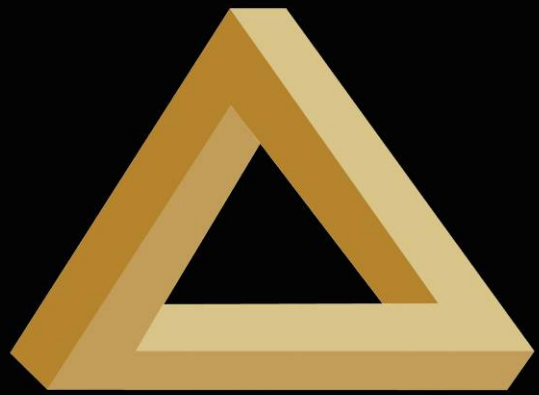


TRIUM

트 리 엄

Effective Use of Environmental Forensics for Determining Liability on Unknown Sources of Petroleum Hydrocarbons

Presented by:
Court Sandau, PhD, PChem

REMTECH 2010 – October 22, 2010

Environmental Forensic Investigations

The systematic examination of environmental information, which will likely be used in litigation, to allocate responsibility for contamination

Success relies on an understanding of a variety of disciplines and knowing which tools are best suited for a particular case

Birth of Environmental Forensics

Exxon Valdez 1989

Gulf of Mexico

- 400+ cases pending
- Worth estimated at $37.6 billion
- Many cases will rely on environmental forensics for link to BP

- $6.1 billion spent
- 145,000 claims worth $319 million

Easiest to Attack Data Quality

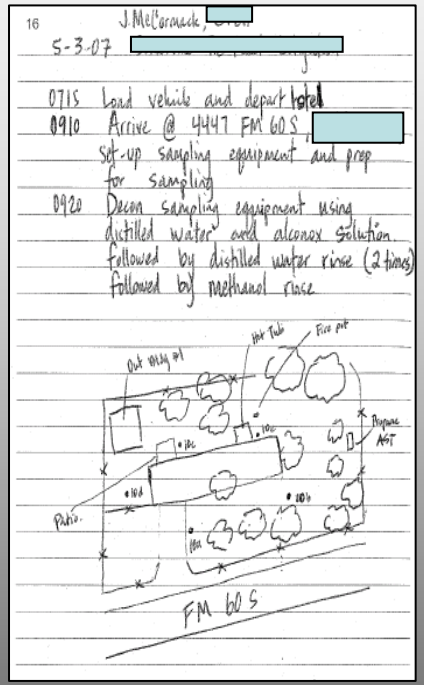
- **Occam's razor** - the simplest explanation or strategy tends to be the best one - *Franciscan friar, William of Ockham*

Data Quality –Sample Collection to Delivery to Laboratory

- Sampling plan
  - Methodology, SOP, previous experience sampling matrix
- Documentation, documentation, documentation
- Chain of custody
- Validating samples were preserved

Sampling

Documentation

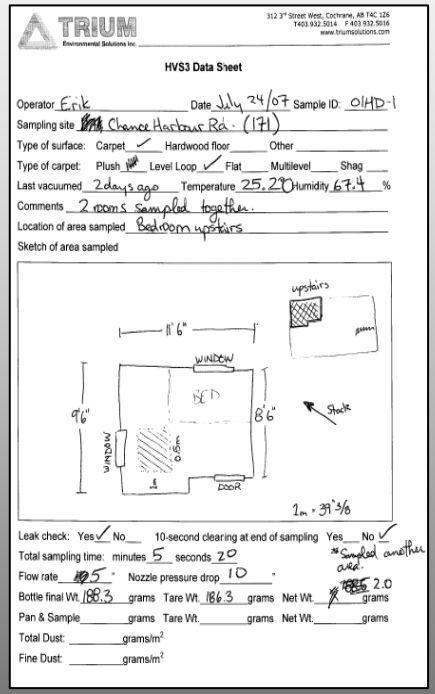

16 J. McCormack

5-3-07

0715 Load vehicle and depart hotel
0910 Arrive @ 4447 FM 605,
Set-up sampling equipment and prep for sampling
0920 Decon sampling equipment using distilled water and alconox solution followed by distilled water rinse (2 times) followed by methanol rinse

Hot Tub
Fire pit
Out bldg #1
Propane tank
Patio
FM 605

Field Notes


TRIUM
Environmental Solutions Inc.
312 3rd Street West, Cochrane, AB T4C 1Z6
T403.932.5014 F 403.932.5016
www.triumsolutions.com

