Source Identification of Hydrocarbons Following Environmental Releases

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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

| Carbon# | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| B.P (°C)| 4.2| 5.1| 6.5| 7.6| 9.8| 12.6| 13.1| 17.4| 36| 21.8| 25.5| 21.3| 27.0| 27.7| 30.2| 31.8| 33.9| 38.3| 35.8| 36.9| 38.0| 39.1| 40.2| 41.7| 42.2| 43.1| 44.0|
| D.P (°C)| 44| 31| 97| 151| 239| 313| 343| 384| 421| 436| 486| 519| 546| 575| 601| 625| 680| 741| 785| 851| 714| 735| 761| 796| 838| 888| 940|

- Gasoline
- Mineral Spirits
- #1 Diesel
- #2 Diesel
- Jet, Jet A
- Gas Oil, Fuel Oil
- Heavy Diesel
- Lubricating Oils
Is this the same product or something different?
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

Ion 85.00 L870724-25-1000

Ion 85.00 L870724-23-100

Ion 85.00 L870724-24-100

Ion 85.00 L870724-26-100
WHAT IS THIS?

OBVIOUS LUBE OIL
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”
SCAN FOR TERPANES

Ion 191.00 L870724-4

Ion 191.00 L870724-5
SCAN FOR TERPANES SOURCE OILS

Ion 191.00 L870724-26-1000

Ion 191.00 L870724-22-1000

Ion 191.00 L870724-23-100

Ion 191.00 L870724-24-100
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 SOURCE OILS

Ion 218.00 L870724-26-1000

Ion 218.00 L870724-22-1000

Ion 218.00 L870724-23-100

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
SCAN FOR TRIAROMATIC STERANES

Ion 231.00 L870724-5

Ion 231.00 L870724-4

Ion 231.00 L870724-8
TRIAROMATIC STERANES SOURCE OILS

Ion 231.00 L870724-26-1000

Ion 231.00 L870724-22-1000

Ion 231.00 L870724-23-100

Ion 231.00 L870724-24-100
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
ISOALKANES AND ISOPRENOIDS

Ion 113.00 L870724-5

Ion 113.00 L870724-4

Ion 113.00 L870724-8
ISOALKANES AND ISOPRENOIDS

Ion 113.00 BP Crude MC252

Ion 113.00 Diesel #2

Ion 113.00 Fuel Oil #2

Ion 113.00 Louisiana crude oil
Ion 85.00 L870724-5 - alkanes

Ion 113.00 L870724-5 - isoprenoids
ISOALKANES AND ISOPRENOIDS SOURCE OILS

1. Ion 113.00 L870724-26-100(*)

2. Ion 113.00 L870724-22-1000

3. Ion 113.00 L870724-23-100

4. Ion 113.00 L870724-24-100
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

Ion 97.00 L870724-4

Ion 97.00 L870724-8

ALKYLCYCLOHEXANES
ALKYLCYLOHEXANES

Ion 97.00 Diesel #2

Ion 97.00 Fuel Oil #2

Ion 97.00 BPMC252 crude oil

Abundance
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

Ion 231.00 Diesel #2

Ion 231.00 Fuel Oil #2

Ion 231.00 Louisiana crude oil
Ion 123.00 L870724-5 - sesquiterpanes

Ion 191.00 terpanes

Ion 218.00 steranes
Ion 123.00 BP MC252 crude oil sesquiterpanes

Ion 191.00 BP MC252 crude oil terpanes

Ion 218.00 BP MC252 crude oil steranes
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.
Island Sands Southern Louisiana
Oil in water,
Venice, Louisiana
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
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
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

\[
\frac{27bbR + 27bbS}{28bbR + 28bbS + 29bbR + 29bbS}
\]
\[
\frac{28bbR + 28bbS}{27bbR + 27bbS + 29bbR + 29bbS}
\]
\[
\frac{29bbR + 29bbS}{27bbR + 27bbS + 28bbR + 28bbS}
\]
1. C26, 20S-triaromatic sterane \(-C_{26}TA(20S)\)
2. C26, 20R-triaromatic sterane + C27, 20S-triaromatic sterane \(-C_{26}TA(20R) + C_{27}TA(20S)\)
3. C28, 20S-triaromatic sterane \(-C_{28}TA(20S)\)
4. C27, 20R-triaromatic sterane \(-C_{27}TA(20R)\)
5. C28, 20R-triaromatic sterane \(-C_{28}TA(20R)\)
**Table 1 Summary of diagnostic ratios**

<table>
<thead>
<tr>
<th></th>
<th>Absolute Difference</th>
<th>Critical Difference</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terpanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27TS/27TM</td>
<td>0.1156</td>
<td>0.15649</td>
<td>Match</td>
</tr>
<tr>
<td>29ab/30ab</td>
<td>0.017</td>
<td>0.064882</td>
<td>Match</td>
</tr>
<tr>
<td>31abS/31abR</td>
<td>0.175</td>
<td>0.197212</td>
<td>Match</td>
</tr>
<tr>
<td>32abS/32abR</td>
<td>0.2451</td>
<td>0.187819</td>
<td>No Match</td>
</tr>
<tr>
<td>33abS/33abR</td>
<td>0.038</td>
<td>0.202592</td>
<td>Match</td>
</tr>
<tr>
<td><strong>Steranes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(27bbR + 27bbS)/(28bbR + 28bbS + 29bbR + 29bbS)</td>
<td>0.003</td>
<td>0.0892</td>
<td>Match</td>
</tr>
<tr>
<td>(28bbR + 28bbS)/(27bbR + 27bbS + 29bbR + 29bbS)</td>
<td>0.019</td>
<td>0.0528</td>
<td>Match</td>
</tr>
<tr>
<td>(29bbR + 29bbS)/(27bbR + 27bbS + 28bbR + 28bbS)</td>
<td>0.0247</td>
<td>0.0712</td>
<td>Match</td>
</tr>
<tr>
<td><strong>Triaromatic Steranes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C26TA(20S)/C28TA(20S)</td>
<td>0.029</td>
<td>0.0741</td>
<td>Match</td>
</tr>
<tr>
<td>C27TA(20R)/C28TA(20R)</td>
<td>0.045</td>
<td>0.1263</td>
<td>Match</td>
</tr>
<tr>
<td>C28TA(20R)/C28TA(20S)</td>
<td>0.109</td>
<td>0.1197</td>
<td>Match</td>
</tr>
<tr>
<td><strong>PAHs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3-DBT/C3-Phen</td>
<td>0.047</td>
<td>0.0411</td>
<td>No Match</td>
</tr>
<tr>
<td>C2-DBT/C2-Phen</td>
<td>0.01</td>
<td>0.0315</td>
<td>Match</td>
</tr>
</tbody>
</table>
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 ≤ critical difference = match
• If absolute difference > critical difference = no match
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
  - 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