



Source Identification of Hydrocarbons Following Environmental Releases

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Minerals



Coal



Environmental Tribology



Food & Pharmaceutical Industrial



RIGHT SOLUTIONS RIGHT PARTNER



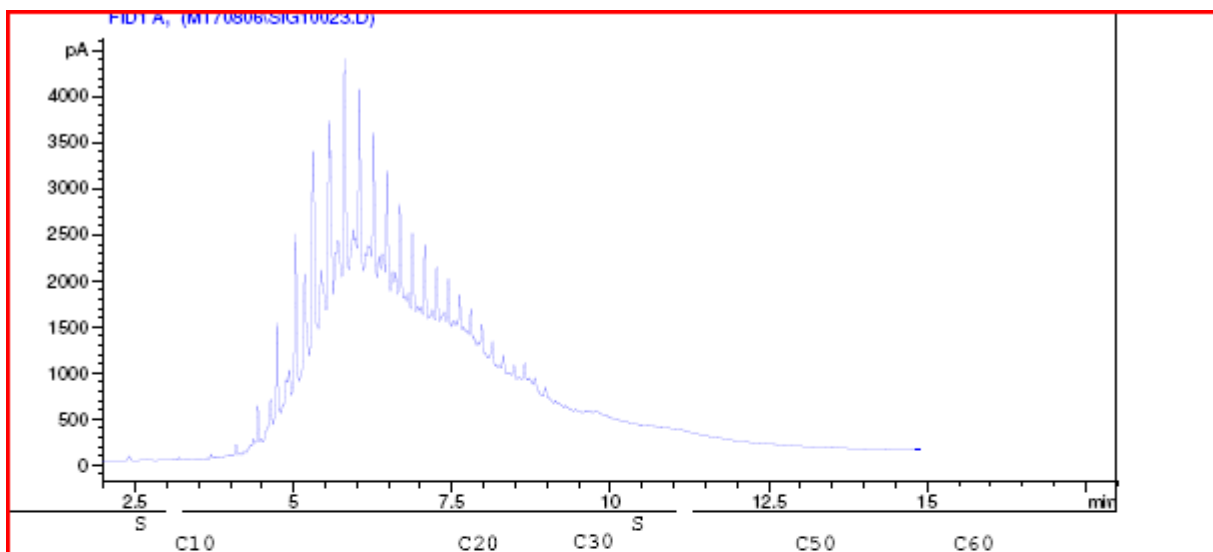
Acknowledgements

- Court Sandau, PhD, P.Chem, Trium
- Marco Kaltofen, P.E., Boston Chemical Data Corp
- Eileen Gueuthal and her staff, ALS Centre of Ex.
- Jarrod Roberts, ALS Centre of Excellence



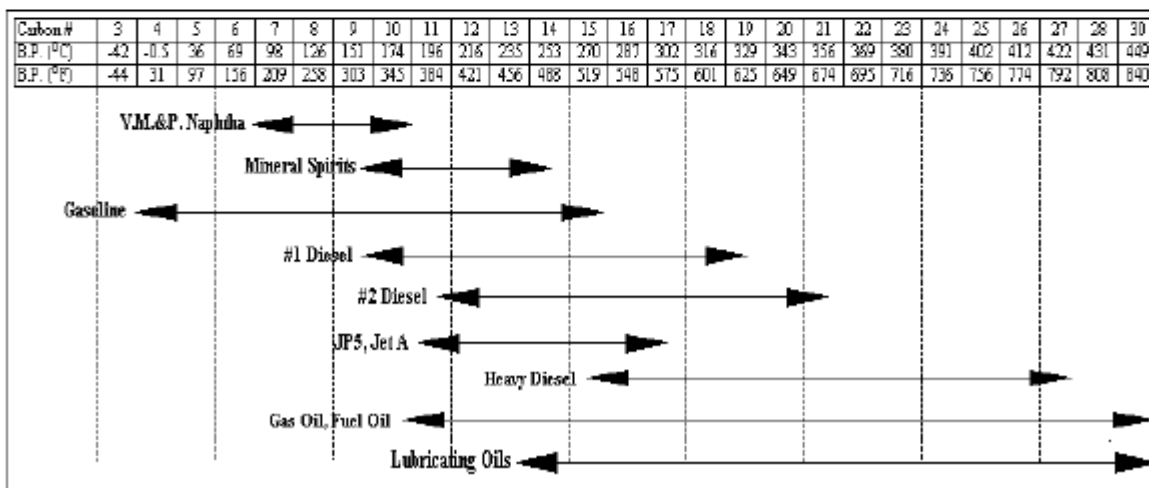
Forensic Analyses

- Laboratories routinely analyze for total petroleum hydrocarbons using the CCME protocol
- As part of the analyses chromatograms of observed products are obtained
- Based upon these chromatograms, laboratories suggest possible petroleum products
- This is by no means definitive analysis, unless a source sample is available to compare against
- Many petroleum products give rise to similar chromatograms, e.g. distinguishing between diesel #1, turbine fuel and kerosene; distinguishing between certain jet fuels, distinguishing between gasolines



S=Surrogate

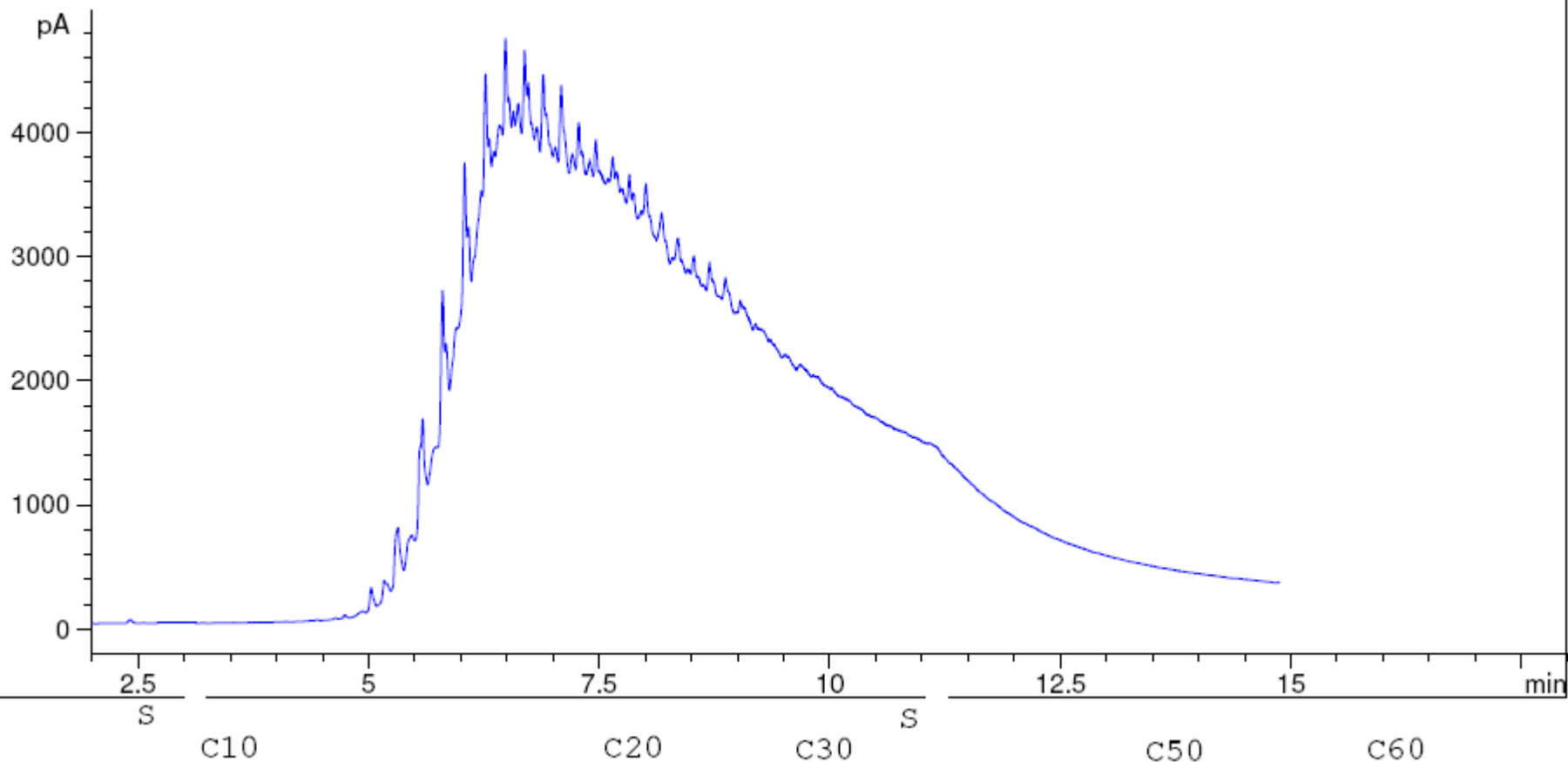
Boiling Point Distribution Range for Petroleum Based Fuel Products



Is this the same product or something different?



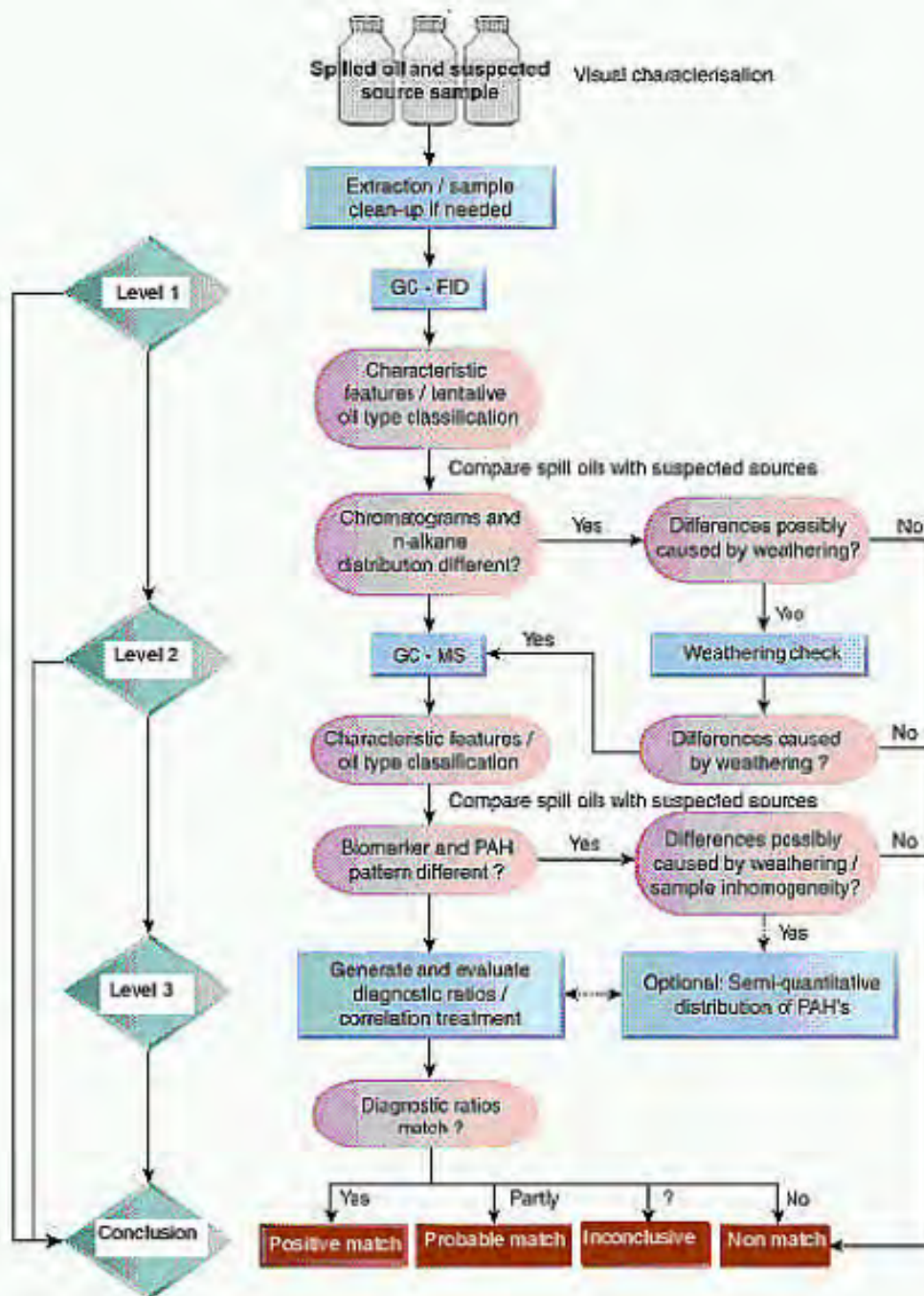
FID1 A, (MT70806\SIG10025.D)



Source Determination



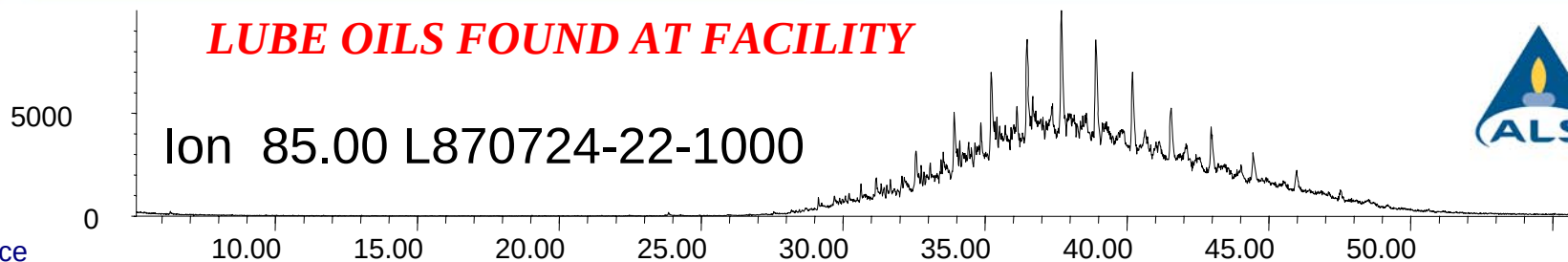
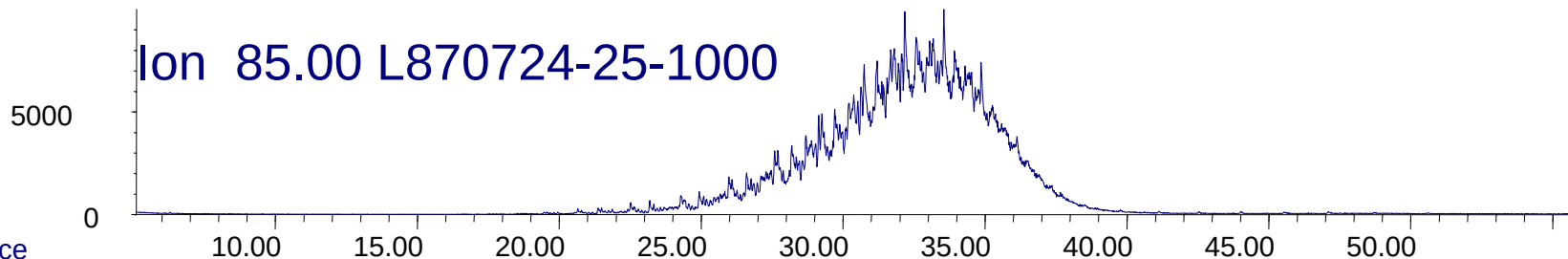
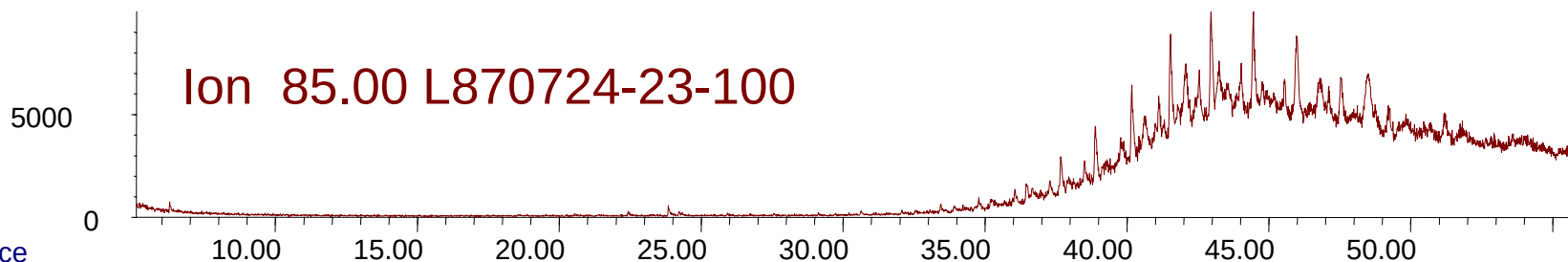
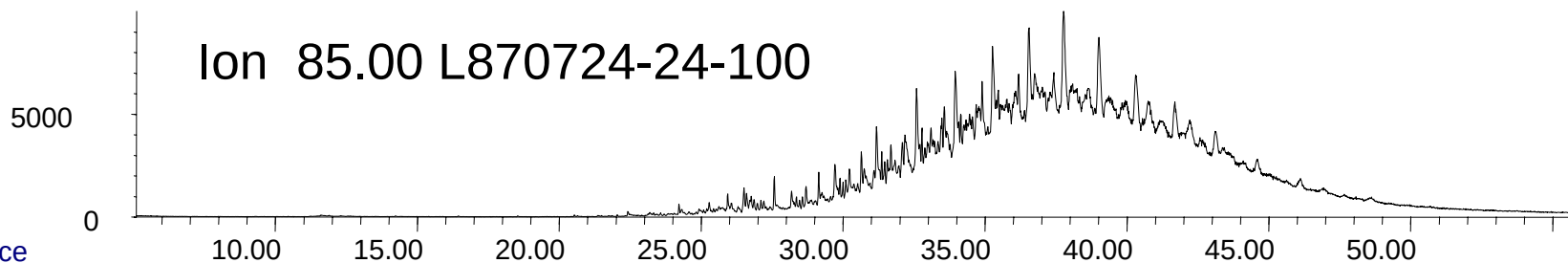
- Simple chromatograms – obtained following TPH analysis are useful but insufficient to prove sources of hydrocarbons
- They provide the least defensible evidence
- For litigation we require several independent lines of evidence.
- Most requests for forensic analyses arise from reclamation. In most instances there is no source product to compare against
- Opinions given during such investigations can have far reaching consequences, including implicating persons responsible as well as liability for cleanup.
- Laboratories conducting such analyses need to be correct or risk lawsuits themselves.
- If chromatograms are not enough to do the job what do we need?



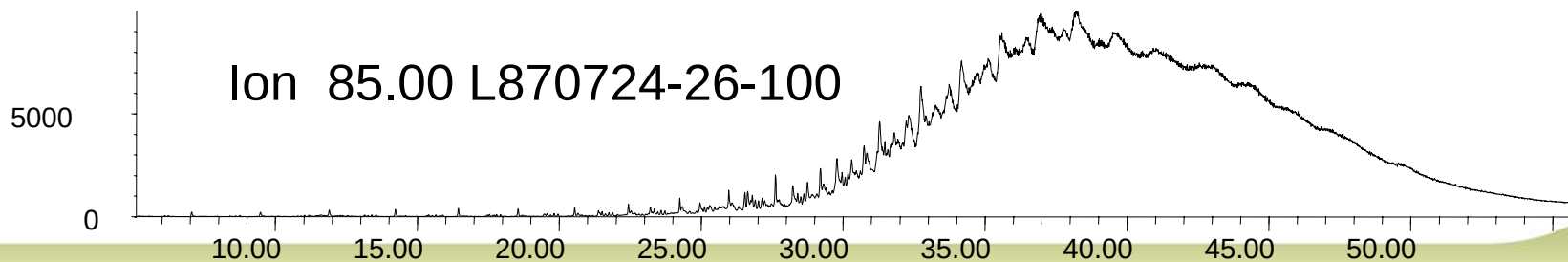
Case Study

- Lube oil blending facility – S.E. Asia
- Adjacent property had fuel storage tanks
- Crude oil pipeline ran through property
- Several wells drilled on property revealed significant LNAPL
- Remediation required at great cost
- The question was whether free product came from the blending facility?



