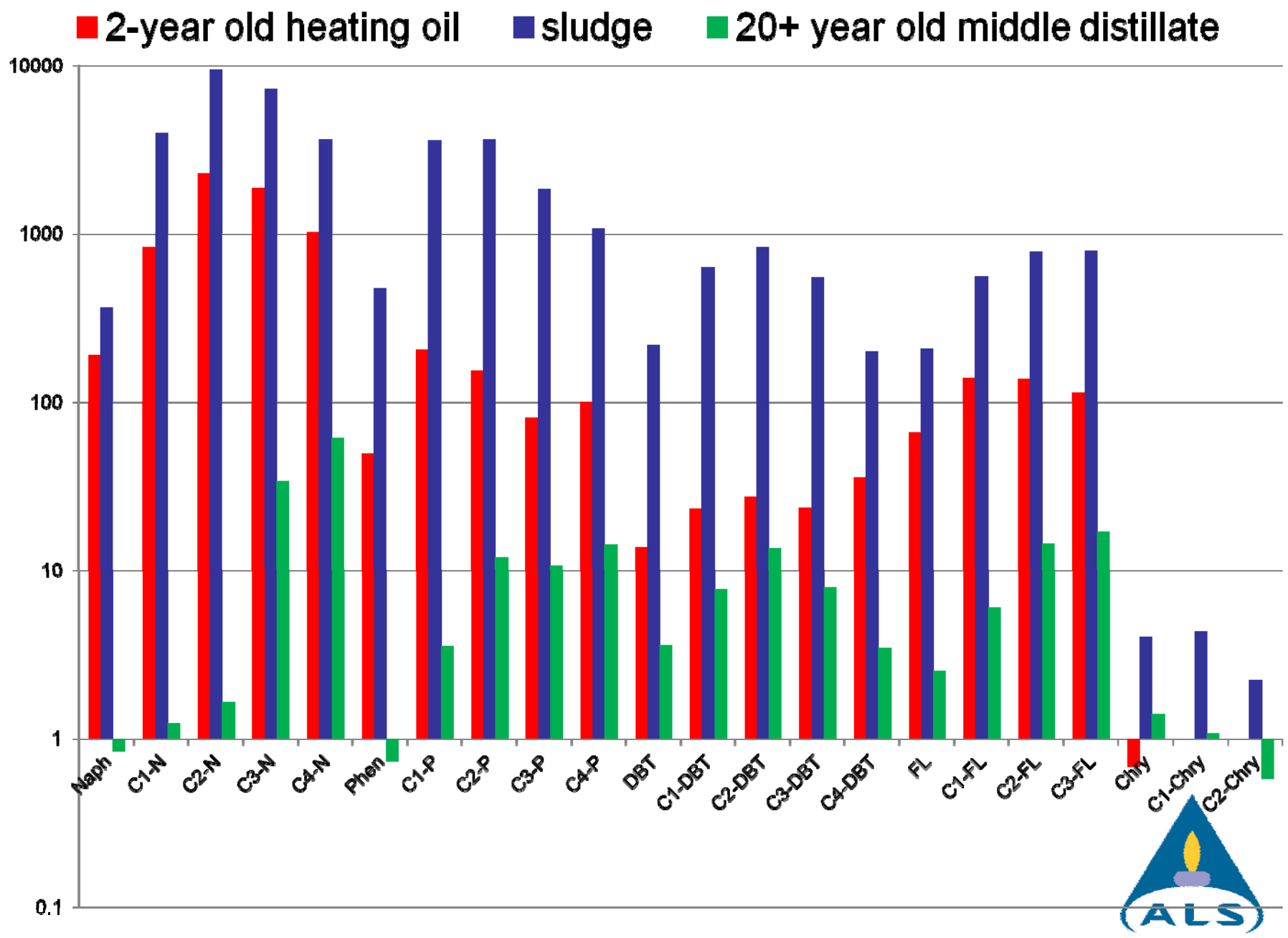

Abundance
Ion 105.00 20+ year old middle distillate
alkylbenzenes
250000
200000
150000
100000
50000
0
Time-->
Abundance
16.00 16.50 17.00 17.50 18.00 18.50 19.00 19.50 20.00 20.50 21.00 21.50 22.00 22.50
Ion 105.00 2 year old heating oil
500000
400000
300000
200000
100000
Time-->
Abundance
16.00 16.50 17.00 17.50 18.00 18.50 19.00 19.50 20.00 20.50 21.00 21.50 22.00 22.50
Ion 105.00 Sludge
400000
300000
200000
100000
Time-->
16.00 16.50 17.00 17.50 18.00 18.50 19.00 19.50 20.00 20.50 21.00 21.50 22.00 22.50
ALS

Summary

- Based upon the C/L method as well as depletion of organic chemical classes we could conclude that sludge represents fuel that is less than 5-6 years old
- This is bad news for our client
- BUT WAIT!
- Are these fuels different?
- What can we attribute the difference to?
- Will this help assign an age to the sludge and vindicate our client?

SESQUITERPANES




2-year old heating oil
sludge
20+ year old middle distillate
10000
1000
100
10
1
0.1
Naph
C1-N
C2-N
C3-N
C4-N
Phen
C1-P
C2-P
C3-P
C4-P
DBT
C1-DBT
C2-DBT
C3-DBT
C4-DBT
FL
C1-FL
C2-FL
C3-FL
Chry
C1-Chry
C2-Chry

PAH Distribution

PAH Compounds	2-year fuel	sludge
Alkylated naphthalenes/alkylated phenanthrenes	10.5	2.3
Alkylated phenanthrenes/Total PAHs	0.08	0.27
Alkylated Dibenzothiophenes /Total PAHs	1.7	6.1
Percent 3-ring PAHs	5.8	7.4
Percent 4-ring PAHs	0.4	3.3
Percent 5-6 ring PAHs	0.1	0.1