HVS3 Data Sheet

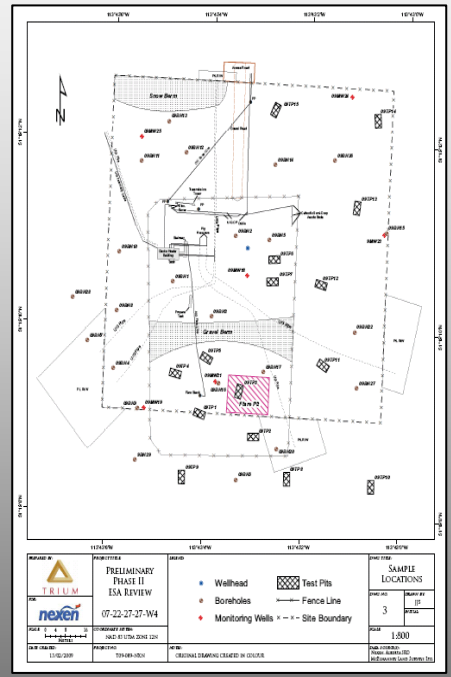
Operator Erik Date July 24/07 Sample ID: 01HD-1
Sampling site Chance Harbour Rd. (171)
Type of surface: Carpet ✓ Hardwood floor ____ Other ____
Type of carpet: Plush ✓ Level Loop ✓ Flat ____ Multilevel ____ Shag ____
Last vacuumed 2 days ago Temperature 25.29 Humidity 67.4 %
Comments 2 rooms Sampled together.
Location of area sampled Bedroom upstairs
Sketch of area sampled

upstairs
11' 6"
WINDOW
BED
96"
86"
WINDOW
DOOR
Stairs
2m = 39 3/6

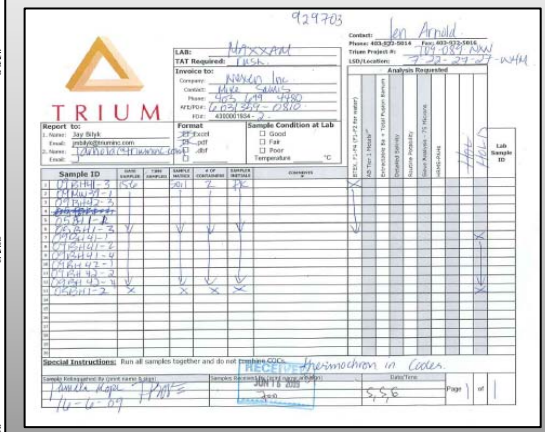
Leak check: Yes ✓ No ____ 10-second clearing at end of sampling Yes ____ No ✓
Total sampling time: minutes 5 seconds 20
Flow rate 10.5 Nozzle pressure drop 10
Bottle final Wt. 188.3 grams Tare Wt. 186.3 grams Net Wt. 2.0 grams
Pan & Sample ____ grams Tare Wt. ____ grams Net Wt. ____ grams
Total Dust: ____ grams/m²
Fine Dust: ____ grams/m²

* Sampled another unit.

Sampling Forms



Maps


TRIUM
Report to:
Format
Sample Condition at Lab
Sample ID
Special Instructions: Run all samples together and do not analyze COC.
Thermochron in Cooler.

COCs

Maintaining Custody

Legally, a sample is under custody if:

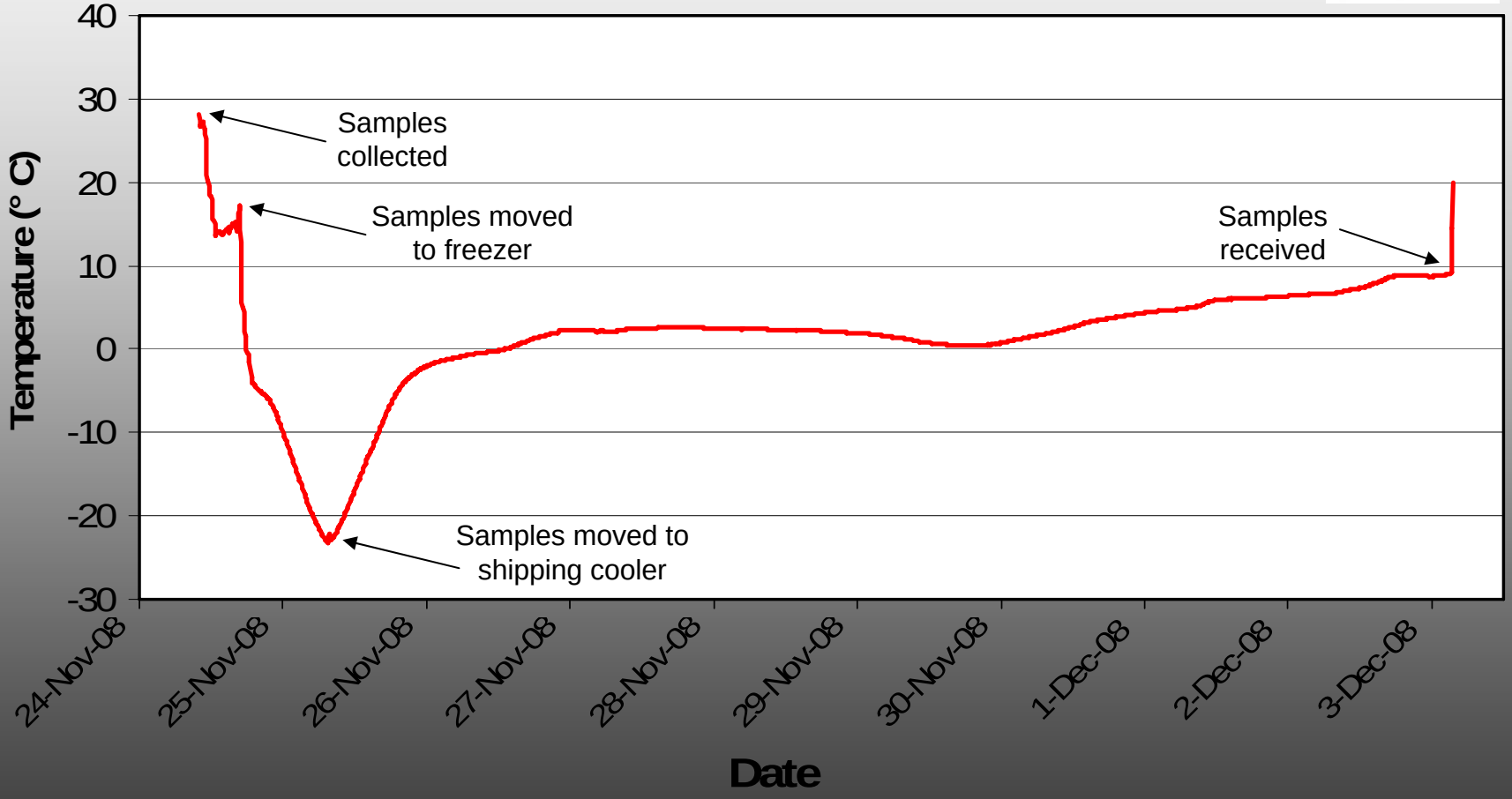
- the sample is in a person's possession
- the sample is in a person's view after being in possession
- the sample was in the person's possession and then was locked up to prevent tampering
- the sample is in a designated secure area