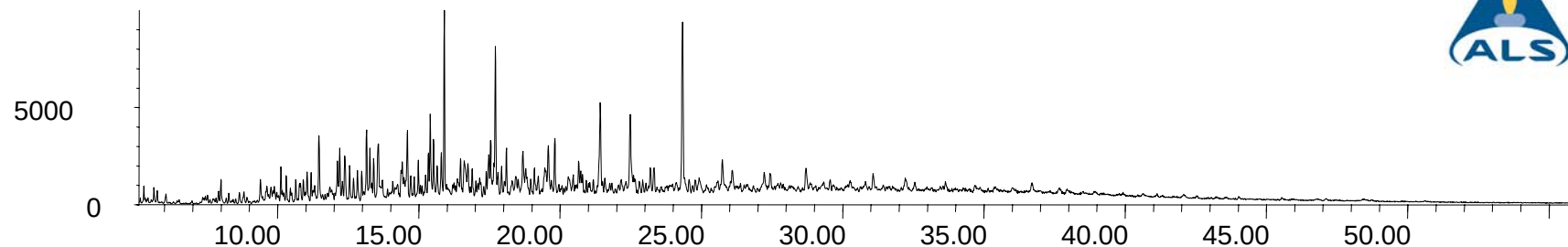
LUBE OILS FOUND AT FACILITY**Ion 85.00 L870724-22-1000**Time-->
Abundance**Ion 85.00 L870724-25-1000**Time-->
Abundance**Ion 85.00 L870724-23-100**Time-->
Abundance**Ion 85.00 L870724-24-100**Time-->
Abundance**Ion 85.00 L870724-26-100**

Time-->



Abundance

Ion 85.00 L870724-4

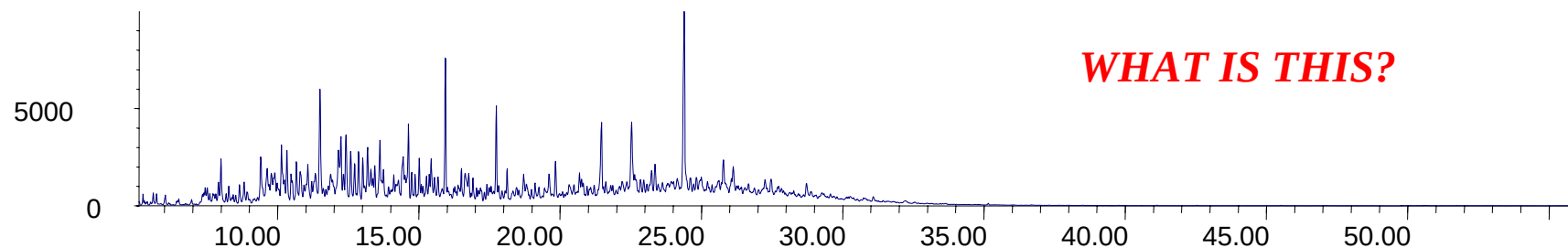


Time-->

Abundance

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WHAT IS THIS?

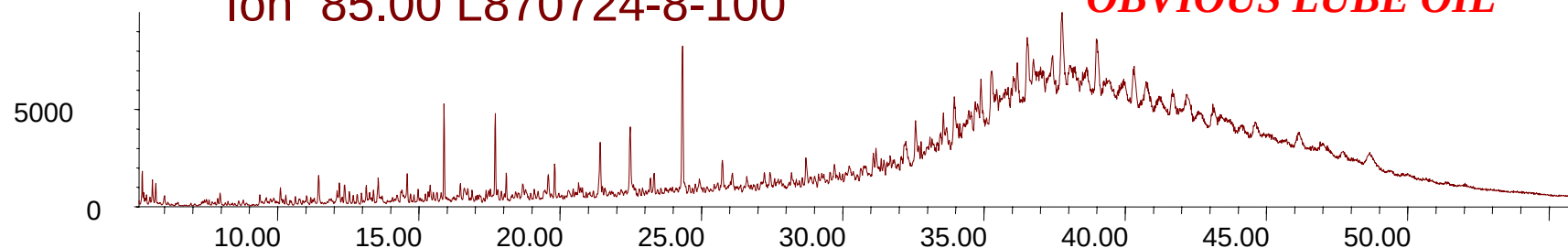


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Abundance

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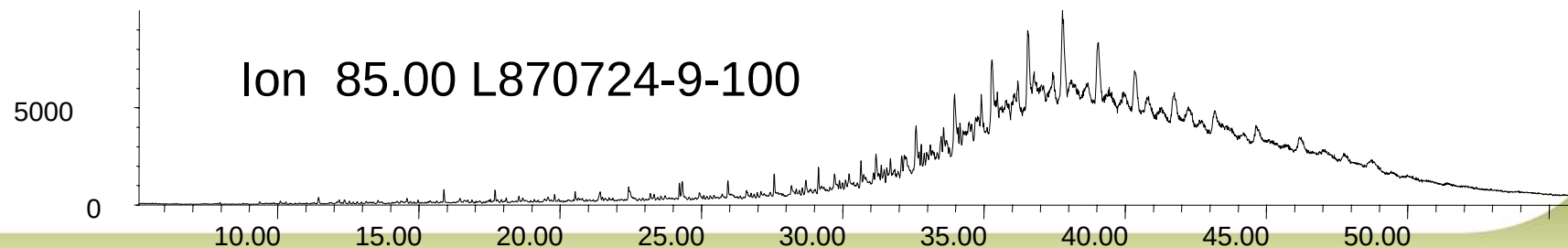
OBVIOUS LUBE OIL



Time-->

Abundance

Ion 85.00 L870724-9-100



Time-->



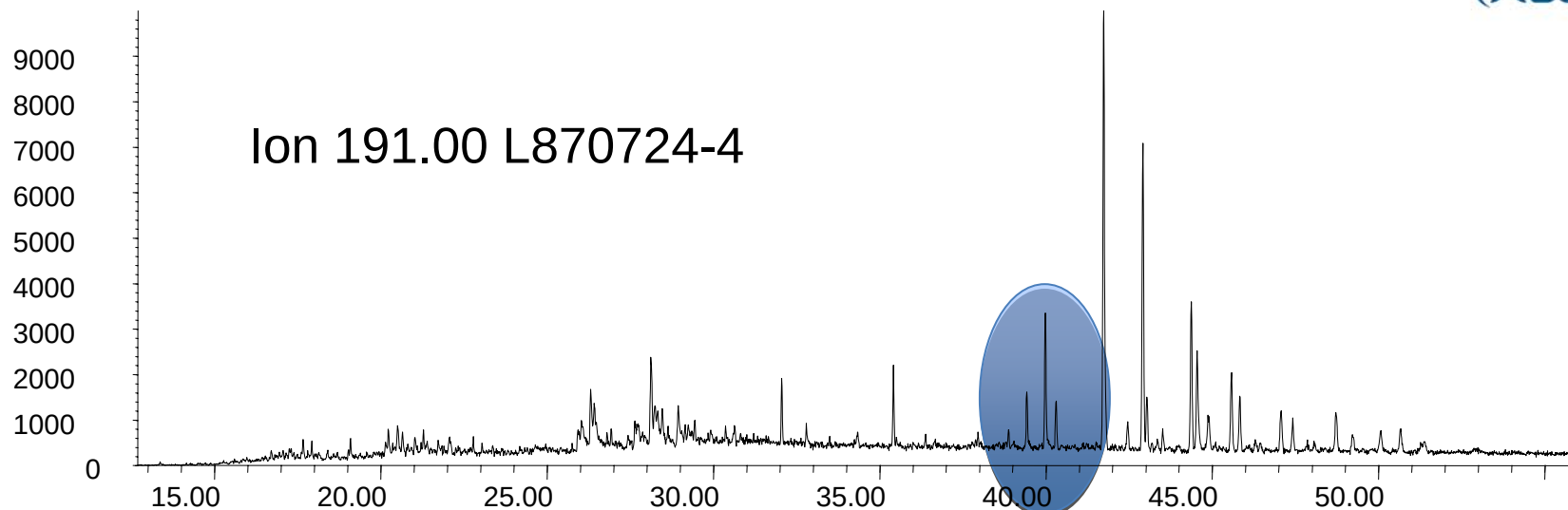
Chromatogram Conclusions

- Sample -8 and -9 obviously contain lube oil
- Sample -4 and -5 contain another product
- Sample -8 may contain lube oil + another product
- In order to determine what the other products are we need to investigate further
- Need to look at petroleum “biomarkers”

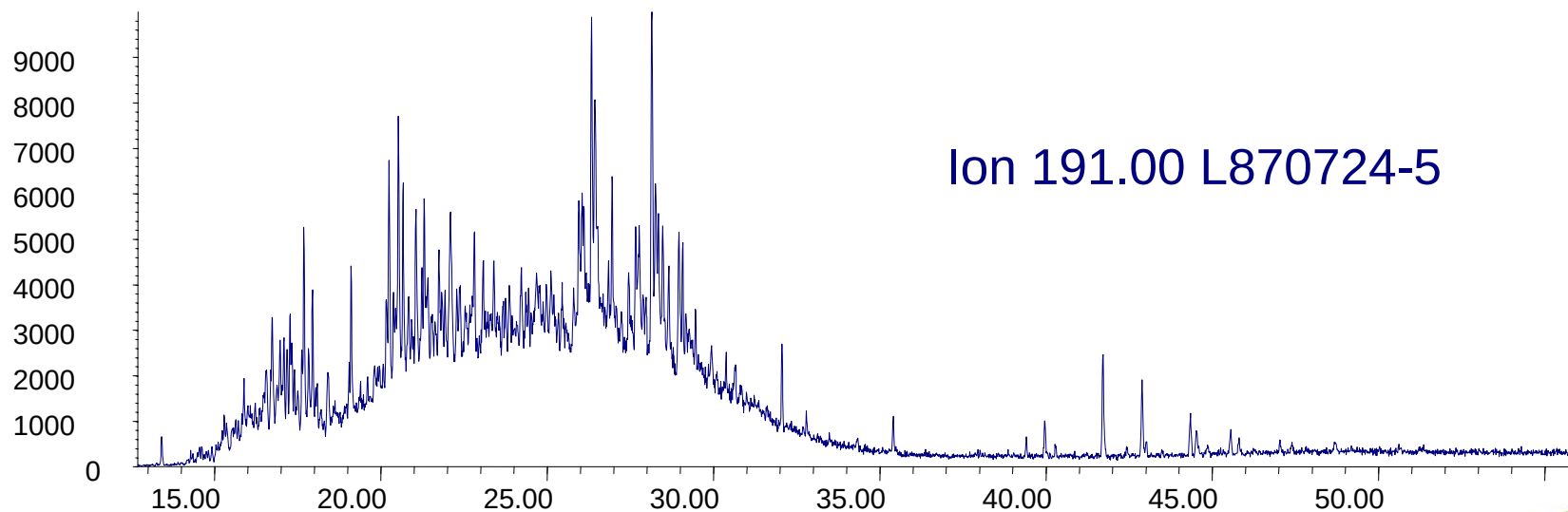
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SCAN FOR TERPANES



Time-->
Abundance

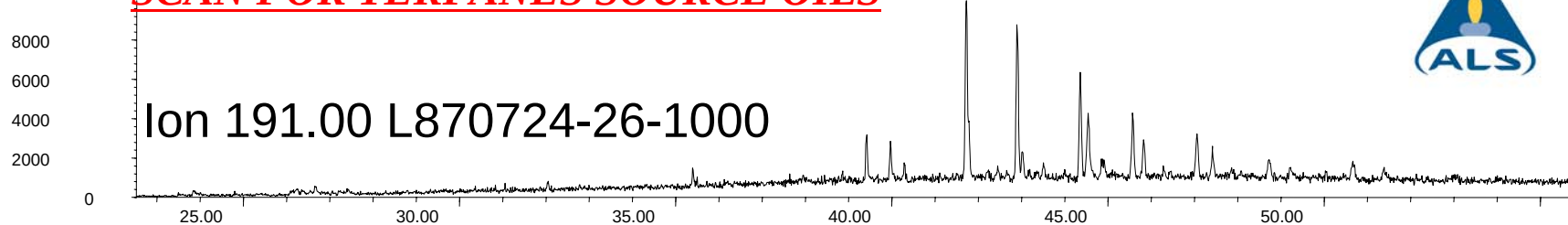


Time-->

SCAN FOR TERPANES SOURCE OILS

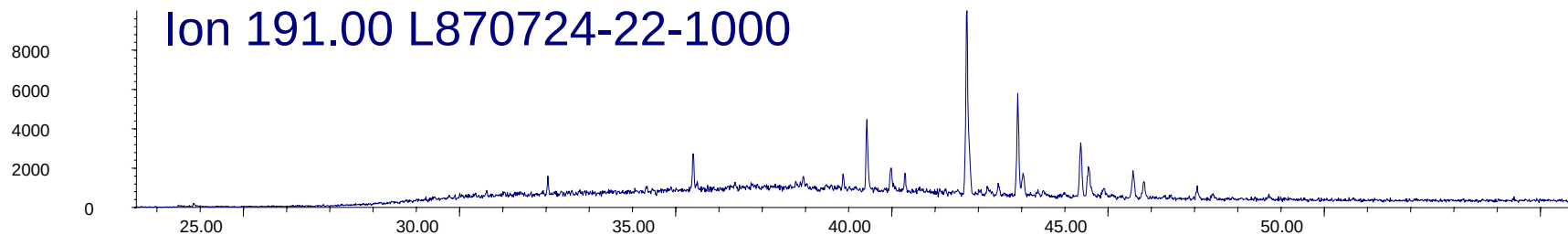


Ion 191.00 L870724-26-1000



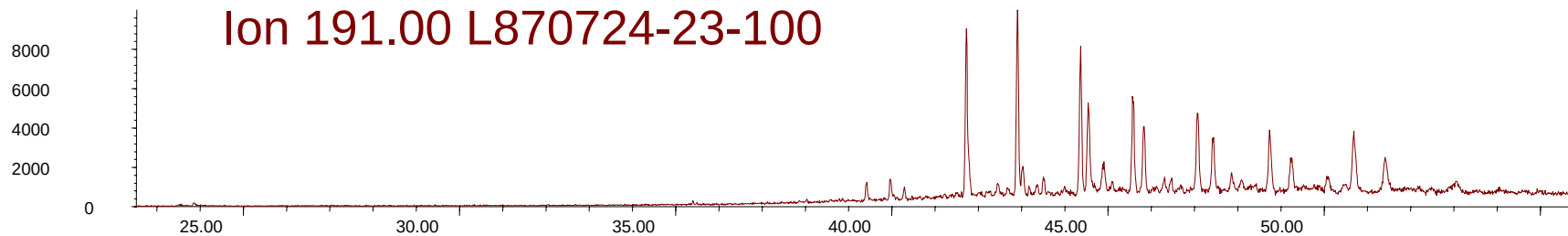
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Ion 191.00 L870724-22-1000



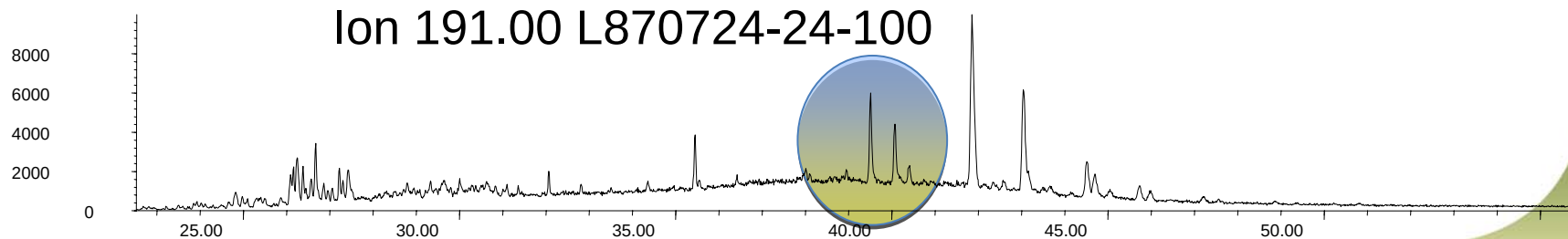
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Ion 191.00 L870724-23-100



Time-->
Abundance

Ion 191.00 L870724-24-100

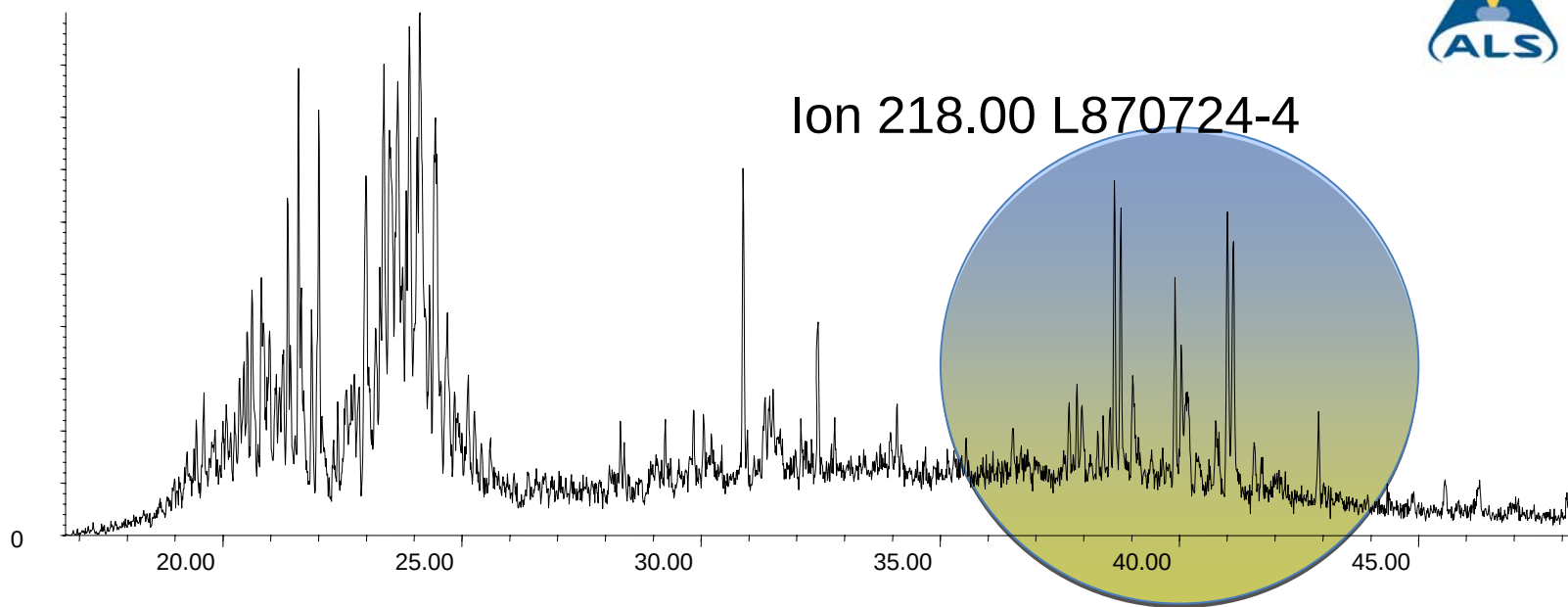


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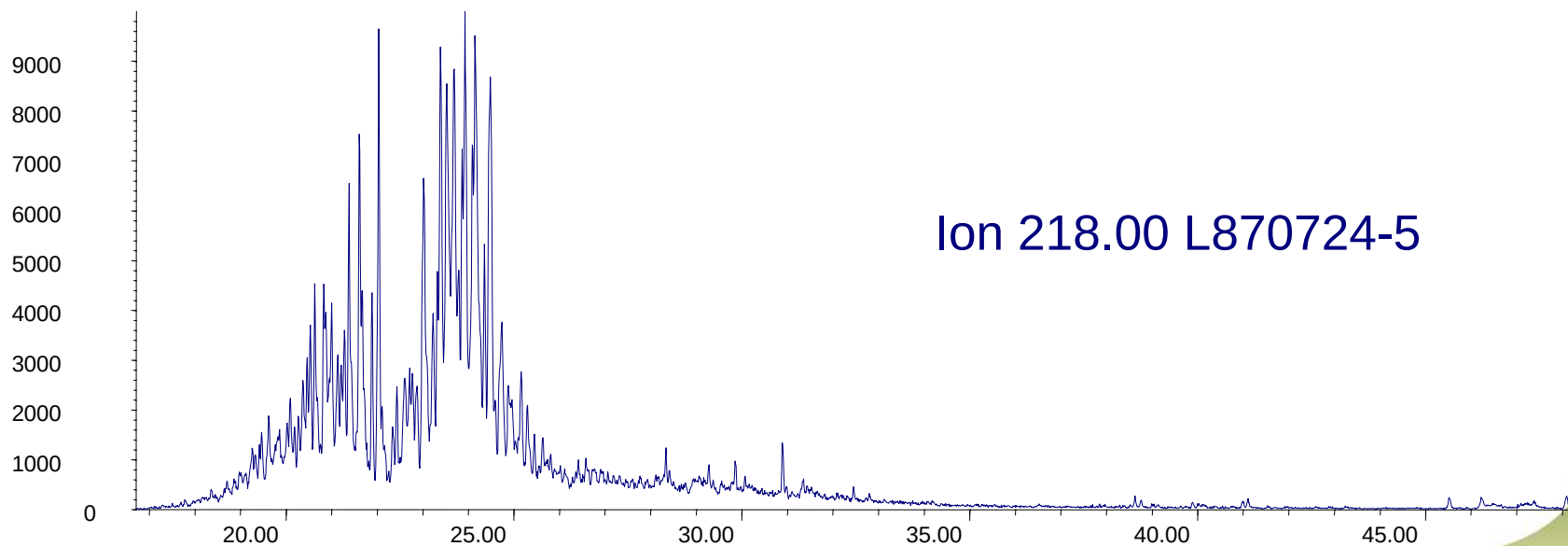
Conclusions Terpane Analyses