Critical Difference Analysis

Ratio	2-year heating fuel	Sludge	Conclusion
Sesquiterpanes			
DR-SES1/SES2	2.230	1.943	Match
DR-SES3/SES5	0.306	0.376	No Match
DR-SES4/SES6	0.957	0.792	No Match
DR-SES5/SES10	0.915	1.198	No Match
DR-SES10/SES10+5	0.522	0.455	Match
Alkanes & Isoprenoids			
n-C17/pristane	1.95	1.85	Match
n-C18/phytane	2.04	1.94	Match
Pristane/phytane	1.42	1.19	No Match

Critical Difference Analysis

PAHs	2-year heating fuel	Sludge	Conclusion
DR-4MeDBT/1-MeDBT	2.816	6.424	No Match
DR-2MeP/1-MeP	1.966	1.86	Match
DR-2MePyr/4-MePyr	0.849	1.212	No Match
DR-1MePyr/4-MePyr	0.628	0.79	No Match
DR-C2DBT/C2-P	0.179	0.228	No Match
DR-C3DBT/C3P	0.292	0.298	Match
BaA/Chry	1.490	0.400	No Match
BeP/Bap	0.882	0.754	No Match
Total Matches			**6/16**

Critical Difference Analysis

Sesquiterpanes	2-yr Fuel	Sludge	Difference	Critical Difference	Conclusion
DR-SES1/SES2	2.230	1.943	0.287	0.292	Match
DR-SES3/SES5	0.306	0.376	0.070	0.048	No Match
Difference = absolute difference between pair of ratios					
Critical Difference = mean between ratios * repeatability limit (14%)					
Conclusions = Match if difference < than critical difference					
Conclusions = No Match if difference > critical difference					
Reference: Hansen et al (2007)					

Critical Difference Analysis

- The 2-year old fuel is distinctly different from the sludge sample
- This suggests that the heating fuels are from different sources (crude stocks)