- COC must be documented for all transfers

Relinquishing COC

- Each person that handles samples until (including) receipt at lab must sign/date COC
- Best to have samples sorted for laboratory receipt
- Good practice – samples grouped by analysis requested
- Don’t need sorting issue to be a problem after all the effort put into collecting samples

Validating Preservation



Case Study

Information Before Investigation

- Conducting risk assessment on lube oil facility because of potential vapours from PHCs below the facility…?
  - Our question – what type of PHCs?
- 2+ meters of free product beneath multiple areas on site
- Free product identified as a thick, hydrocarbon material

Site Map – Case Study

Potential Hydrocarbon Sources On-Site

- Diesel (storage tanks, gas station)
- Crude Oil (pipeline, storage facility)
- Gasoline (gas station)
- Lubricating Oil (client's facility)

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Field Study

- Bailed free product samples
- Viscous liquid – bailer needed weight to penetrate interface
- “Wells” filled up while being excavated
- 2+ meters free product
- Sampled product used on facility from tanks

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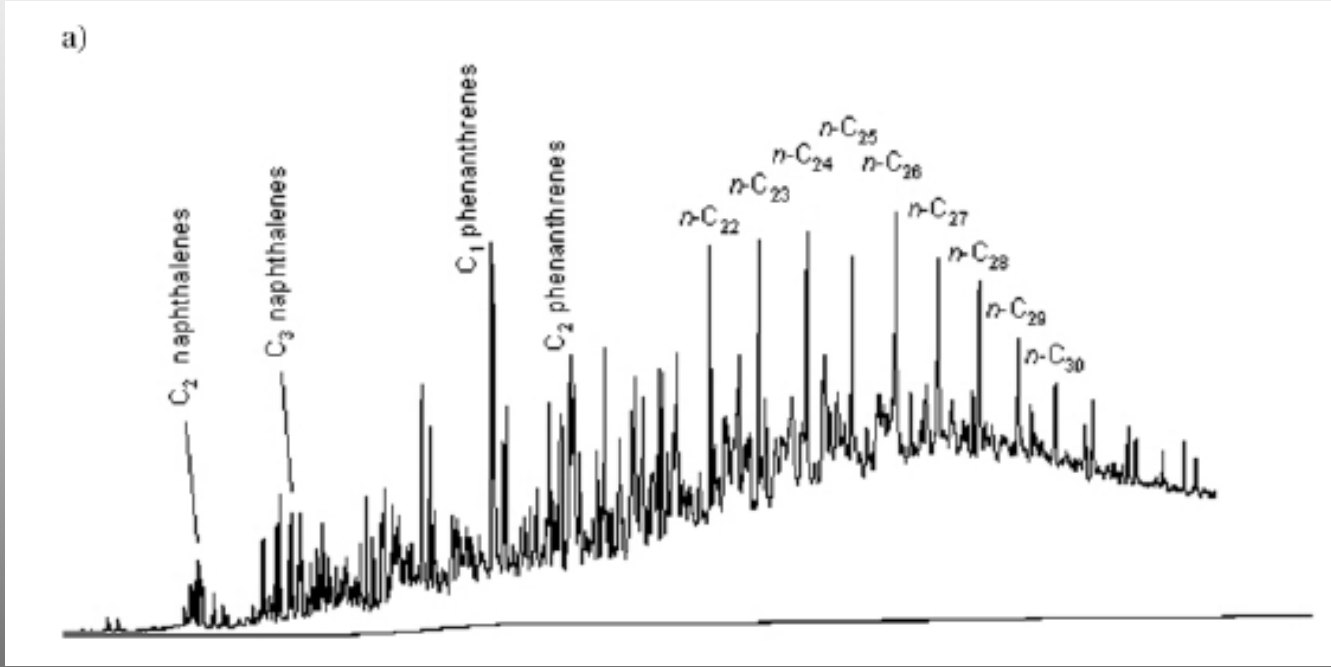
Complexity of PHCs?