- Samples -4 and -5 contain terpanes
- Pattern is similar – although there are observed concentration differences
- Lube oils also contain terpanes, however, patterns and ratios are different than sample -4 and -5

SCAN FOR STERANES



Time-->
Abundance

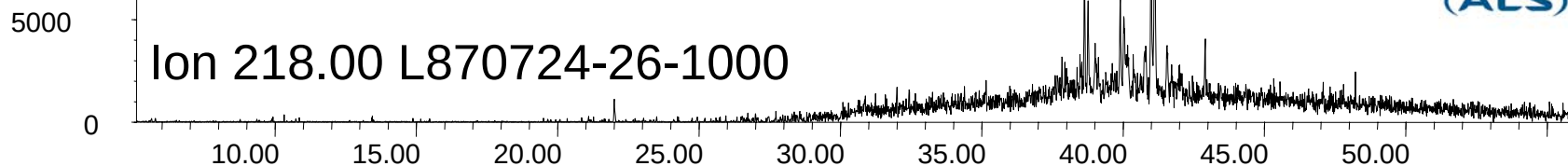


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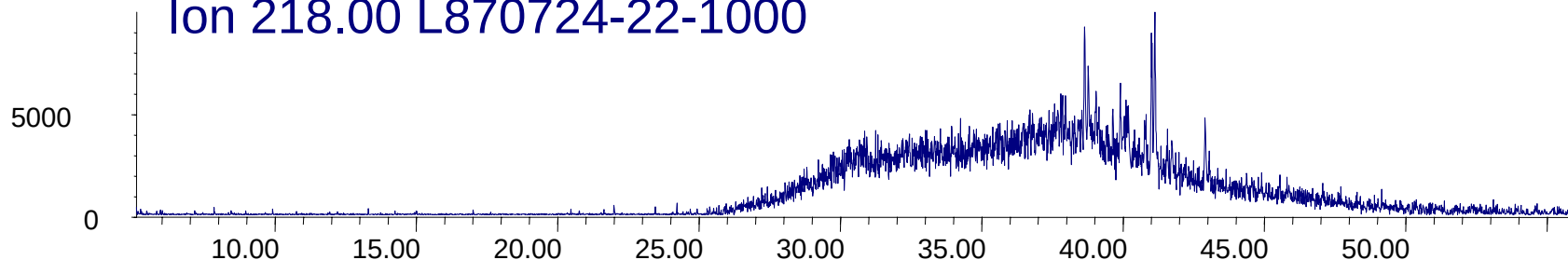
SCAN FOR STERANES SOURCE OILS

Time-->
Abundance

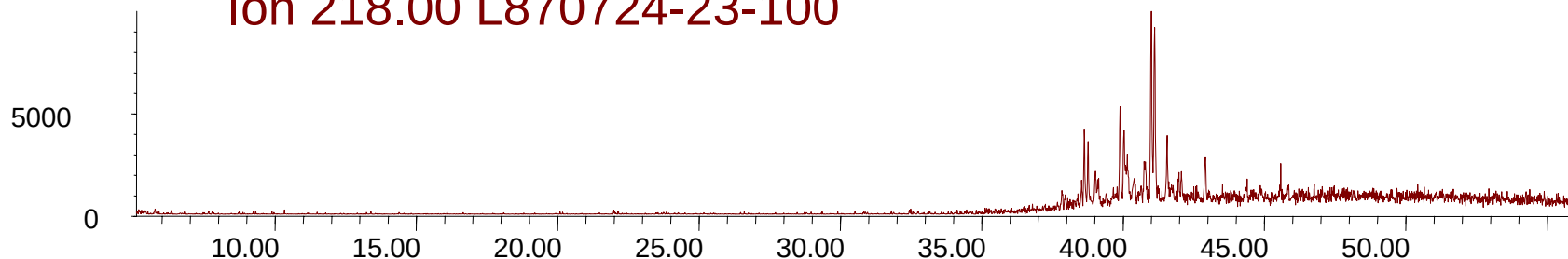
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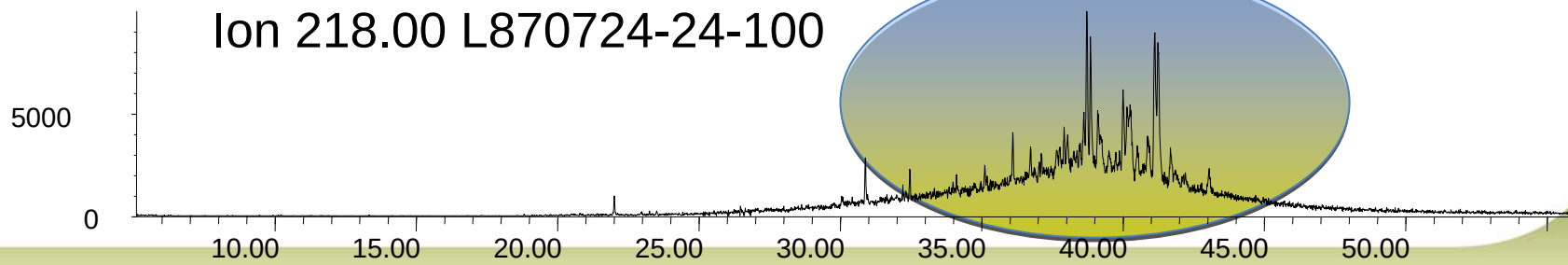
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Time-->

Ion 218.00 L870724-24-100



Sterane analyses

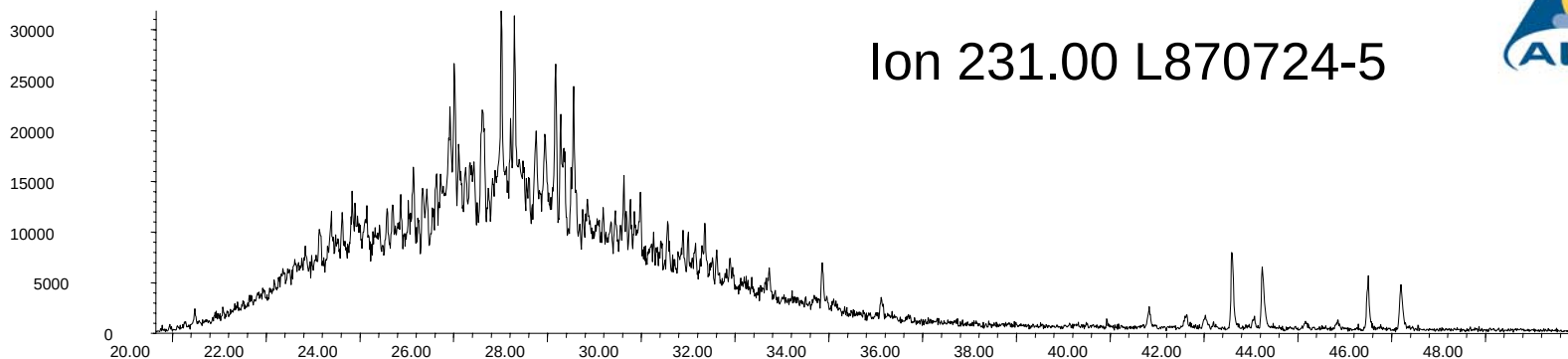
- Present in -4 and -5, although much more concentrated in -5.
- Steranes also present in lube oils, however, patterns and ratios are unique
- Best visual fit is with lube oil -24

Abundance

SCAN FOR TRIAROMATIC STERANES

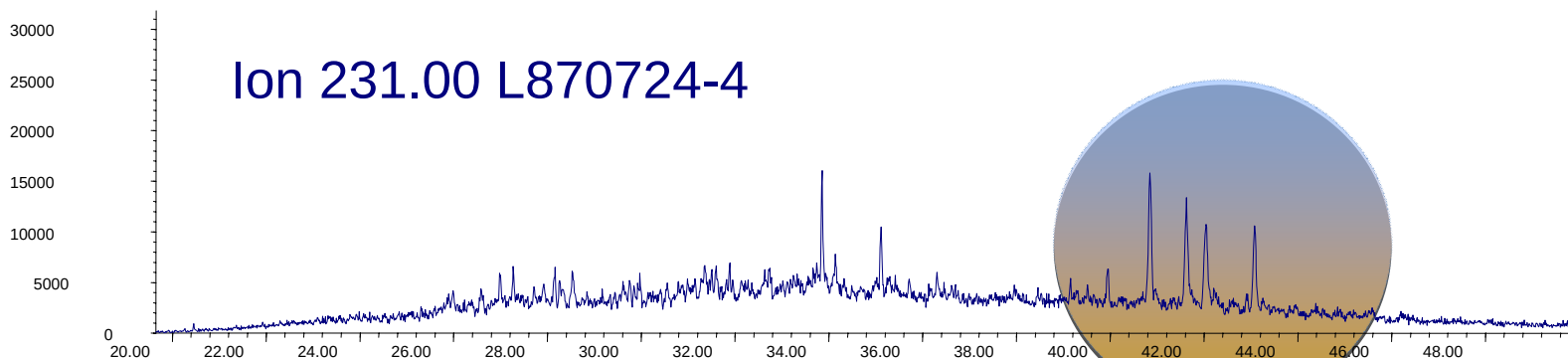


Ion 231.00 L870724-5



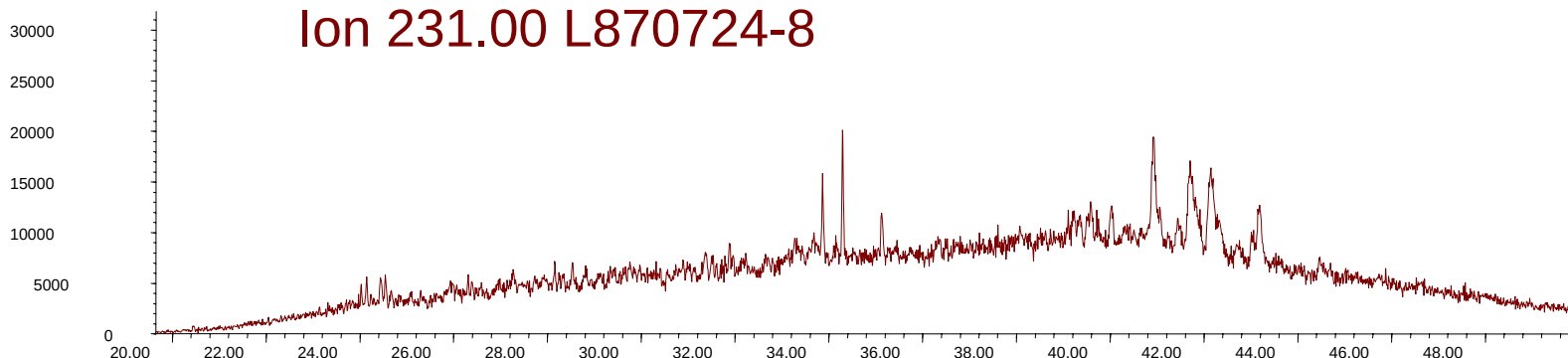
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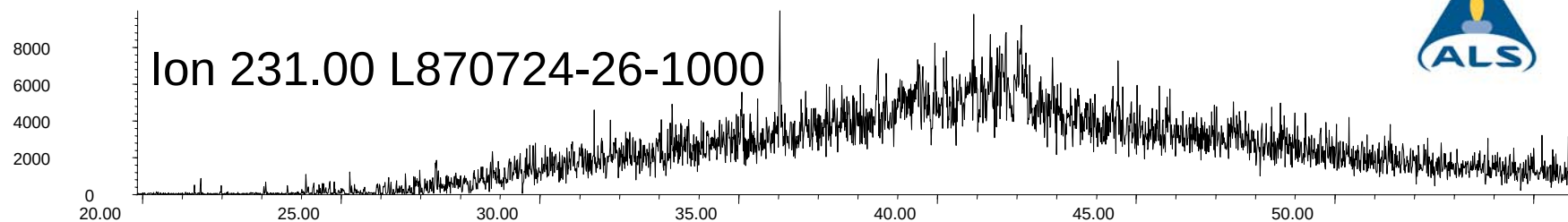
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Ion 231.00 L870724-8

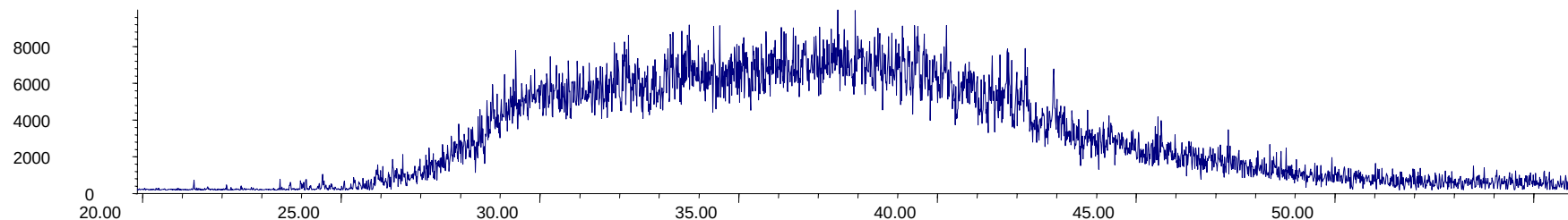


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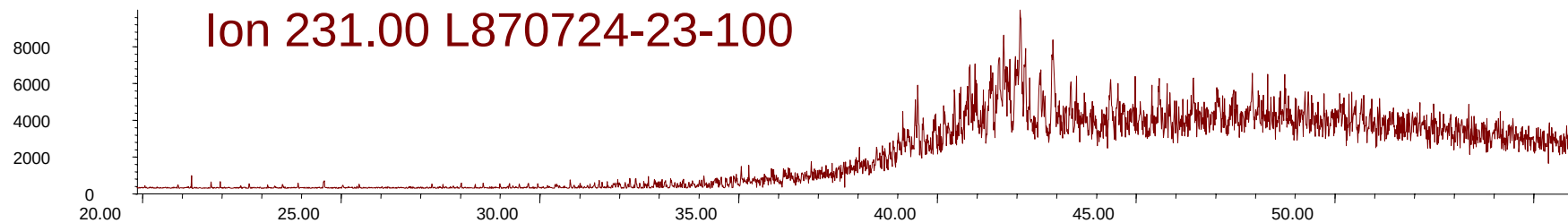
TRIAROMATIC STERANES SOURCE OILS

Time-->
Abundance

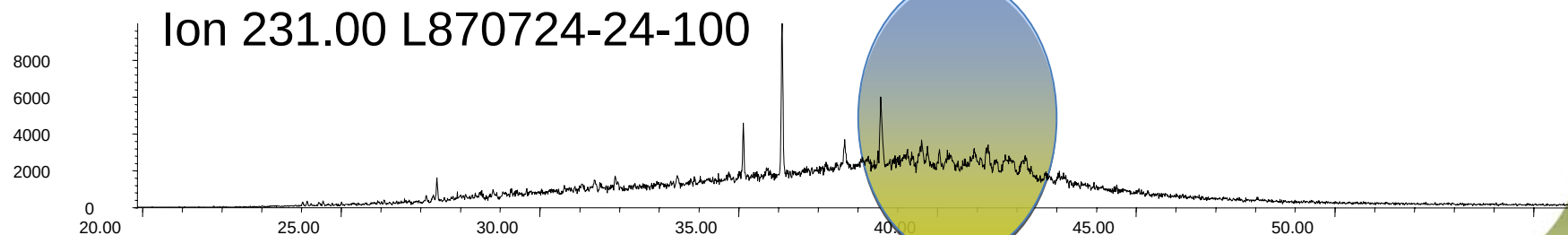
Ion 231.00 L870724-22-1000

Time-->
Abundance

Ion 231.00 L870724-23-100

Time-->
Abundance

Ion 231.00 L870724-24-100



Time-->

Triaromatic Sterane Analyses

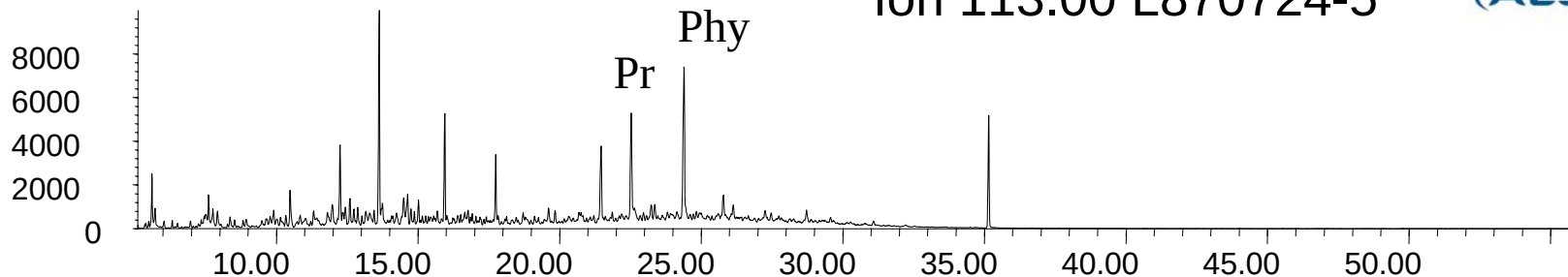
- Samples -4, -5 and -8 contain triaromatic steranes
- These are usually associated with crude oils
- Pattern for -4 and -8 is similar
- Pattern for -5 is different, indicating another petroleum product
- These biomarkers are not found in the lube oils