Elemental Analysis

Element	2-year heating fuel mg/kg	Sludge mg/kg
Aluminum	<10	4830
Cadmium	<0.50	14
Chromium	<0.50	53.1
Copper	<1.0	133
Iron	<100	219,000
Nickle	<2.0	97.9
Lead	<5.0	429
Tin	<5.0	16
Zinc	1.24	846
Sulfur	1300	3600

Conclusions

- Client suggests that sludge from a storage tank represents heating fuel that is 30+ years old
- GC/FID analysis followed by determination of n-C17/pristane, n-C18/phytane as well as pristane/phytane did not suggest a weathered sample
- This was supported by studying profiles of n-alkanes, alkylcycloalkanes, and alkylbenenes which revealed no degradation
- May be explained by the confined space (old storage tank) with minimal opportunity for weathering

Conclusions

- Determination of specific hydrocarbon biomarker ratios (sesquiterpanes, alkanes, isoprenoids, and PAHs) followed by a critical difference analysis revealed that the 2-year old fuel oil and sludge were distinctly different (6/16 matches)
- Comparison of the PAH profiles revealed elevated levels of alkylated naphthalenes, phenanthrenes, fluorenes, dibenzothiophenes and chrysenes in the sludge relative to a 2-year old heating oil

Conclusions

- Higher concentrations of alkylated PAHs and alkylated dibenzothiophenes associated with older fuels.
- Sulfur concentration in the sludge was 3600 mg/kg vs 1300 mg/kg observed for the 2-year old heating fuel
- Comparison to Canadian national averages for home heating fuel suggests sludge dates back to pre-1995 and according to U.S. national standards pre-1987

Conclusions

- The elevated levels of metals, especially iron (219,000 mg/kg) as well as aluminum, zinc, lead, copper, chromium and cadmium provide additional evidence that the sludge represented fuel in contact with a metal tank for many years, likely decades.

ALS Laboratory Group

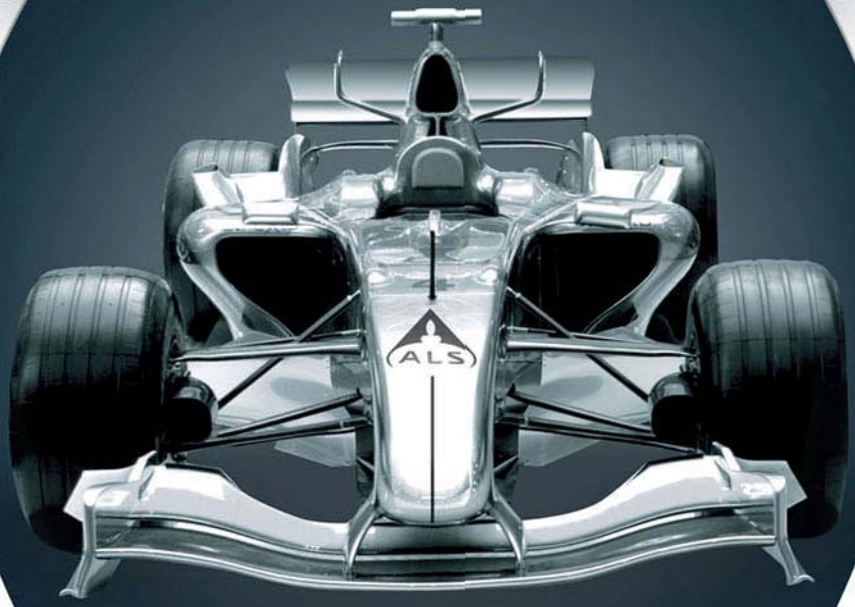
Environmental Testing Services

Performance is Everything!™

QUALITY

INTEGRITY

SERVICE



GLOBAL

ACCREDITED

INNOVATIVE