Conventional GC Analysis



Nelson et al. Environmental Forensics, 7:33–44, 2006

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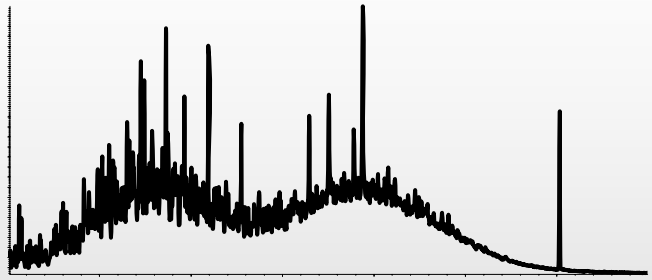
Complexity of PHCs

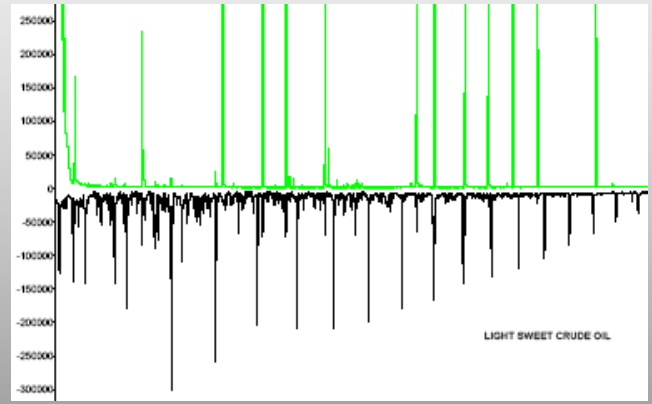
How many compounds are in….

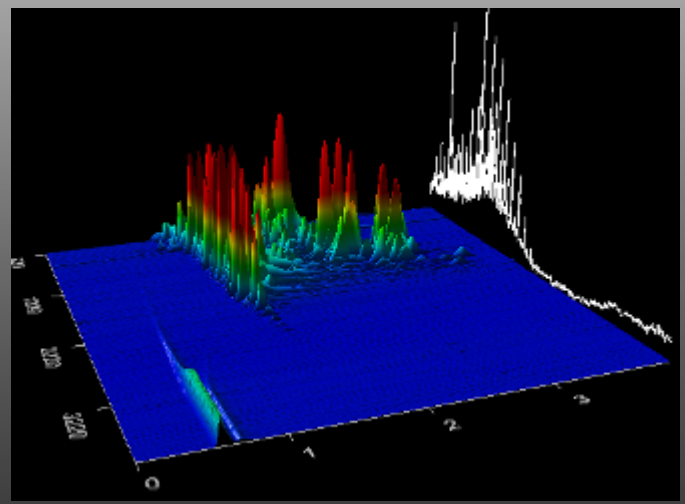
- The atmospheric aerosol from a coniferous forest?
  - **50 compounds** (Kallio, 2006)
- The volatile fraction of roasted coffee beans?
  - **1,000 compounds** (Mondello, 2004)
- Cigarette smoke?
  - **6,000 compounds** (van Mispelaar, 2005)
- Crude oil?
  - **7,500-10,000 compounds** (Dalluge, 2002)

Potential Types of Analyses



- Routine
  - GC-FID
  - GC-MS (full scan)
- Compound Specific Analysis
  - GC-MS (SIM)
    - Targeted analytes (PAHs, biomarkers)
    - Qualitative or quantitative
- Advanced
  - 2D-GC-TOF-MS
    - Advanced separation and detection