Abundance

ISOALKANES AND ISOPRENOIDS

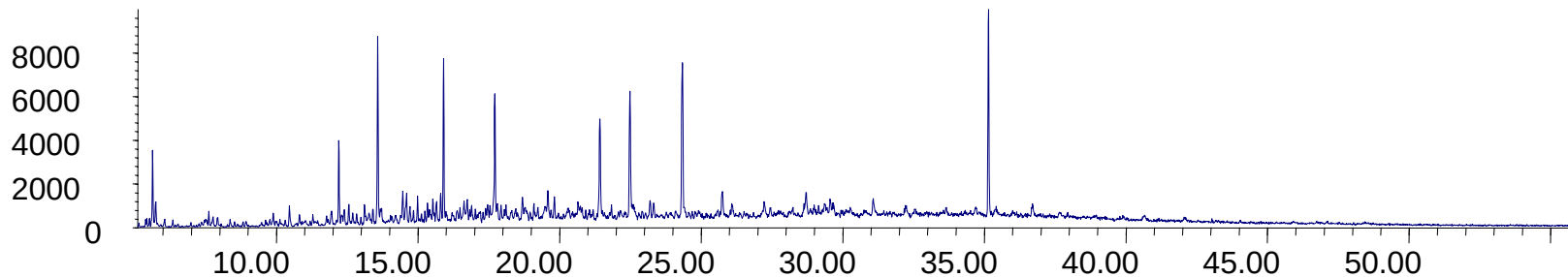


Ion 113.00 L870724-5



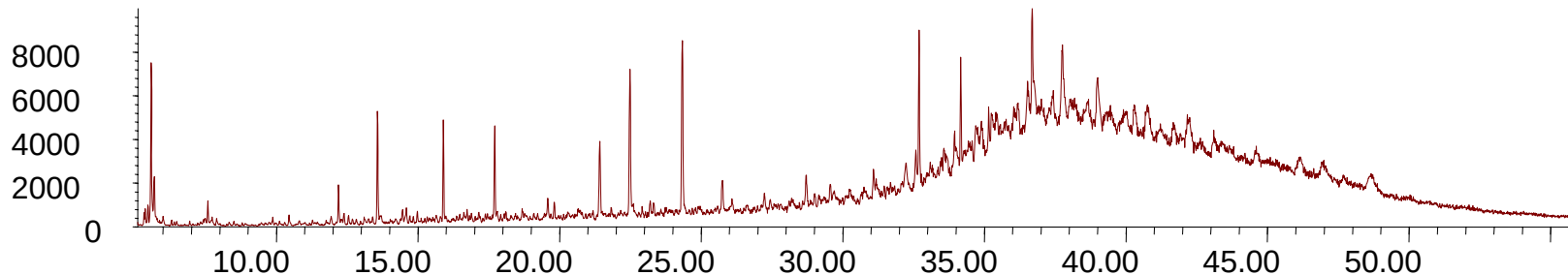
Abundance

Ion 113.00 L870724-4



Abundance

Ion 113.00 L870724-8

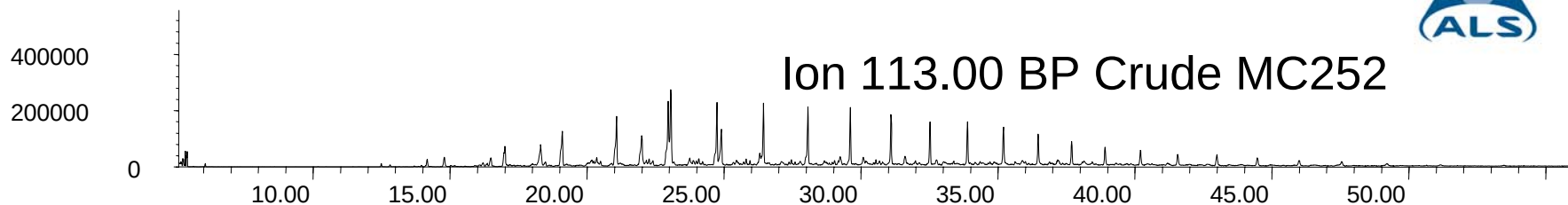


Abundance

ISOALKANES AND ISOPRENOIDS

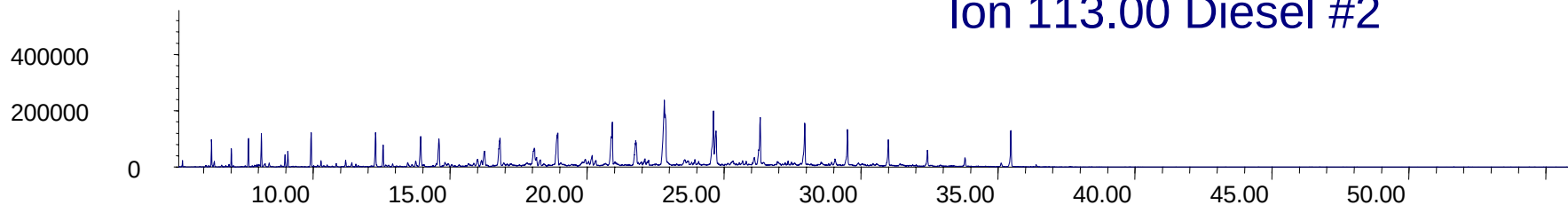


Ion 113.00 BP Crude MC252



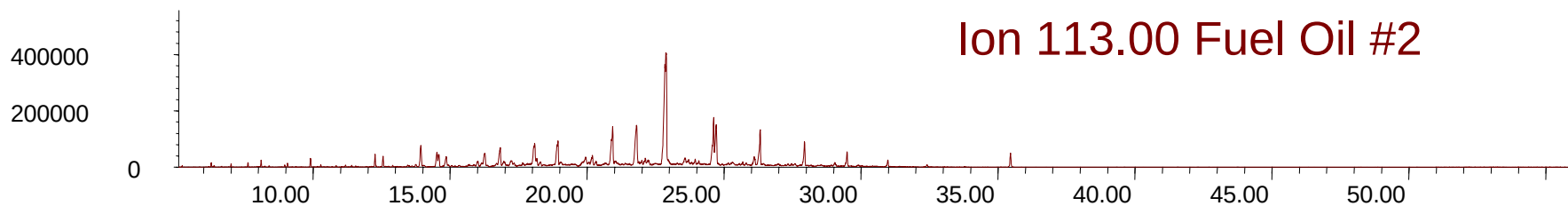
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Abundance

Ion 113.00 Diesel #2



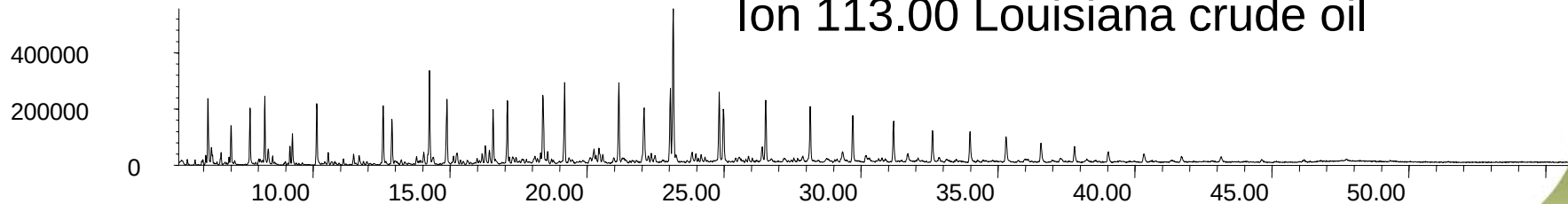
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Abundance

Ion 113.00 Fuel Oil #2



Time-->
Abundance

Ion 113.00 Louisiana crude oil

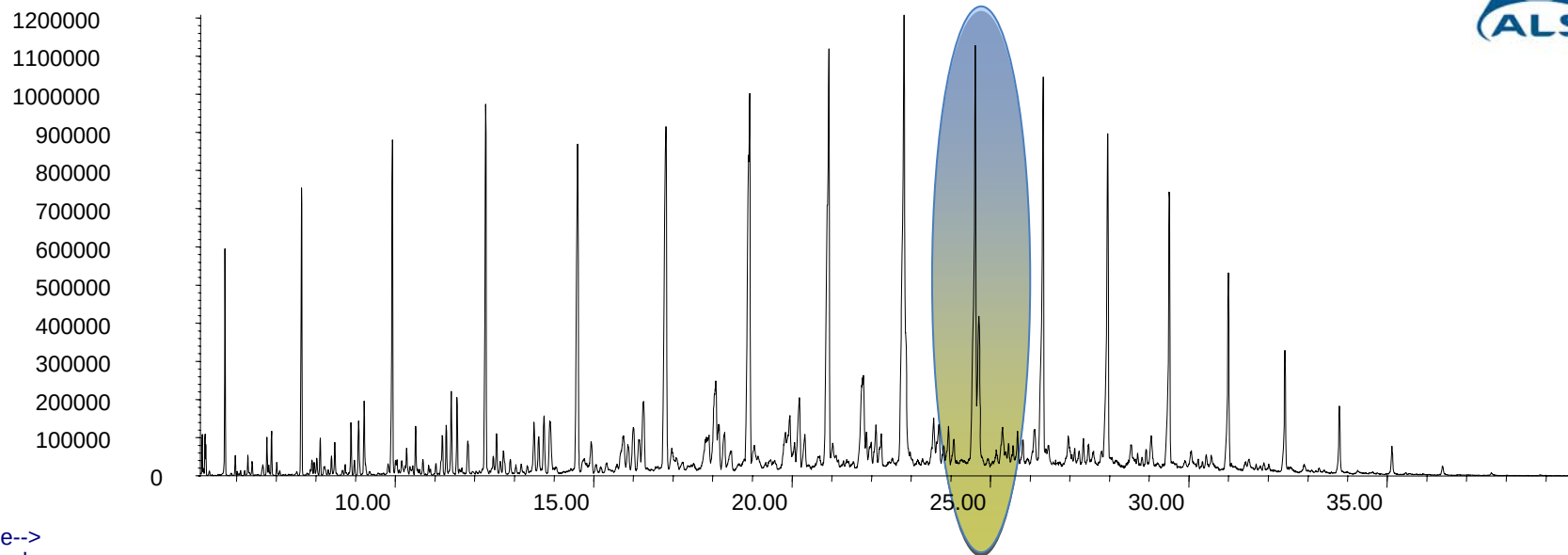


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Abundance

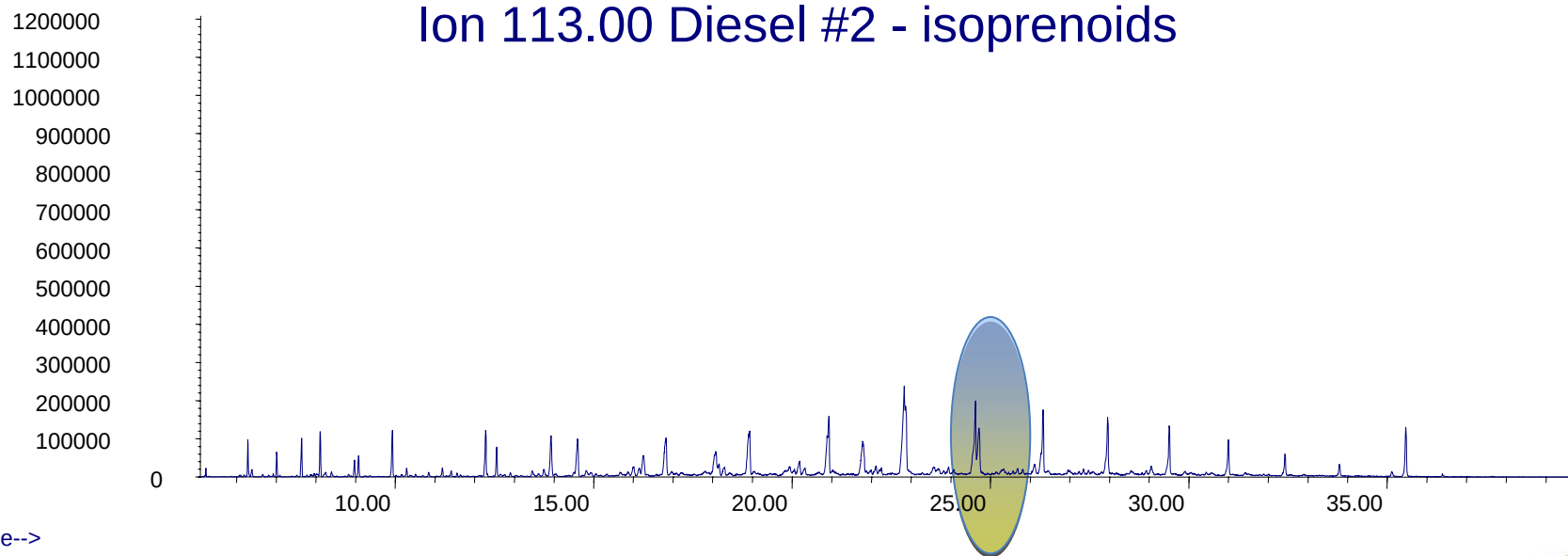


Ion 85.00 Diesel #2 - alkanes



Time-->
Abundance

Ion 113.00 Diesel #2 - isoprenoids

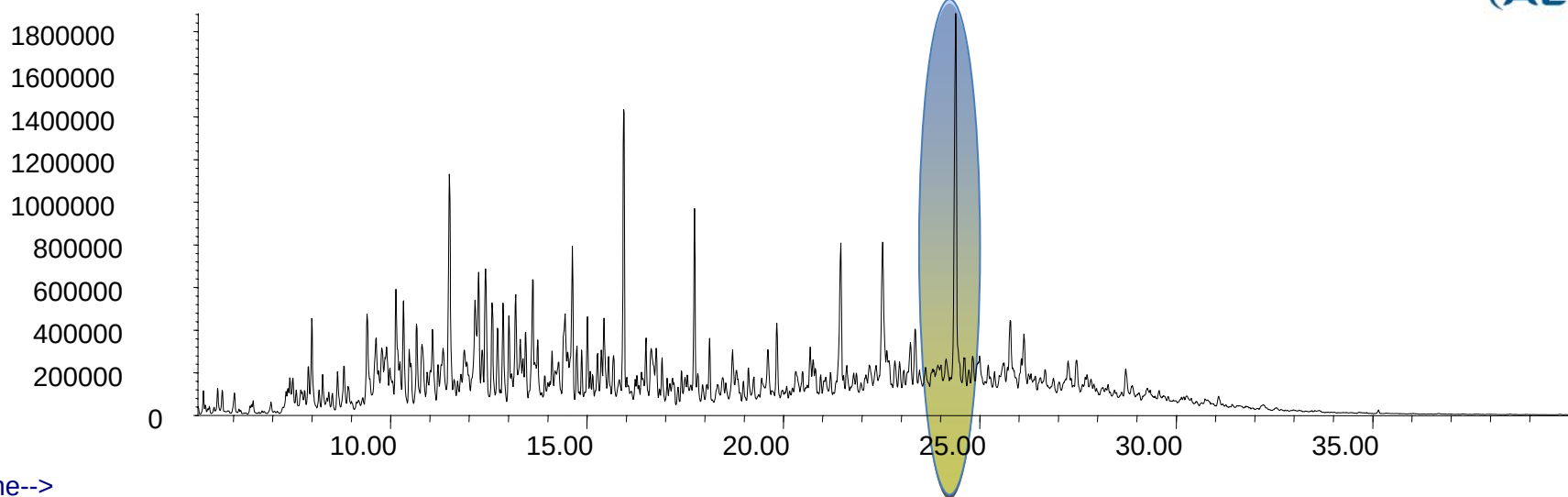


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Abundance

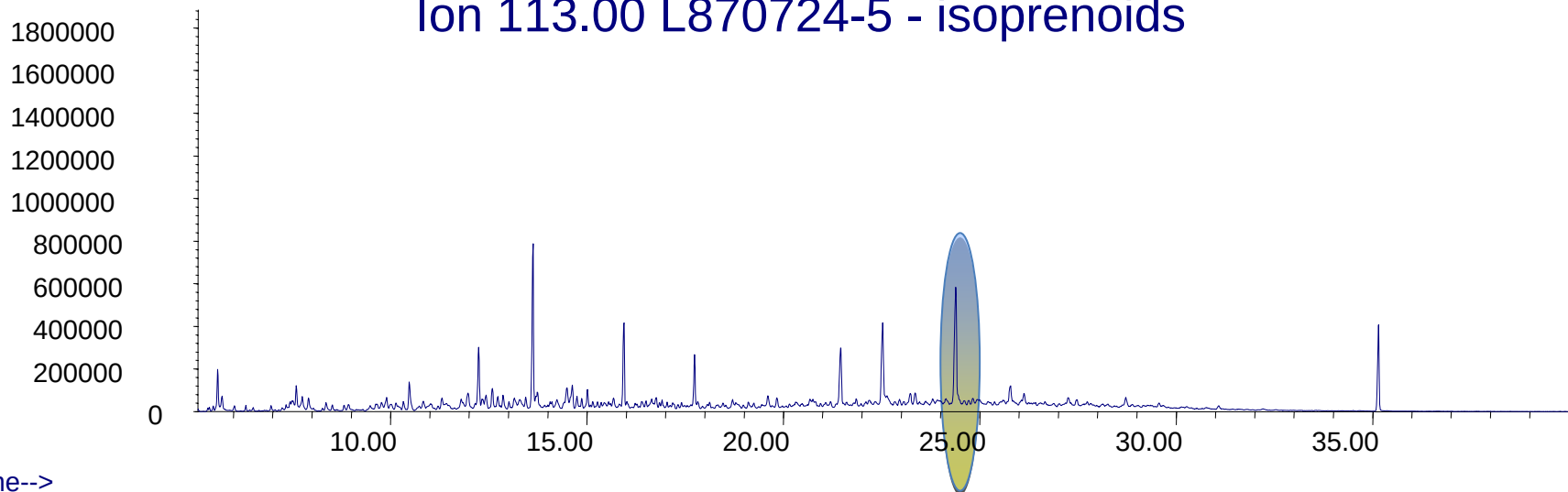


Ion 85.00 L870724-5 - alkanes



Time-->
Abundance

Ion 113.00 L870724-5 - isoprenoids



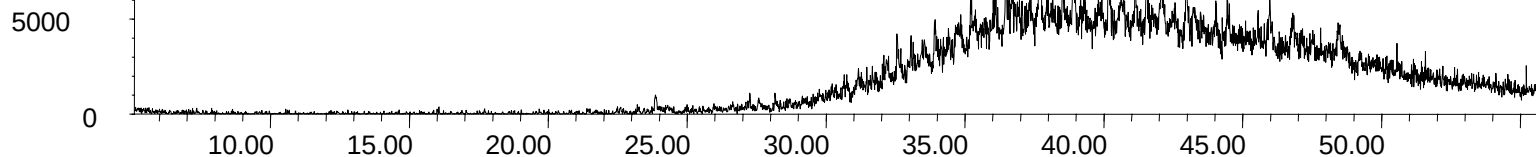
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ISOALKANES AND ISOPRENOIDS SOURCE OILS



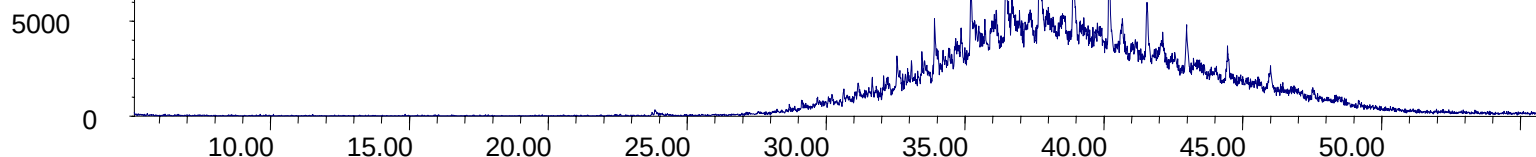
Abundance

Ion 113.00 L870724-26-100(*)



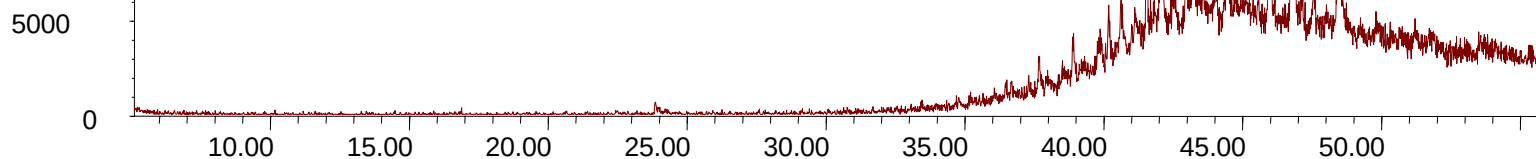
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Abundance

Ion 113.00 L870724-22-1000



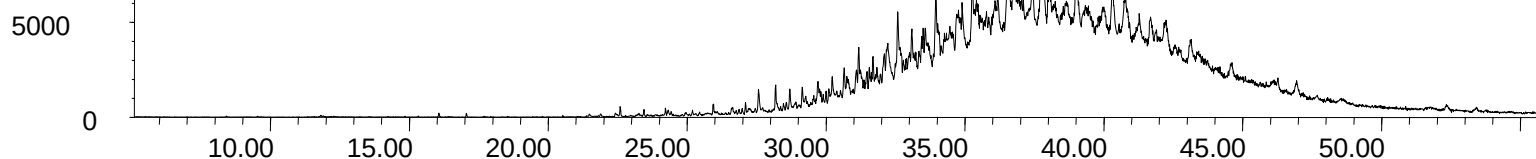
Time-->
Abundance

Ion 113.00 L870724-23-100



Time-->
Abundance

Ion 113.00 L870724-24-100



Time-->

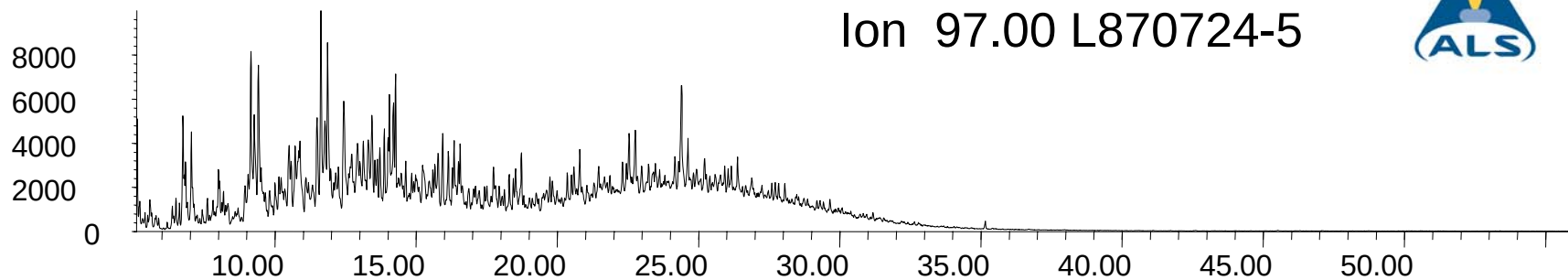


Isoprenoid Analysis

- These biomarkers are more recalcitrant than n-alkanes
- Similar pattern observed in samples -4, -5 and -8
- Not present in lube oils
- Further evidence of a petroleum product other than lube oil
- Ratio of n-alkanes to isoprenoids, and comparison to fresh diesel #2 reveals that samples -4, -5 and -8 severely weathered

ALKYLCYCLOHEXANES

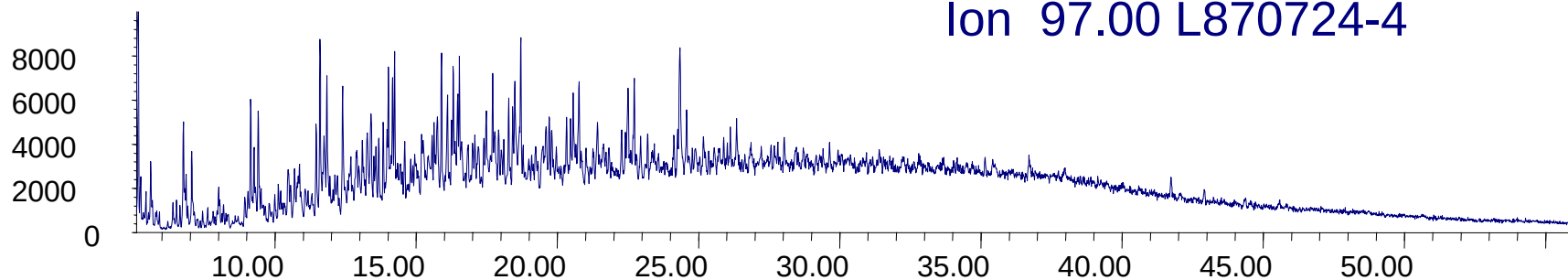
Ion 97.00 L870724-5



Time-->

Abundance

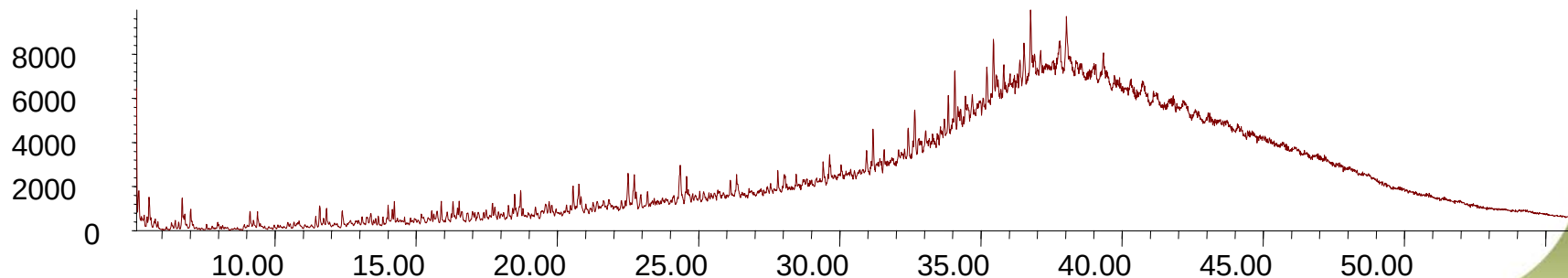
Ion 97.00 L870724-4



Time-->

Abundance

Ion 97.00 L870724-8



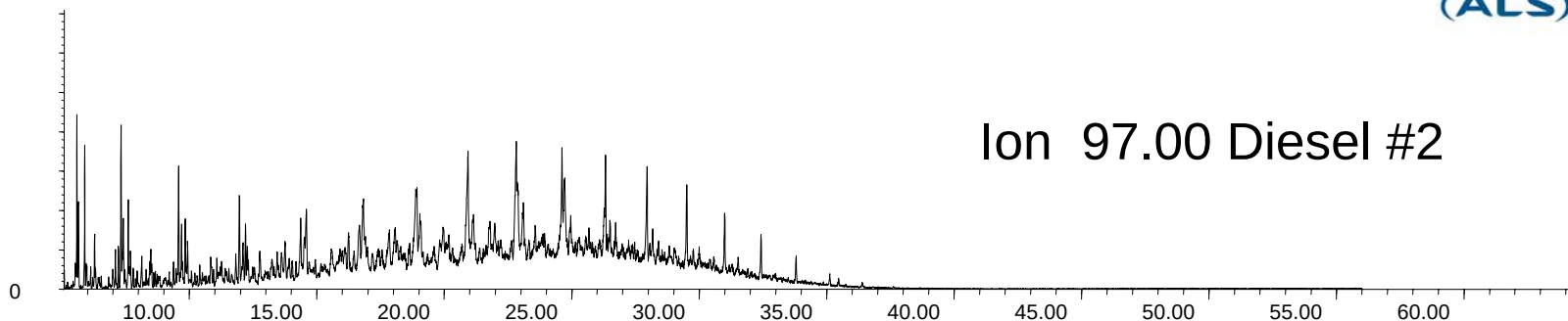
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ALKYLCYCLOHEXANES

Abundance

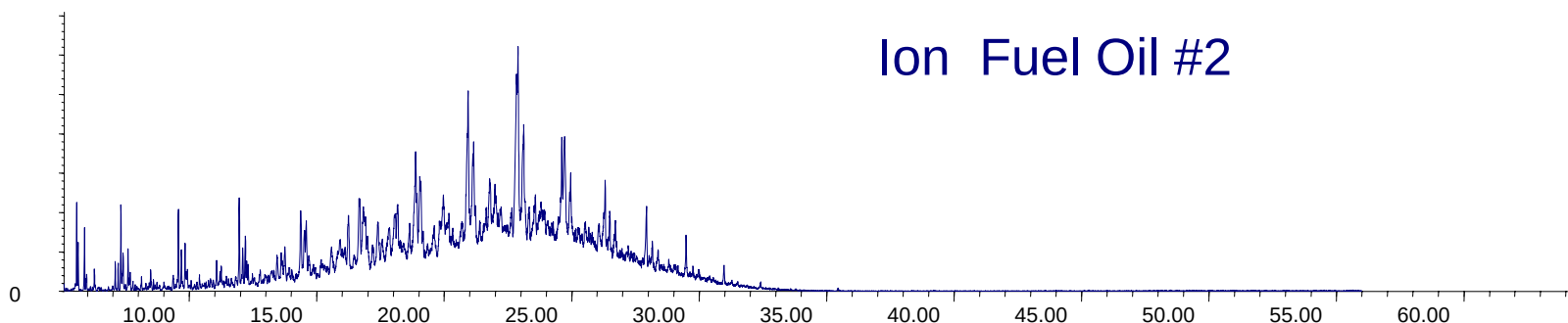
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250000
200000
150000
100000
50000
0



Ion 97.00 Diesel #2

Time-->
Abundance

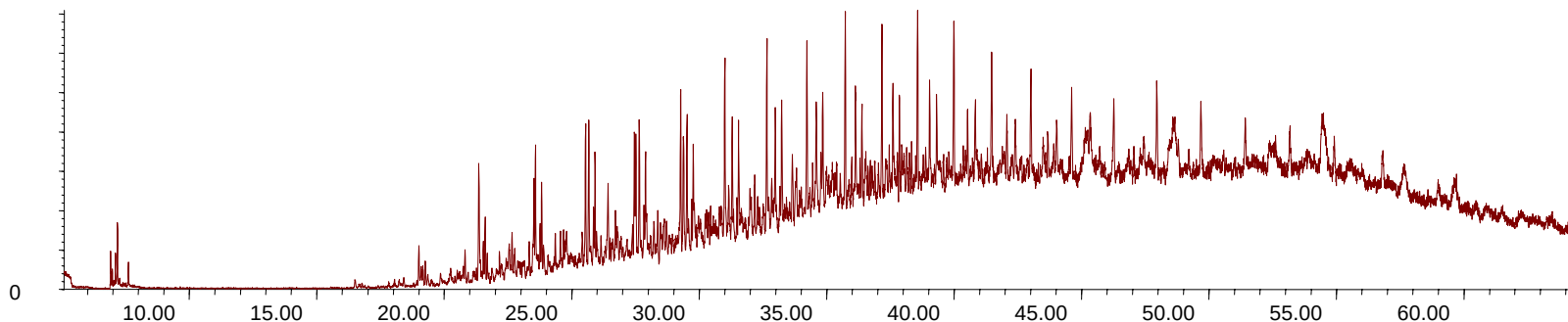
350000
300000
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150000
100000
50000
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Ion Fuel Oil #2

Time-->
Abundance

350000
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250000
200000
150000
100000
50000
0



Ion 97.00 BPMC252 crude oil

Time-->



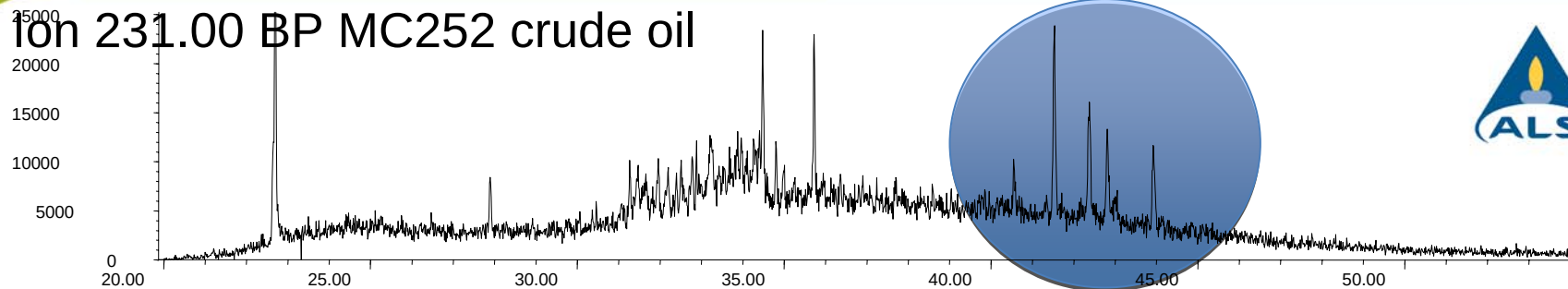
Alkylcyclohexane analysis

- Commonly used for middle distillate forensics (Hostettler and Kvenvolden, 2002)
- Samples -4, -5 and -8 have a similar profile, although sample -8 reveals less product
- Profile observed for samples best fits Diesel #2

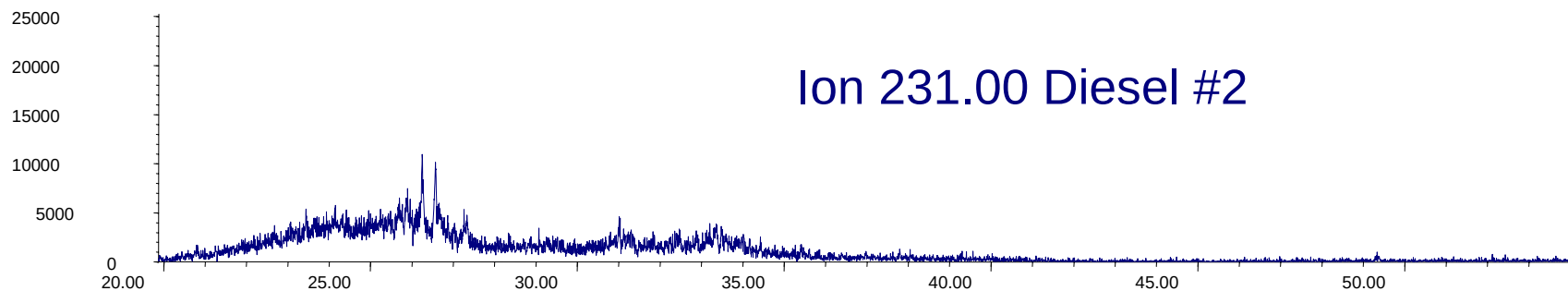
Concern

- Presence of m/z 231 triaromatic steranes not usually associated with middle distillates like diesel
- Analysis of diesel fuels and reclamation samples generated in Western Canada did not detect triaromatic steranes
- Triaromatic steranes commonly found in crude oils
- Sesquiterpanes (m/z 123) are more prevalent than terpanes (m/z 191) and steranes (m/z 218) in middle distillates than in crude oils (Wang et al, 2006; Stout et al, 2005).
- Such an analyses may provide more information to help identify the unknown product present in -4, -5 and -8.