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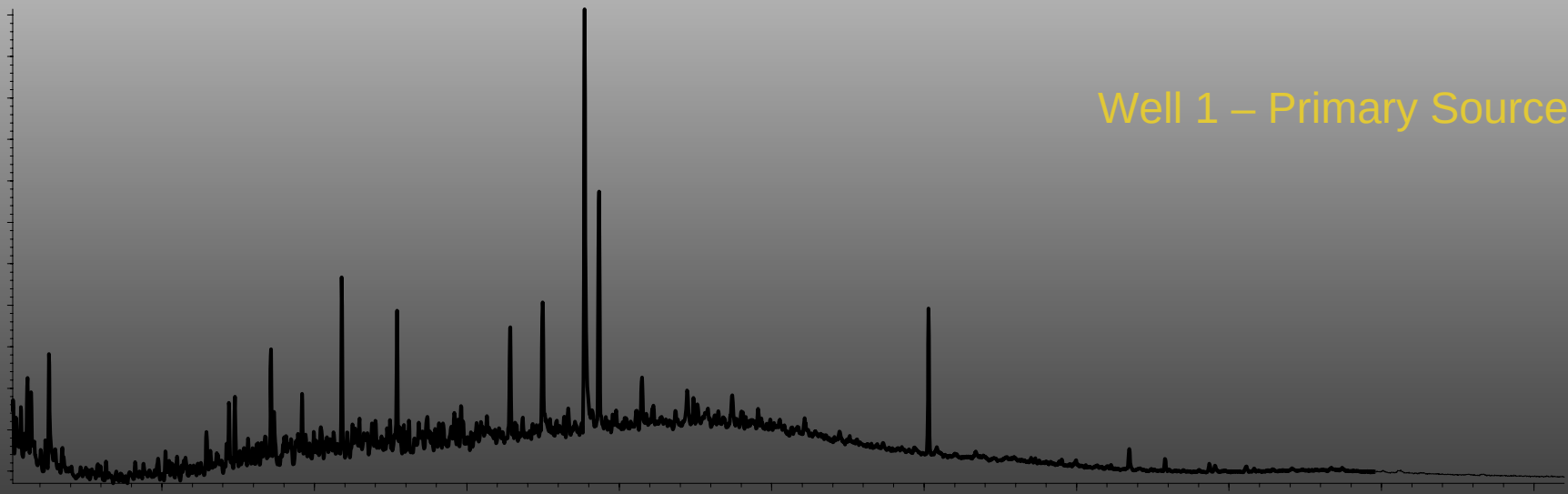
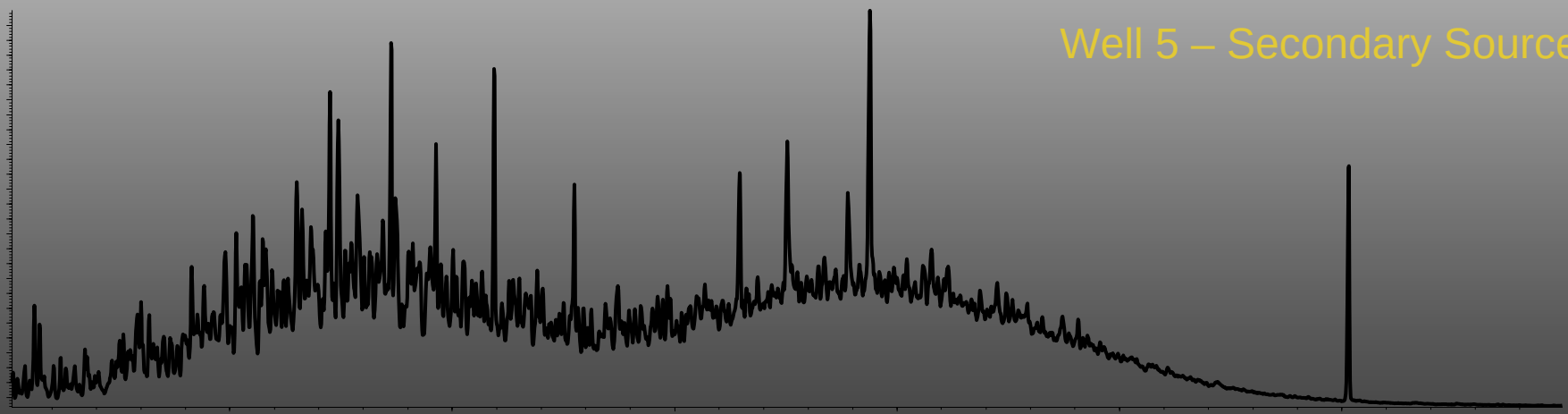
Qualitative Analysis

- Routine PHC spectrum
- Soil - Soxhlet extraction, minor silica cleanup, GC-FID analysis
- Free Product – dilute and shoot
- Results:

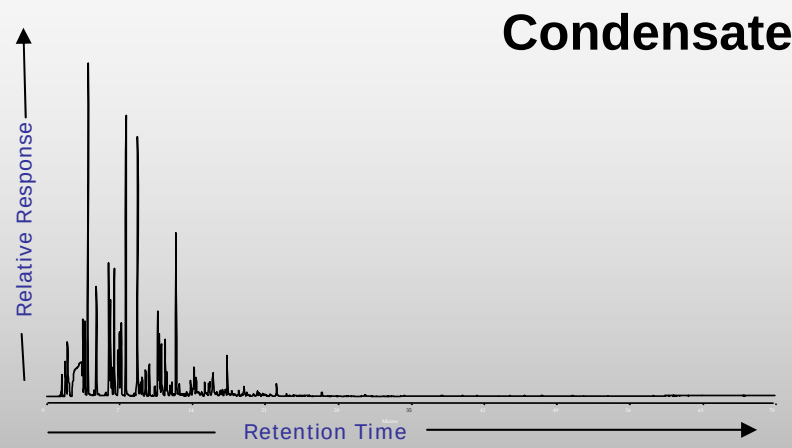


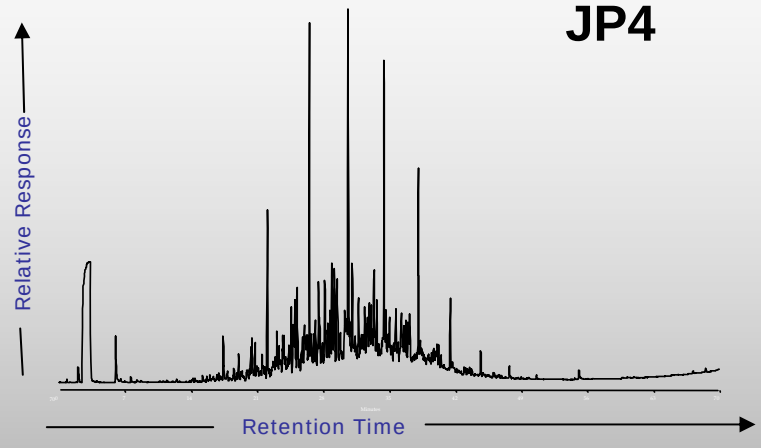
GC-FID

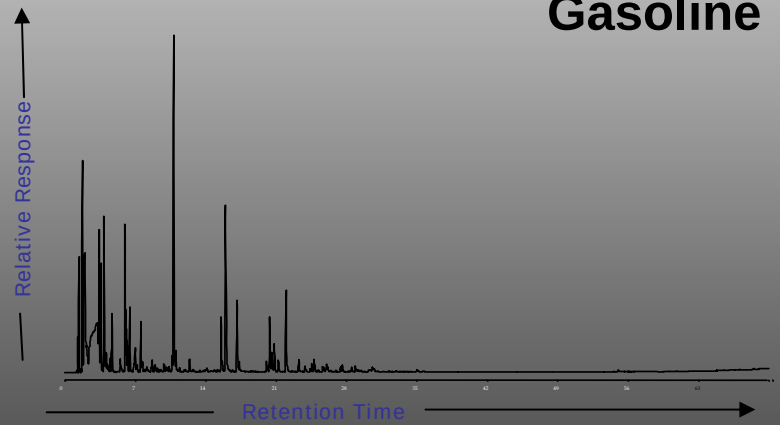
- Cost – low
- Interpretation – easy
- Quantitative for hydrocarbon fractions or TPH
- Time – quick
- Good preliminary look into patterns