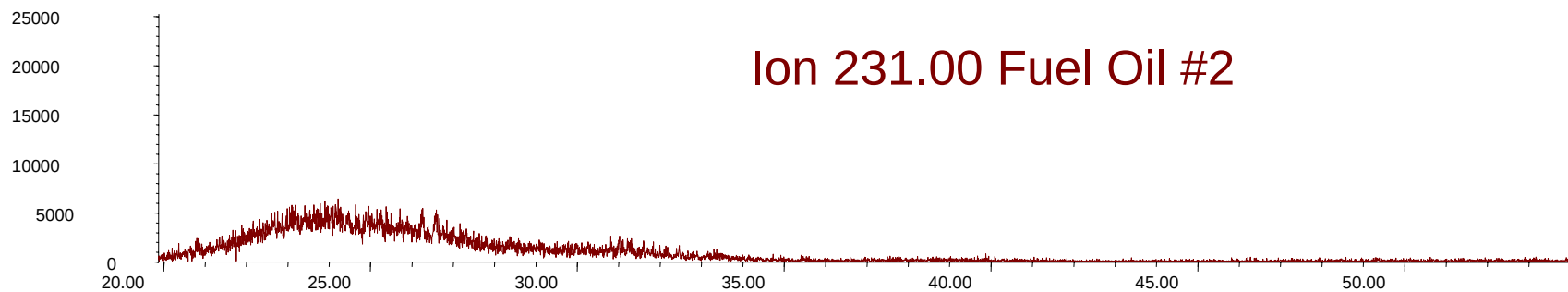
Ion 231.00 BP MC252 crude oil

Time-->
Abundance

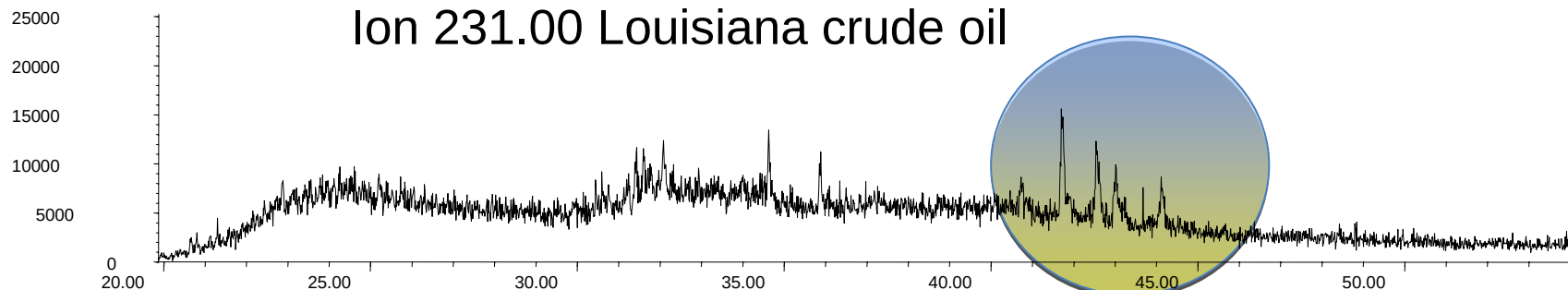
Ion 231.00 Diesel #2

Time-->
Abundance

Ion 231.00 Fuel Oil #2

Time-->
Abundance

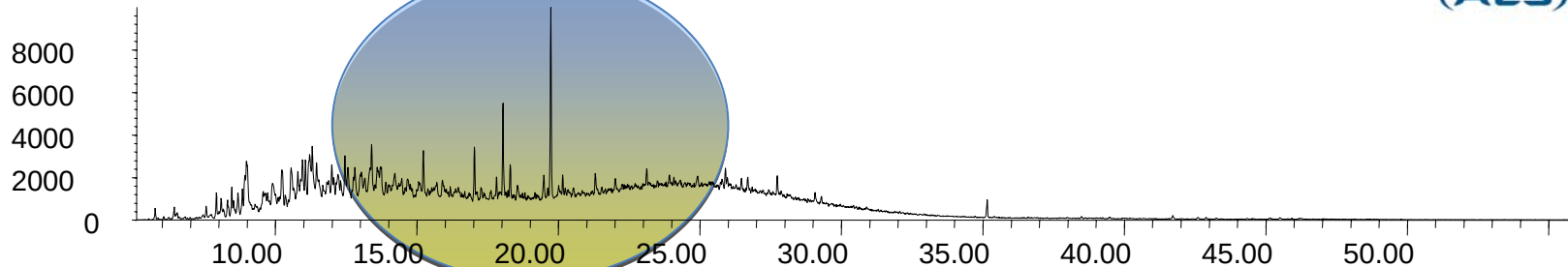
Ion 231.00 Louisiana crude oil



Time-->

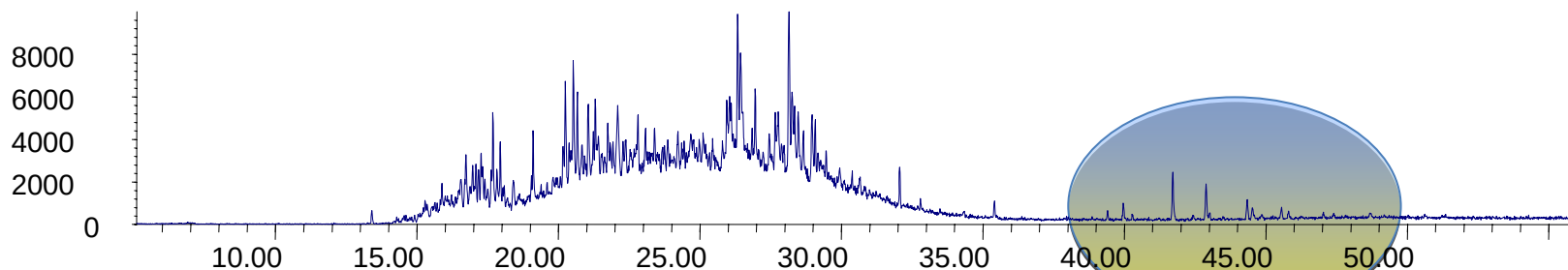
Abundance

Ion 123.00 L870724-5 - sesquiterpanes



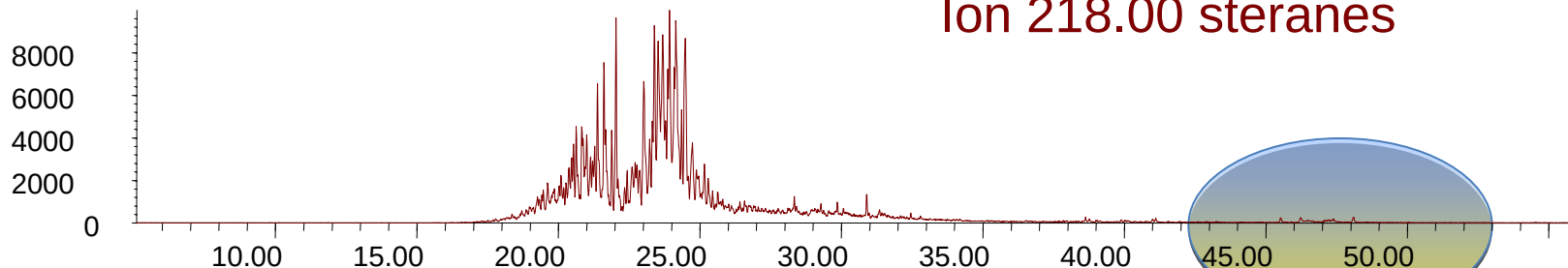
Time-->
Abundance

Ion 191.00 terpanes



Time-->
Abundance

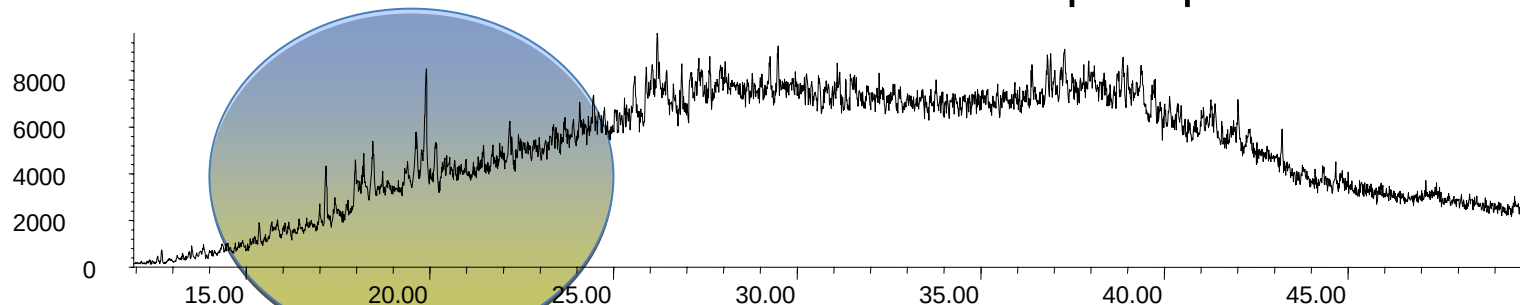
Ion 218.00 steranes



Time-->

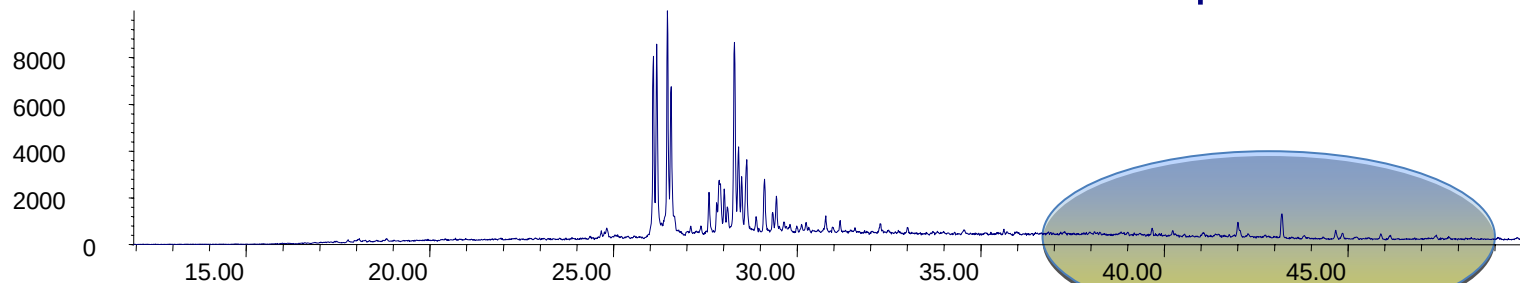
Abundance

Ion 123.00 BP MC252 crude oil sesquiterpanes



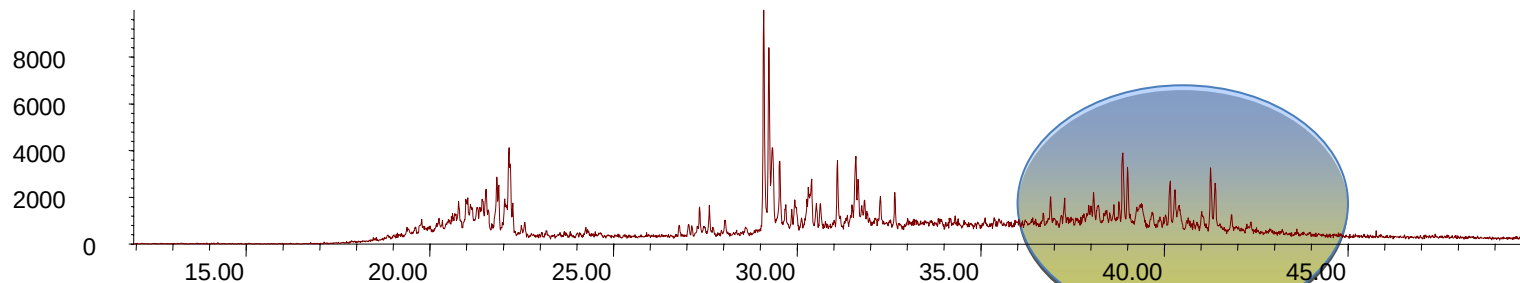
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Abundance

Ion 191.00 BP MC252 crude oil terpanes



Time-->
Abundance

Ion 218.00 BP MC252 crude oil steranes



Time-->

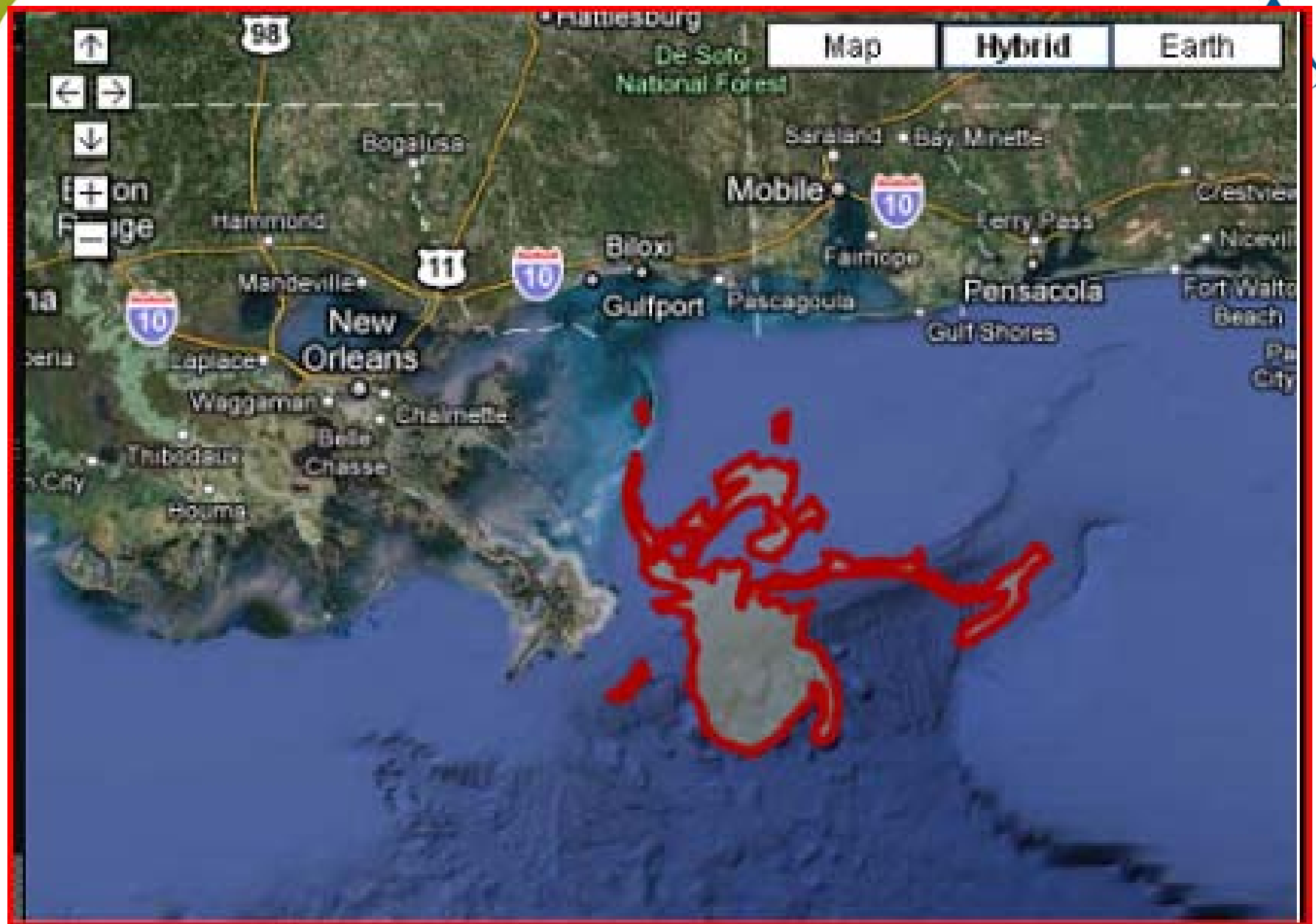
Conclusions Case Study 1

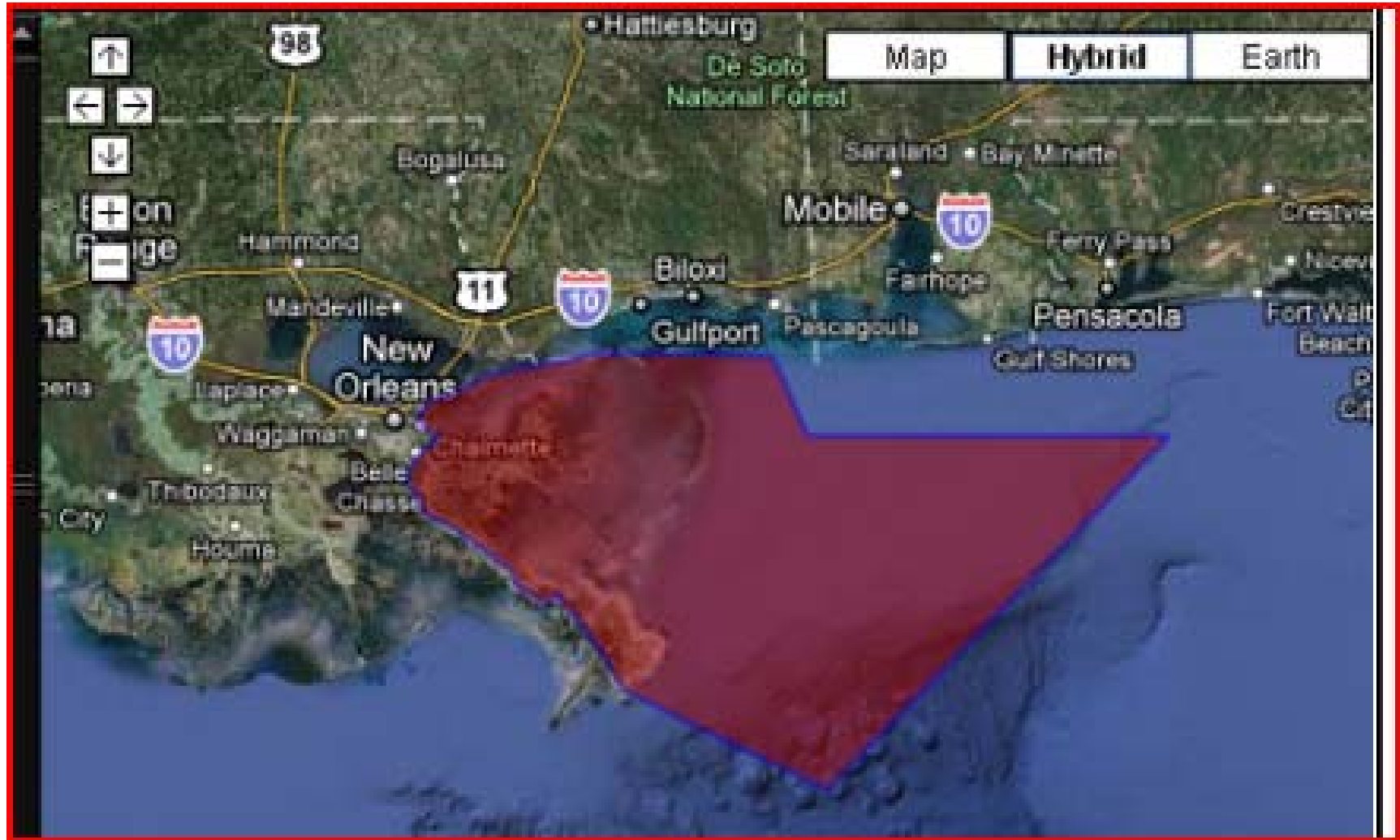


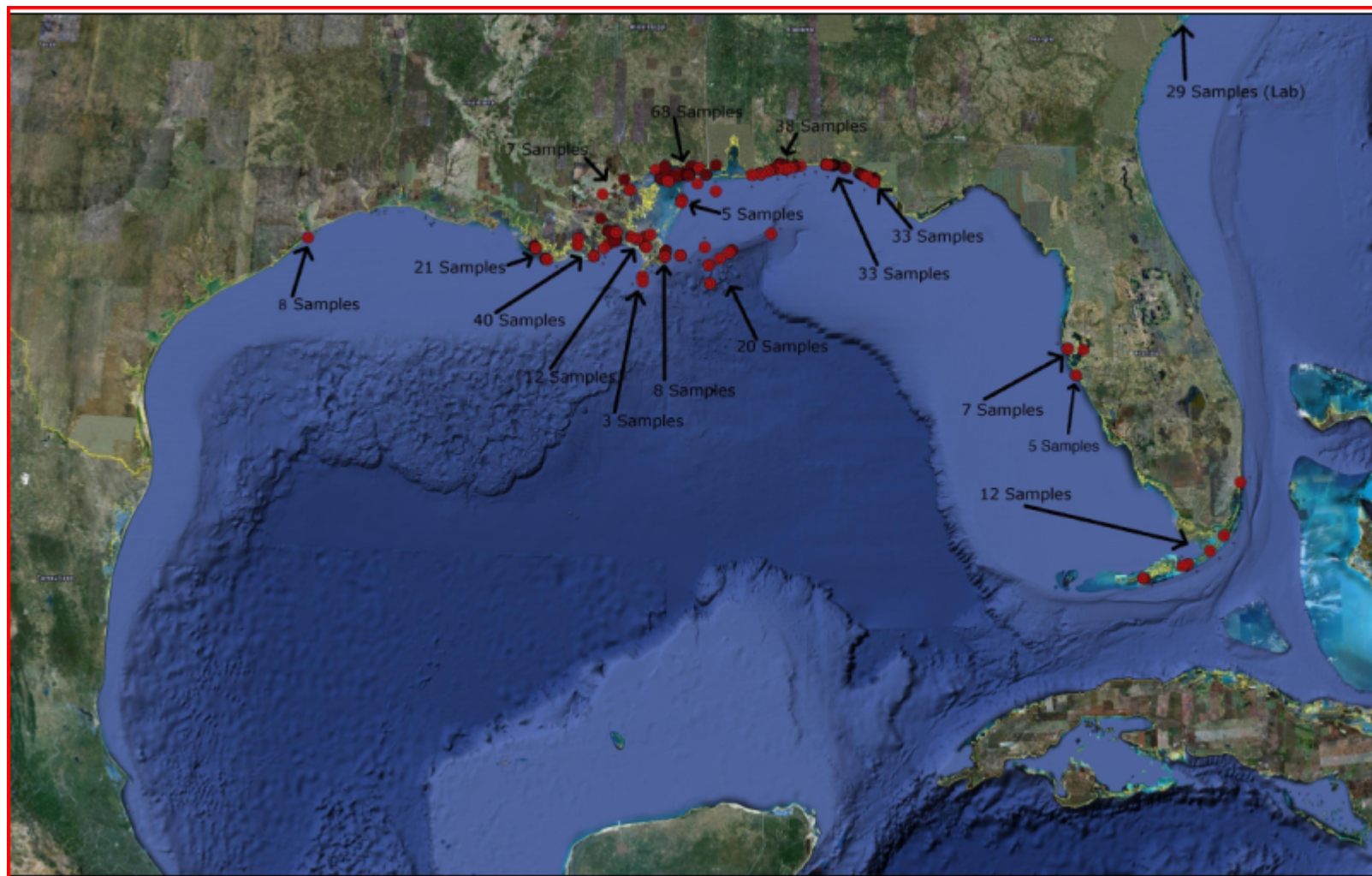
- Sample -4, -5, and -8 contain diesel fuel. This likely associated with activities on adjacent property
- Conclusion supported by isoprenoid, and alkylcyclohexane analyses by comparison with diesel #2 from North America (not source material)
- For diesel fuel the sesquiterpanes (m/z 123) are more prevalent than terpanes (m/z 191) and steranes (m/z 218) (Wang et al, 2006)
- This observation confirmed supporting the presence of diesel fuel #2
- The presence of triaromatic steranes are not usually found in diesel fuels we have analyzed, however, they were reported in S.E. Asia diesel #2 further supporting our conclusions (Wang et al, 2006). Varying TA sterane profile for -4 and -5 can be explained by different spills of diesel
- Sample -8 also contains lubricating oil

Case Study 2 – BP Oil Spill









Island Sands Southern Louisiana





Oil in water,
Venice, Lousiana





Oil on beach,
Pensacola, Florida

Harvesting crab hepatopancreas



We are using oil sorbent pads attached to the anchor to help us find underwater oil plumes...



Tar ball on beach



Fourchon Beach, Louisiana



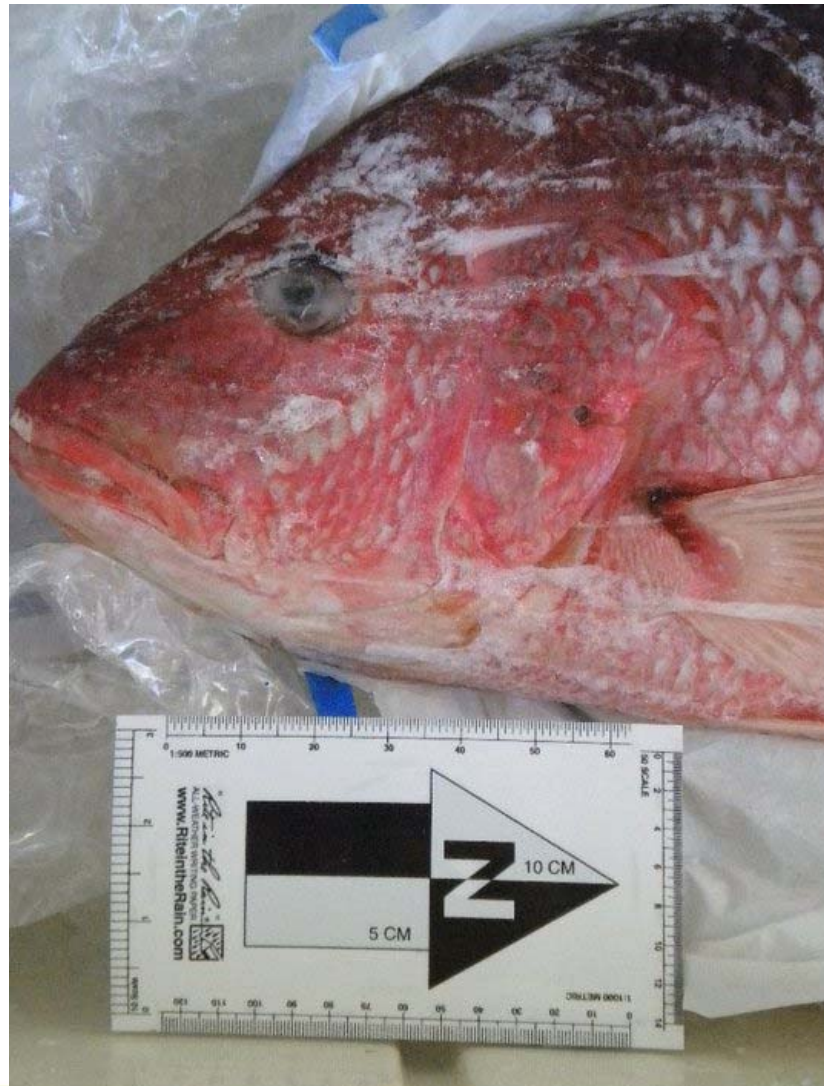
I have been doing night time sampling using
UV light wavelengths to look for oil on the beach
here in St. petersburg, FL



This photo of the beach under IR light looks like it came from an episode of Cops.



The beautiful 11 pound red snapper was caught 35 miles off of Pensacola, with a petroleum-like substance oozing out. It's now at the lab, instead of the dinner table.