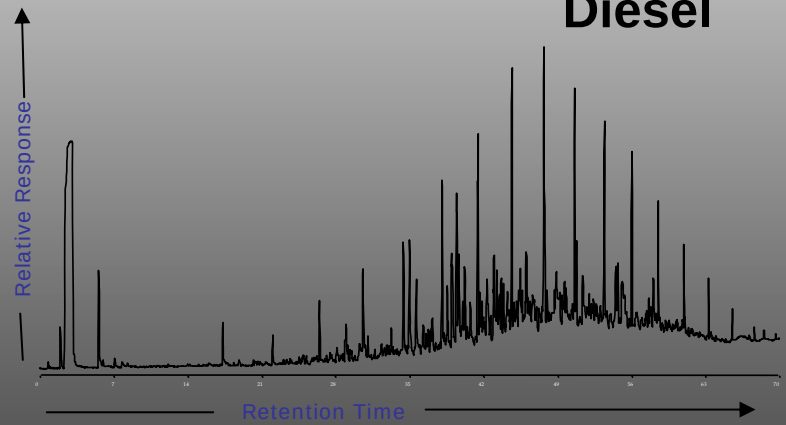


Pattern Recognition



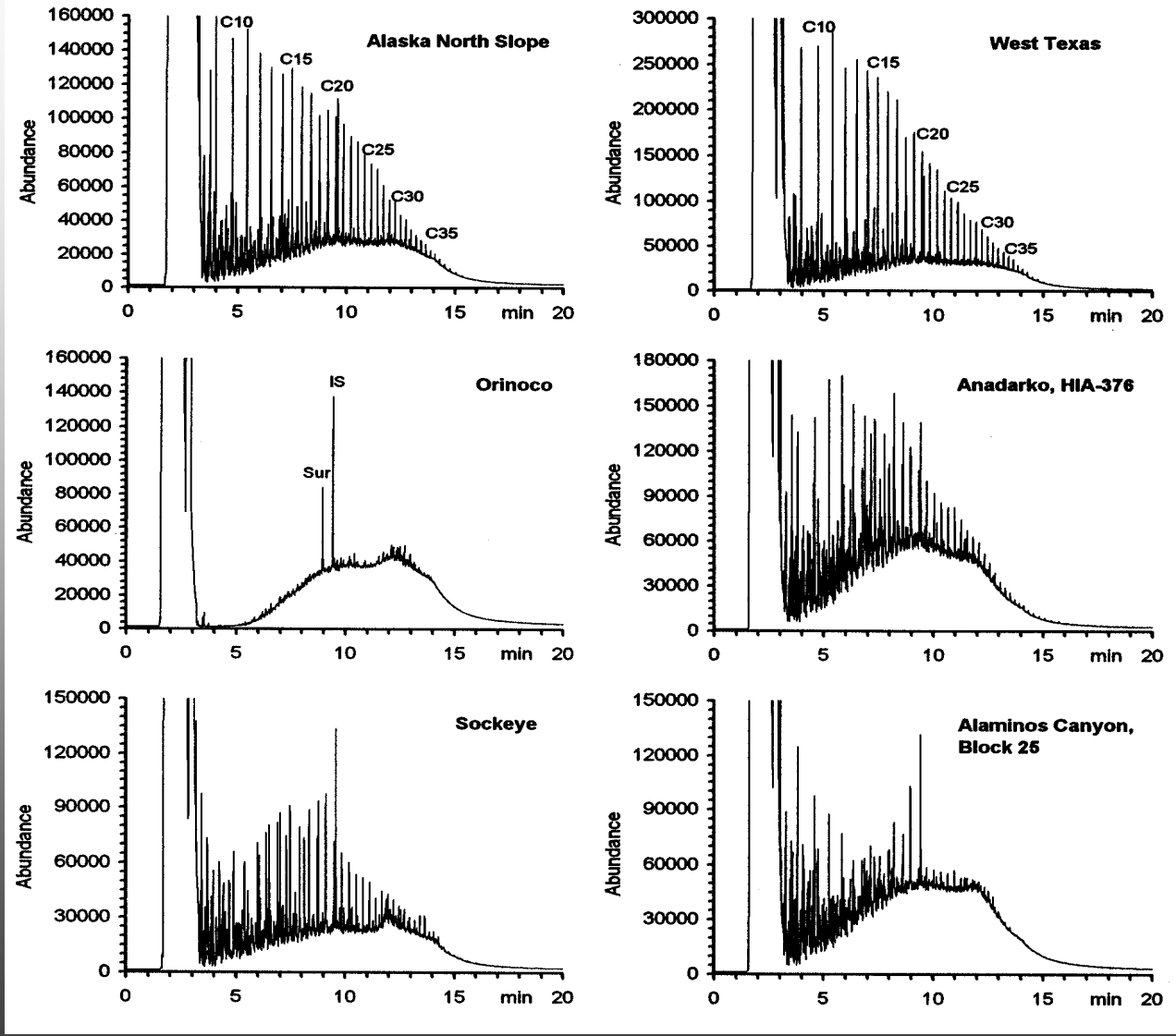






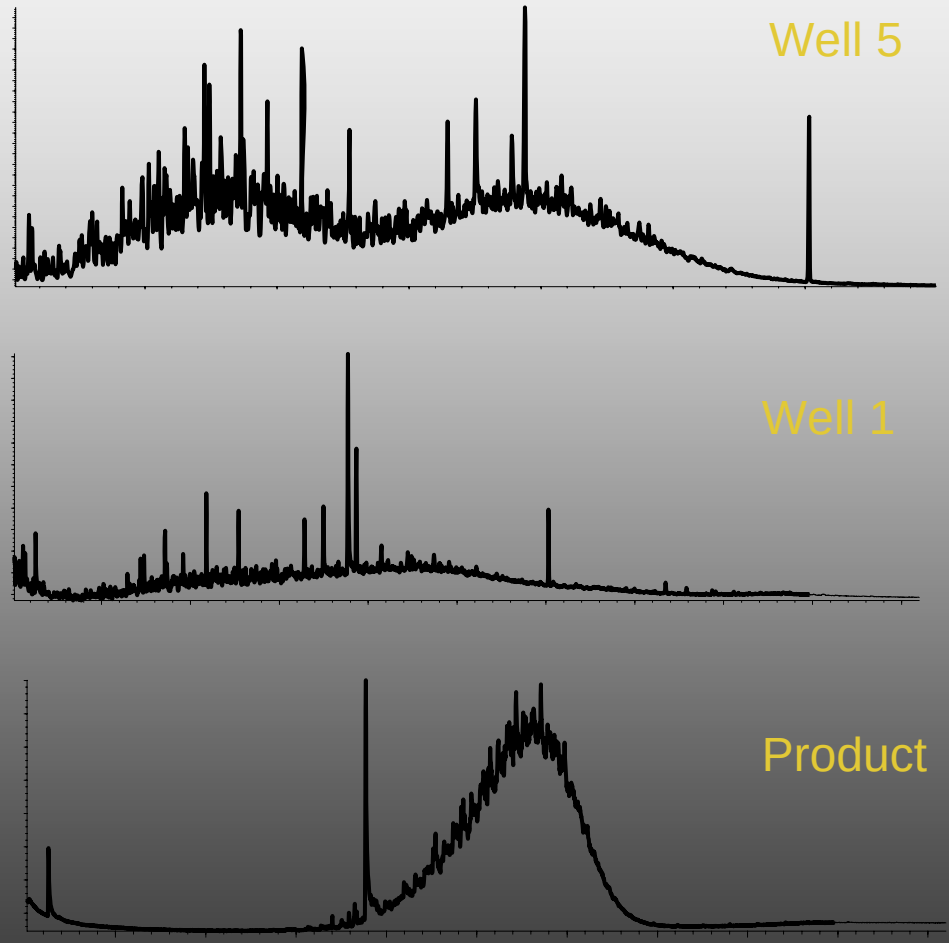
Identifies type of contaminant if sources easily distinguished and preserved