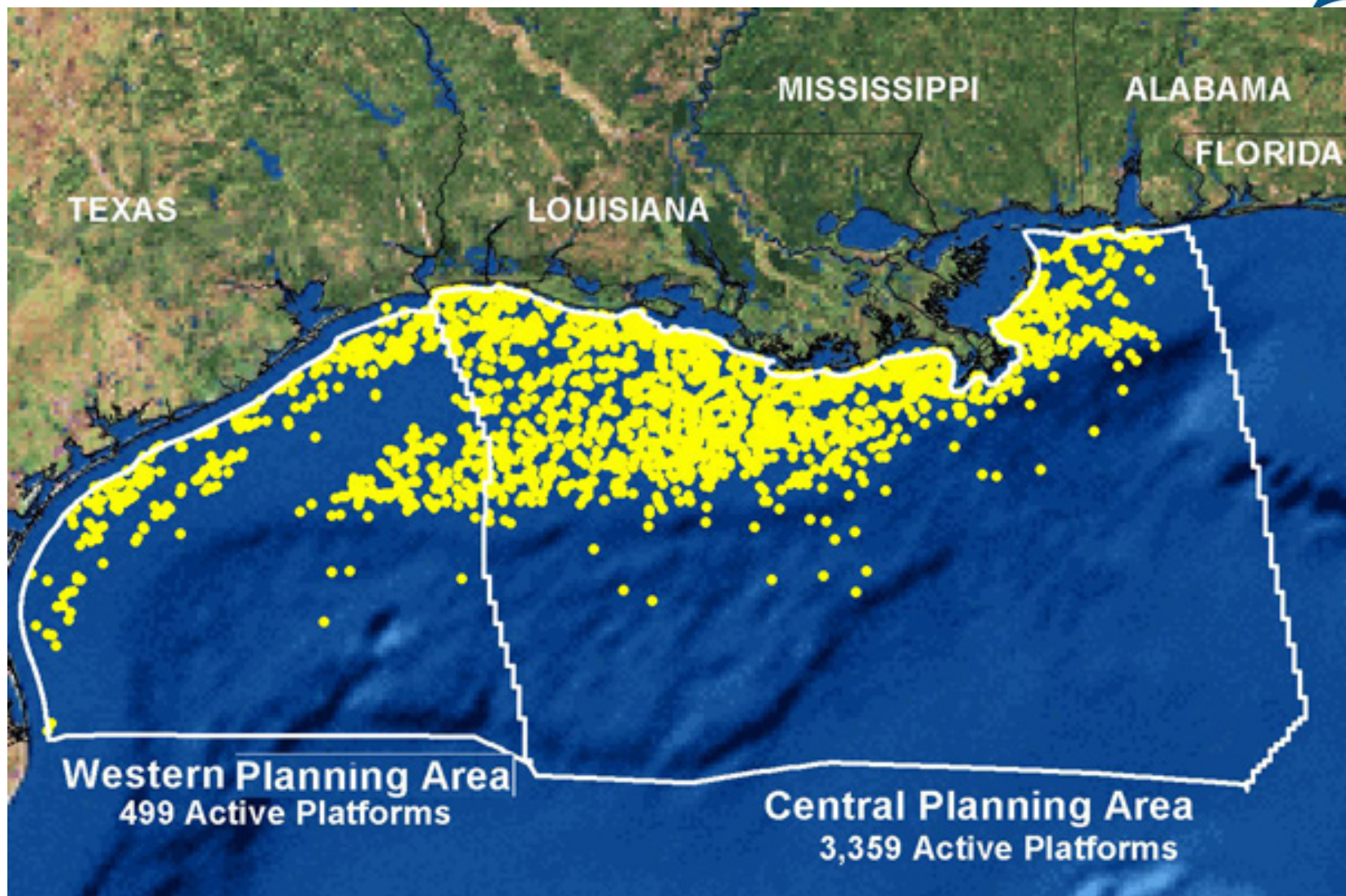
Looking for the oil's leading edge - Key Largo, Gulf side



Forensics for BP Gulf Samples

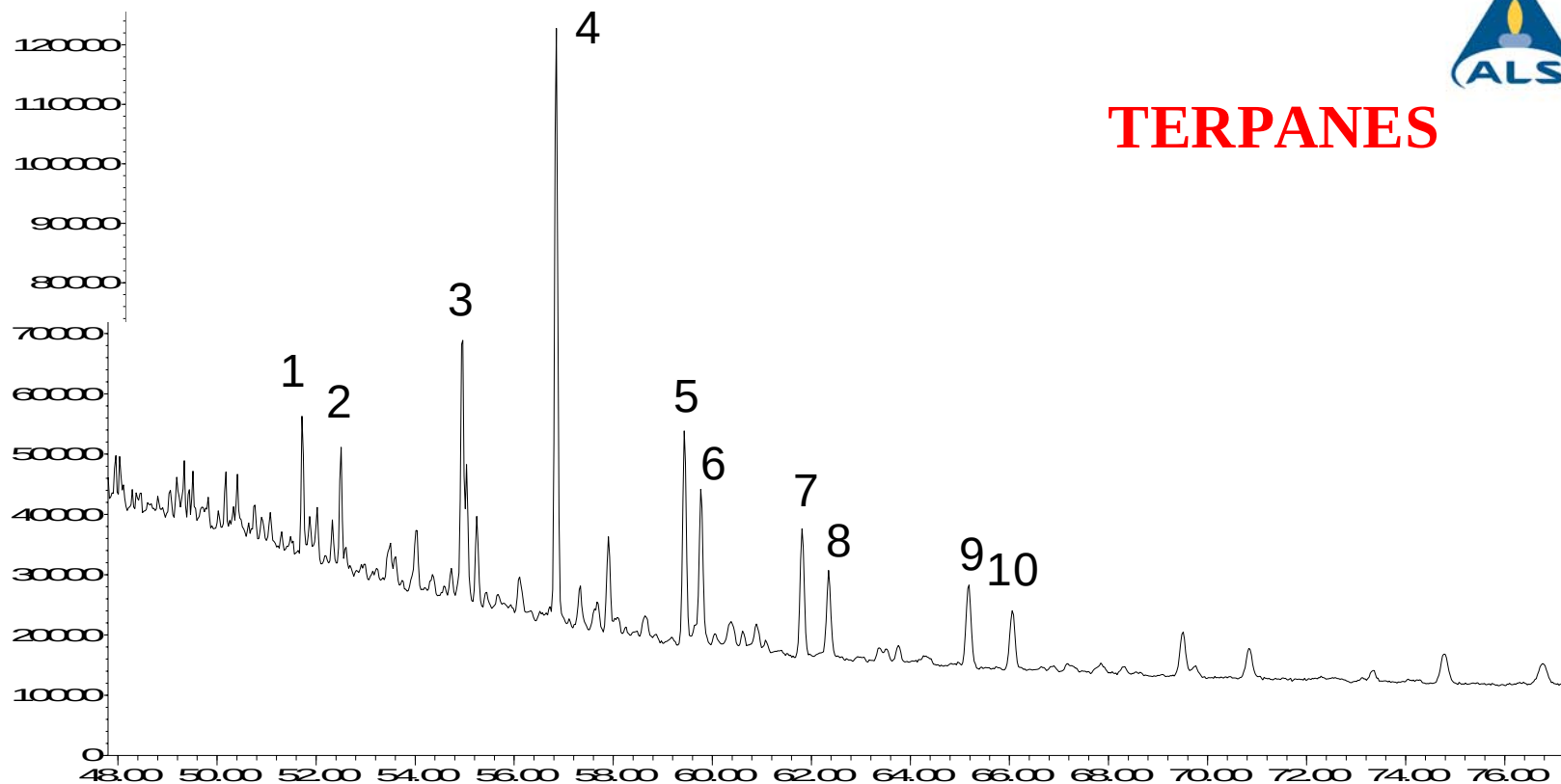


- Approach used for the Korean case study will not work
- Drilling in the Gulf has been going on since 1937
- 3,858 oil and gas platforms in the Gulf since 2006
- Bottom line there is more than BP oil in the Gulf of Mexico
- Considering the environmental and economic impact of the BP Oil Spill we have to be sure that any oil found is undisputably BP Oil, i.e. related to source oil MC252
- Analyses required include: biomarkers (terpanes, steranes, triaromatic steranes, alkanes, isoprenoids, and alkylated PAHs)
- Need ratios of biomarkers and PAHs to generate weight of evidence





TERPANES



Time-->

1. 18a(H)-22,29,30-trisnorhopane - **27Ts**
2. 17a(H)-22,29,30-trisnorhopane - **27Tm**
3. 17a(H),21b(H)-30-norhopane - **29ab**
4. 17a(H),21b(H)-hopane - **30ab**
5. 17a(H),21b(H),22S-homohopane - **31abS**
6. 17a(H),21b(H),22R-homohopane - **31abR**
7. 17a(H),21b(H),22S-bishomohopane - **32abS**
8. 17a(H),21b(H),22R-bishomohopane - **32abR**
9. 17a(H),21b(H),22S-trishomohopane - **33abS**
10. 17a(H),21b(H),22R-trishomohopane - **33abR**

RATIOS

27Ts/27Tm

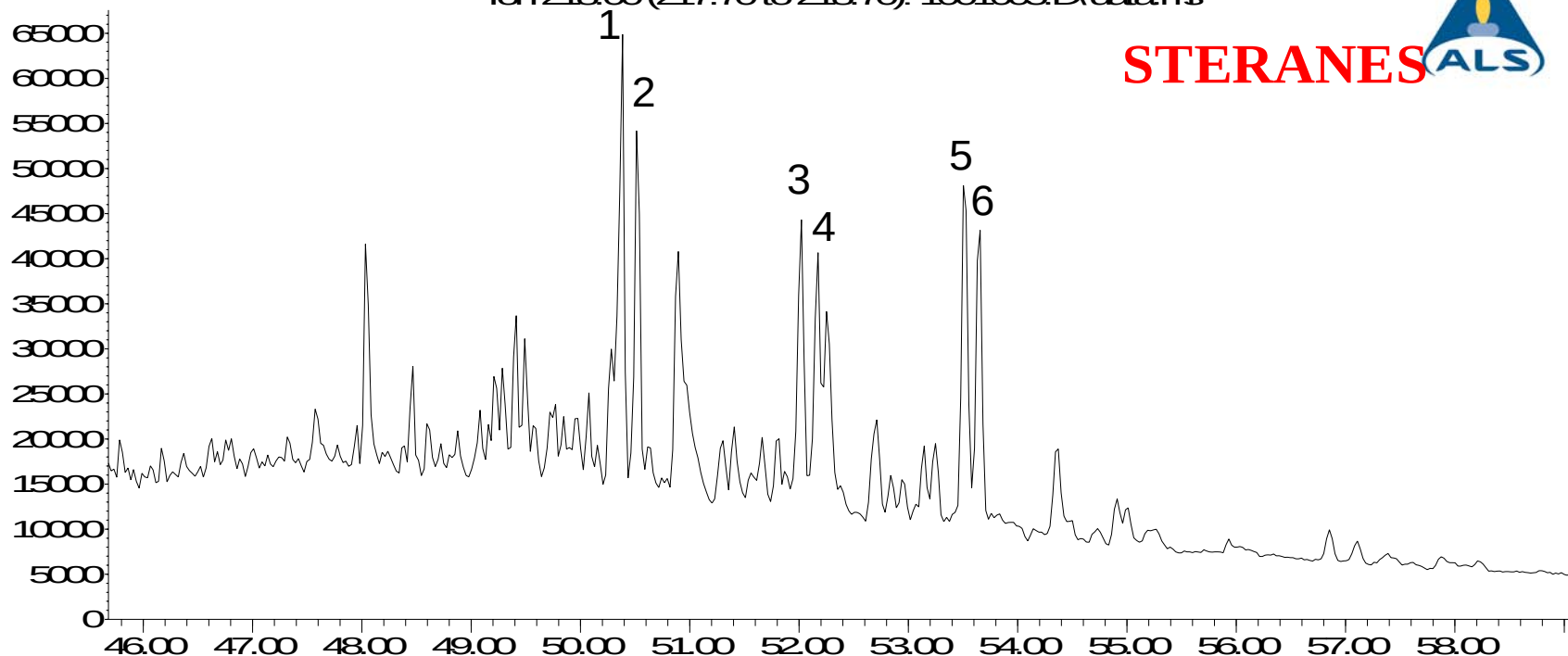
29ab/30ab

31abS/31abR

32abS/32abR

33abS/33abR

Ion 218.00 (217.70 to 218.70): 1001005.D\data.ms



Time→

1. 5a(H), 14b(H),17b(H),20R-cholestane - **27bbR**
2. 5a(H), 14b(H),17b(H),20S-cholestane - **27bbS**
3. 24-methyl-5a(H),14b(H), 17b,20R-cholestane - **28bbR**
4. 24-methyl-5a(H),14b(H),17b,20S-cholestane- **28bbS**
5. 24-ethyl-5a(H),14b(H)m17b,20R-cholestane - **29bbR**
6. 24-ethyl-5a(H),14b(H),17b,20S-cholestane - **29bbS**

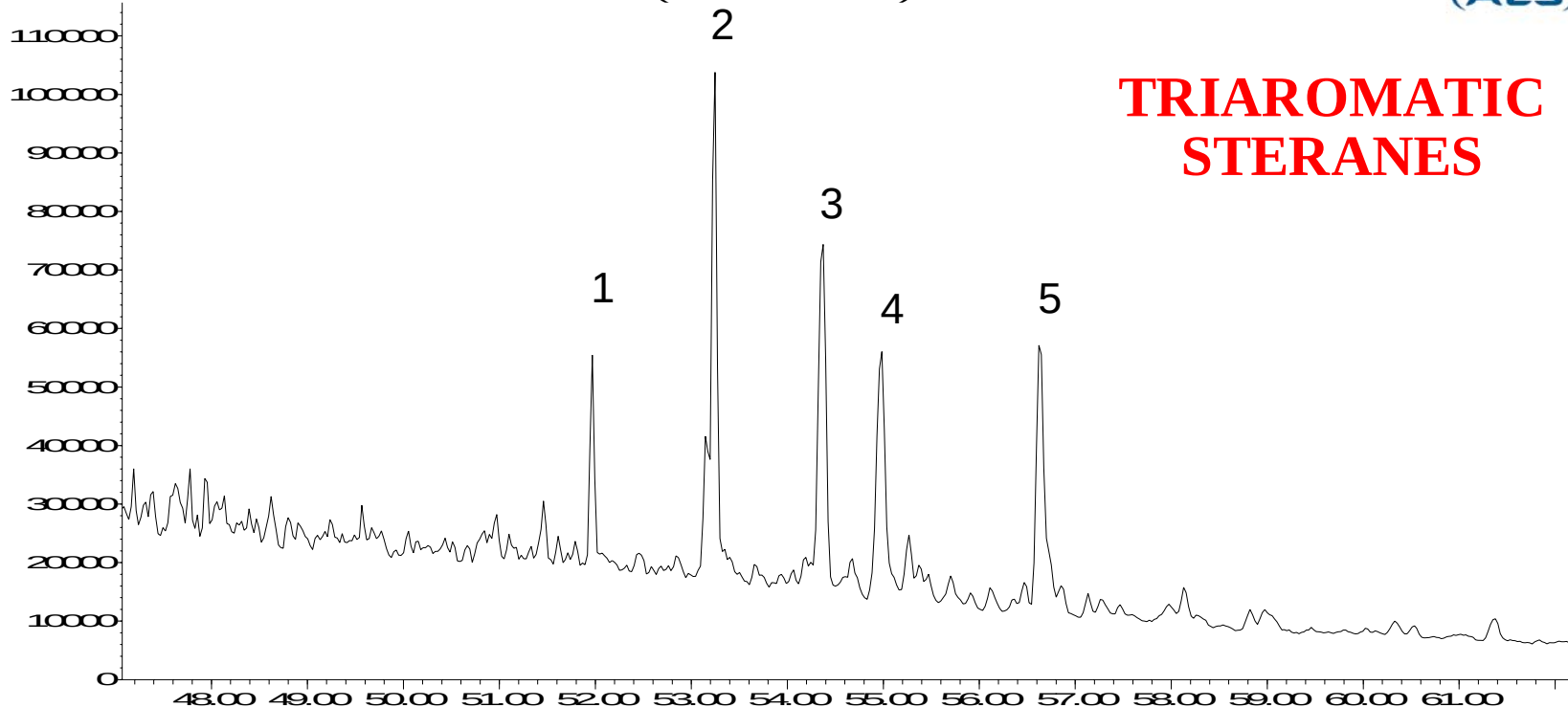
Ratios

$$(27bbR + 27bbS)/(28bbR + 28bbS + 29bbR + 29bbS)$$

$$(28bbR + 28bbS)/(27bbR + 27bbS + 29bbR + 29bbS)$$

$$(29bbR + 29bbS)/(27bbR + 27bbS + 28bbR + 28bbS)$$

Ion 231.00 (230.70 to 231.70): 1001005.D\data.ms



TRIAROMATIC STERANES

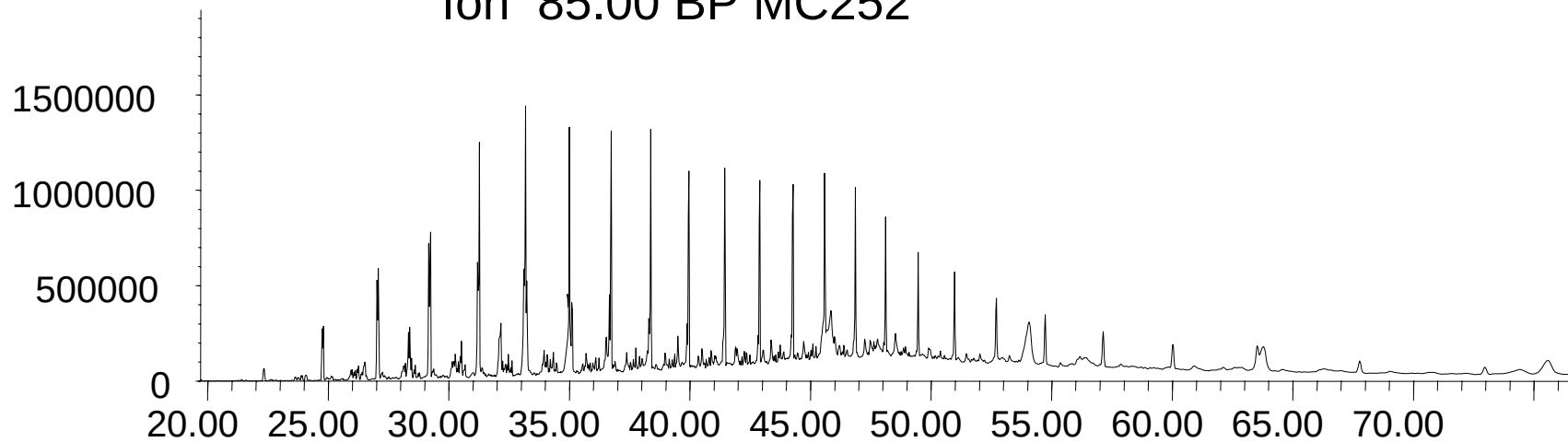
1. C26,20S-triaromatic sterane -**C26TA(20S)**
2. C26, 20R-triaromatic sterane + C27, 20S-triaromatic sterane -**C26TA(20R) + C27TA(20S)**
3. C28, 20S-triaromatic sterane -**C28TA(20S)**
4. C27, 20R-triaromatic sterane -**C27TA(20R)**
5. C28, 20R-triaromatic sterane -**C28TA(20R)**

Time→

Abundance

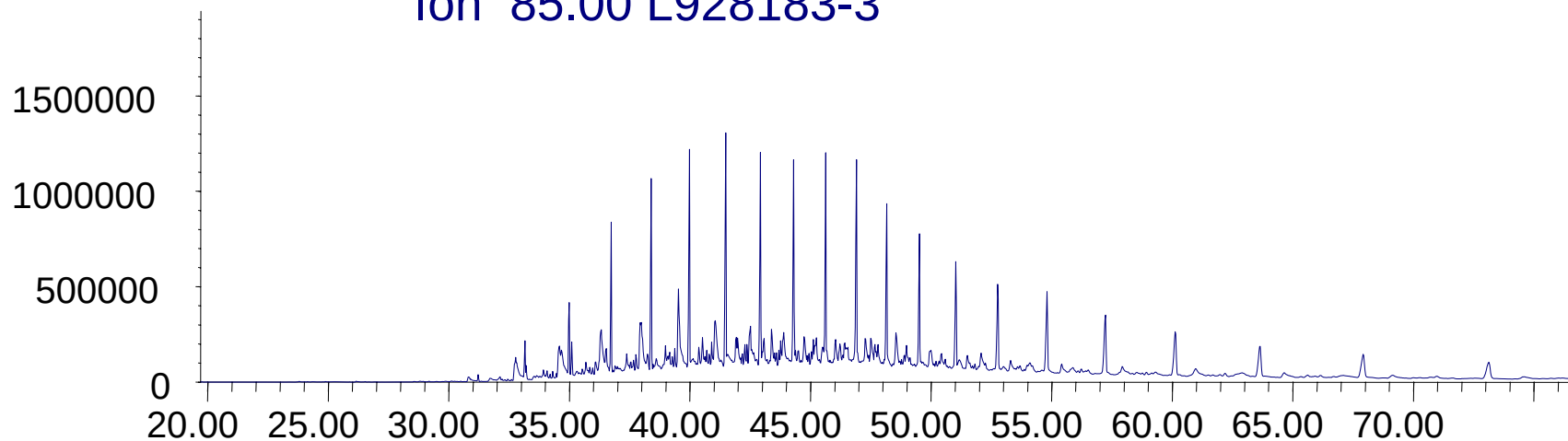


Ion 85.00 BP MC252



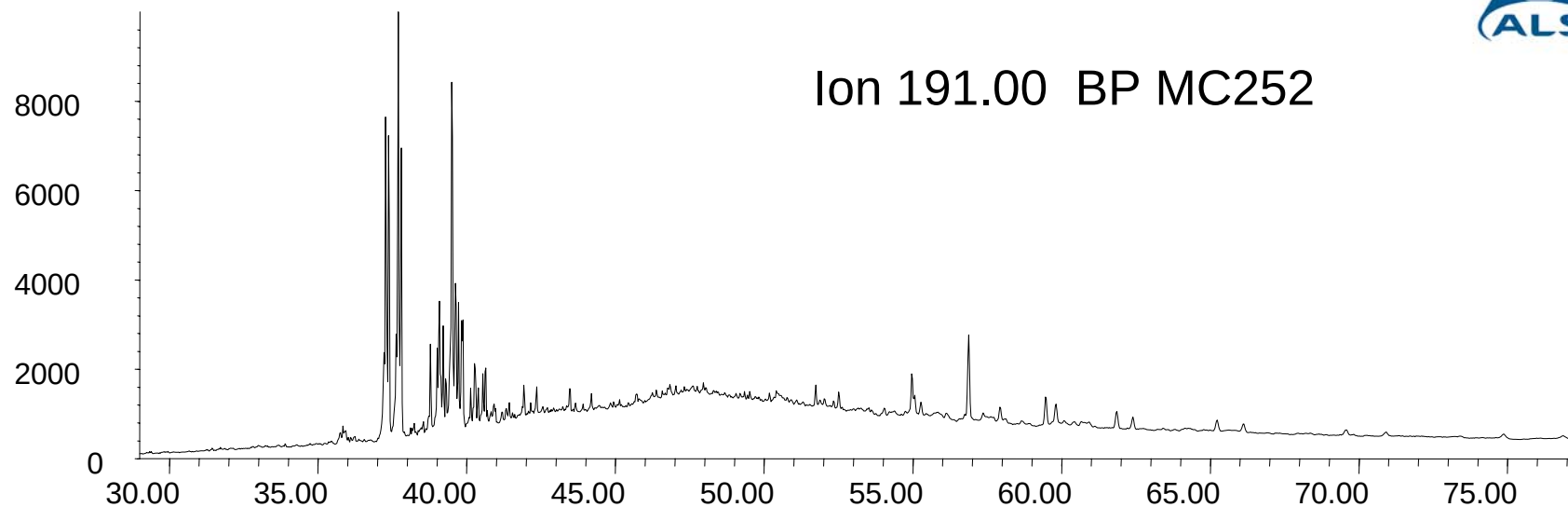
Time-->
Abundance

Ion 85.00 L928183-3

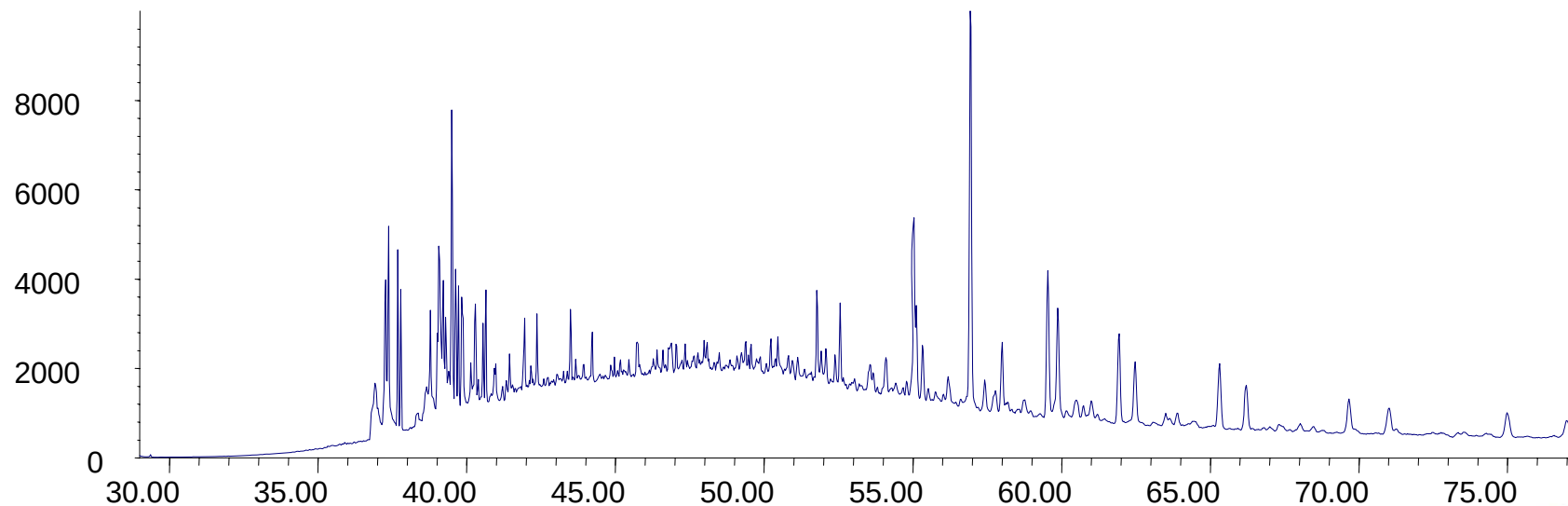


Time-->

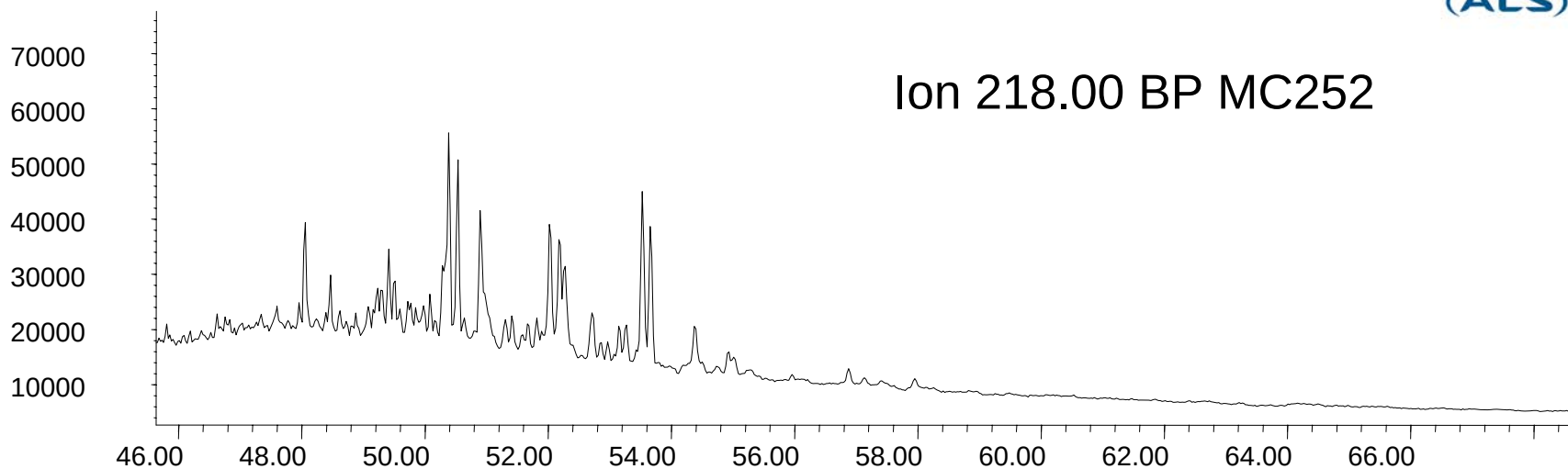
Ion 191.00 BP MC252



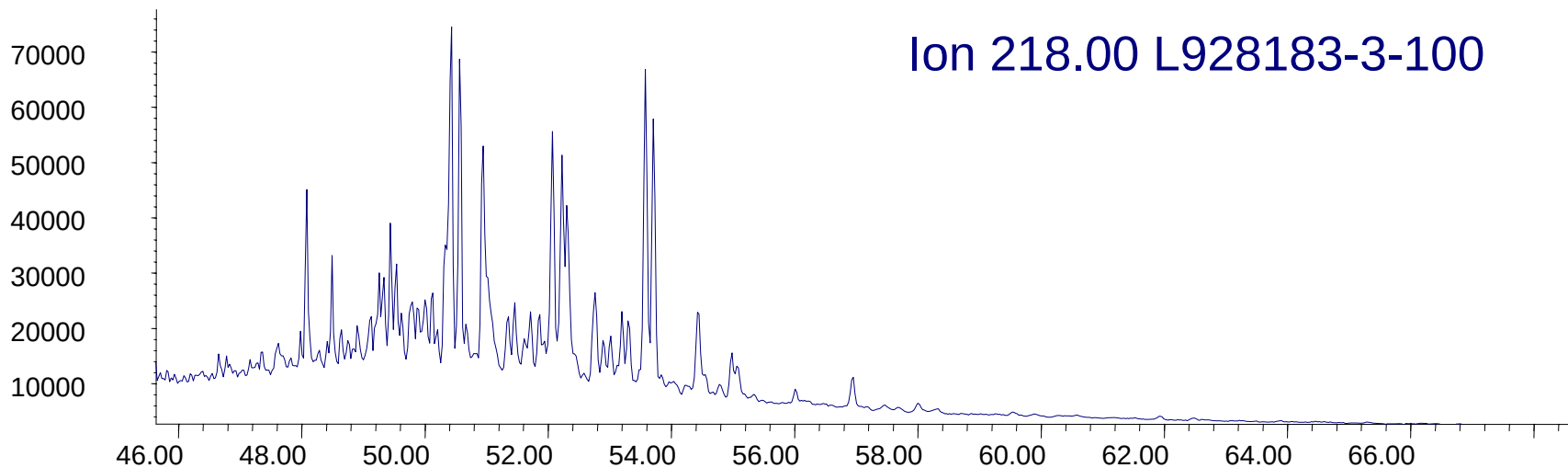
Ion 191.00 L928183-3-100



Ion 218.00 BP MC252

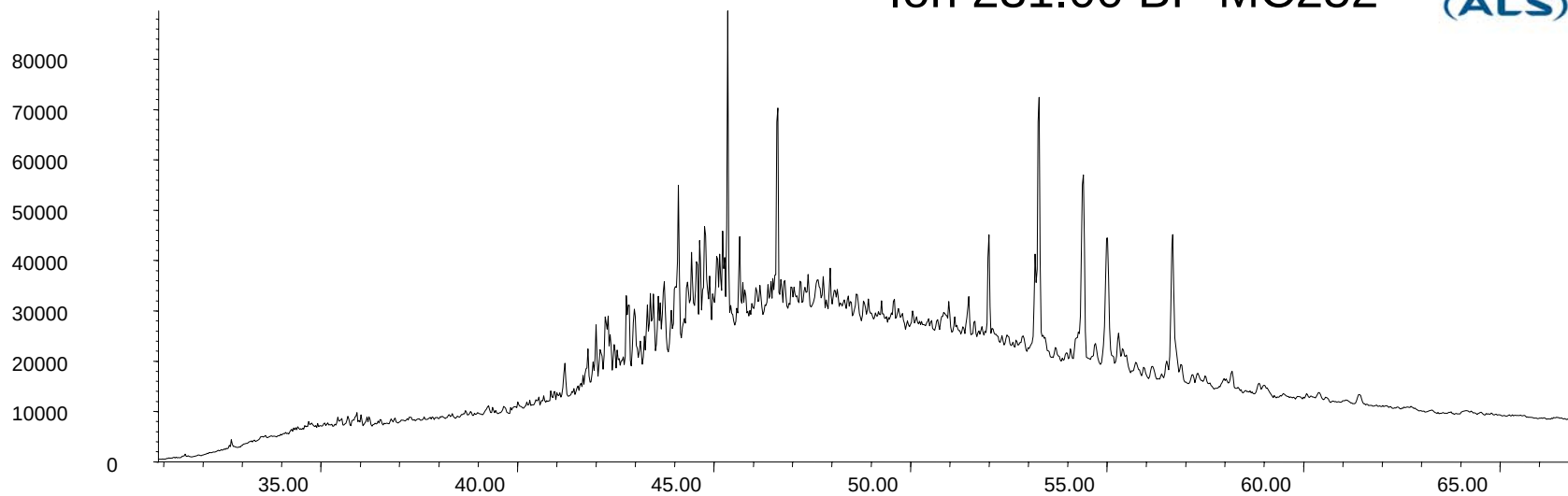


Ion 218.00 L928183-3-100



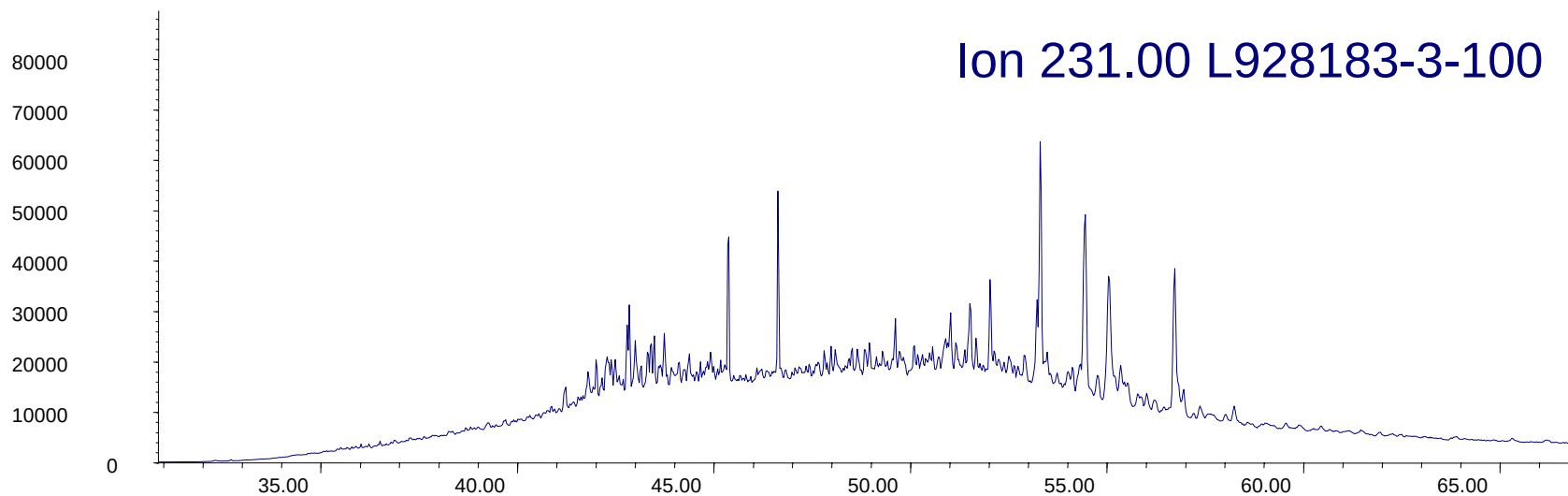
Abundance

Ion 231.00 BP MC252



Time-->
Abundance

Ion 231.00 L928183-3-100



Time-->

Table 1 Summary of diagnostic ratios



	Absolute Difference	Critical Difference	Conclusion
<i>Terpanes</i>			
27TS/27TM	0.1156	0.15649	Match
29ab/30ab	0.017	0.064882	Match
31abS/31abR	0.175	0.197212	Match
32abS/32abR	0.2451	0.187819	No Match
33abS/33abR	0.038	0.202592	Match
<i>Steranes</i>			
(27bbR + 27bbS)/(28bbR + 28bbS + 29bbR + 29bbS)	0.003	0.0892	Match
(28bbR + 28bbS)/(27bbR + 27bbS + 29bbR + 29bbS)	0.019	0.0528	Match
(29bbR + 29bbS)/(27bbR + 27bbS + 28bbR + 28bbS)	0.0247	0.0712	Match
<i>Triaromatic Steranes</i>			
C26TA(20S)/C28TA(20S)	0.029	0.0741	Match
C27TA(20R)/C28TA(20R)	0.045	0.1263	Match
C28TA(20R)/C28TA(20S)	0.109	0.1197	Match
<i>PAHs</i>			
C3-DBT/C3-Phen	0.047	0.0411	No Match
C2-DBT/C2-Phen	0.01	0.0315	Match

Critical Difference Analysis

- Repeatability limit = $2.8 * 5\% = 14\%$
- Critical difference = mean of two ratios * $14/100$
- Absolute difference = difference of two ratios
- If absolute difference $\leq$ critical difference = match
- If absolute difference $>$ critical difference = no match
- Ref: Hansen et al (2007). Emerging CEN Methodology for Oil Spill Identification. In Oil Spill Environmental Forensics: Fingerprinting and Source Identification, Eds. Z. Wang and S.A. Stout, Elsevier, New York

Conclusions

- The techniques presented here are by no means complete. There are many other procedures available, including:
- PAHs with chemometrics – Iqbal et al, 2008; Zeigler et al, 2008; Fernandez-Varela, 2010; and Zemo, 2009
- Nickel/Vanadium ratios – Osuji et al, 2006
- Chemometrics – Gaines et al, 2006; Pasadakis et al, 2008; Hupp et al, 2008
- Sulfur and oxygen heterocyclic aromatics – Zhihuan et al, 2008
- Compound specific isotope analyses – Boyd et al, 2006; Philp et al, 2002; Li et al, 2009

Is the approach used by ALS in the Gulf good enough?



- Thanks for your help gentlemen.
- And by the way, even our most ardent critics, (can you believe we have any?), are impressed with the quality of ALS' lab work, so thanks.
- This is particularly true of some of the more critical university researchers, who have commented favorably on the reports. The methods used are as good or better than anything coming up at this week's JSOST conference here in St. Petersburg.
- Marco Kaltofen, PE, Boston Chemical Data Group



ALS Laboratory Group

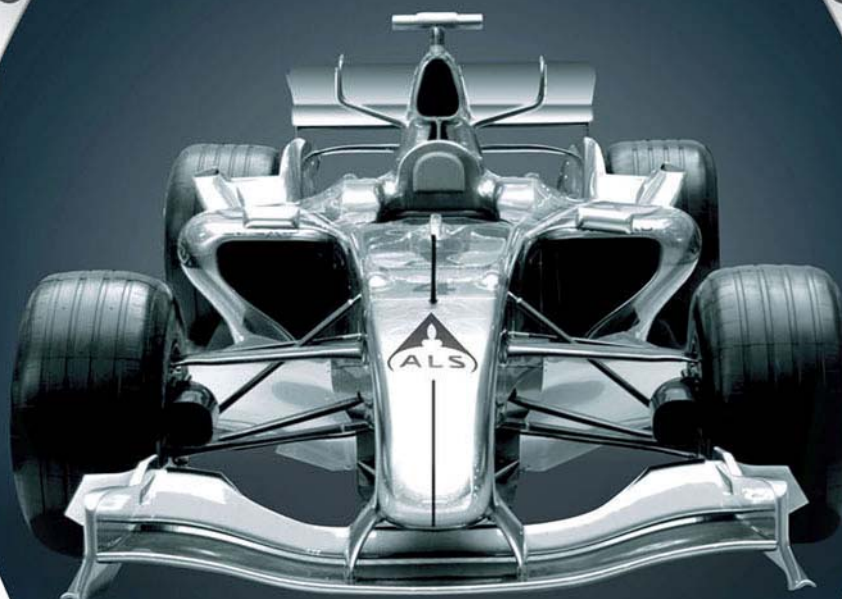
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