GC-FID Chromatograms of Very Different Crude Oils



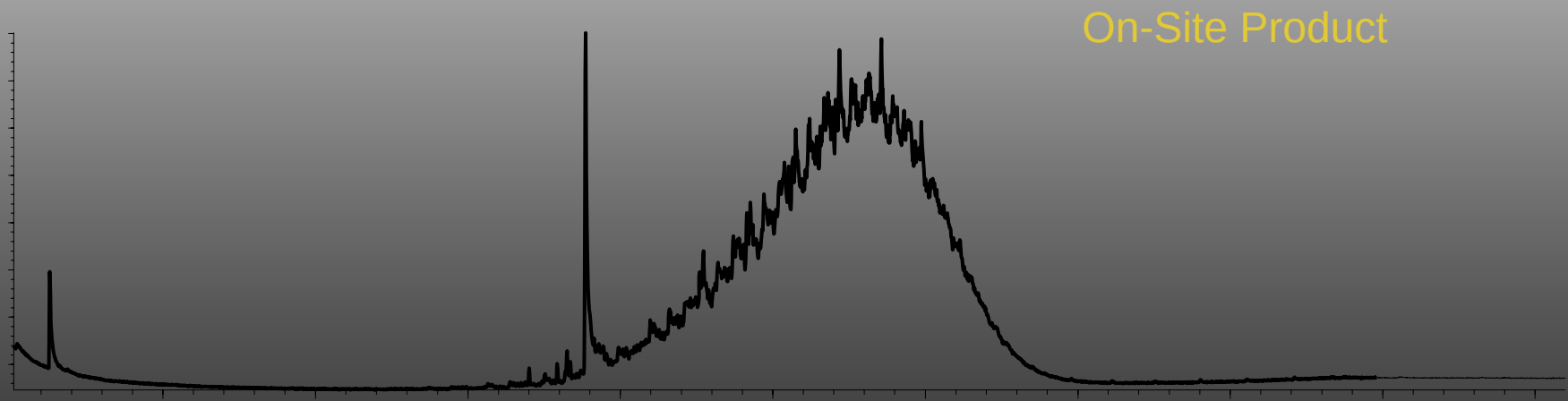
Site Summary

- Free product from wells differ from product produced at facility
  - Lube oils vs. medium distillates



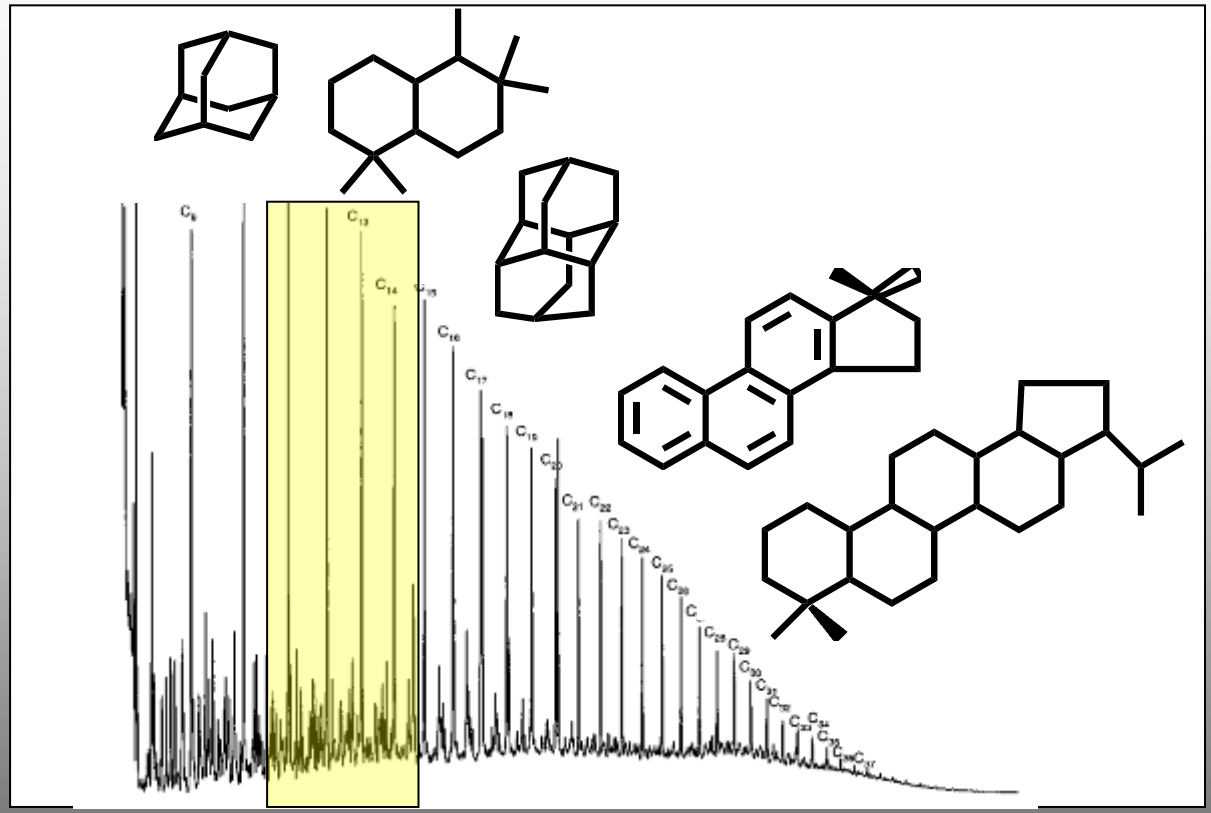
GC-MS (full scan)

- Cost – Medium
- Interpretation – easy to difficult
- Time – slow
- Concentrations must be high enough (no problem – free product)
- Allows chemist to dig into information
- Still qualitative analysis unless internal standards used



Petroleum Biomarkers

- Adamantanes
- Sesquiterpanes
- Diamantanes
- Steranes
- Hopanes

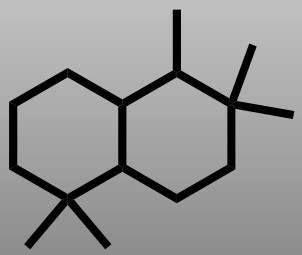


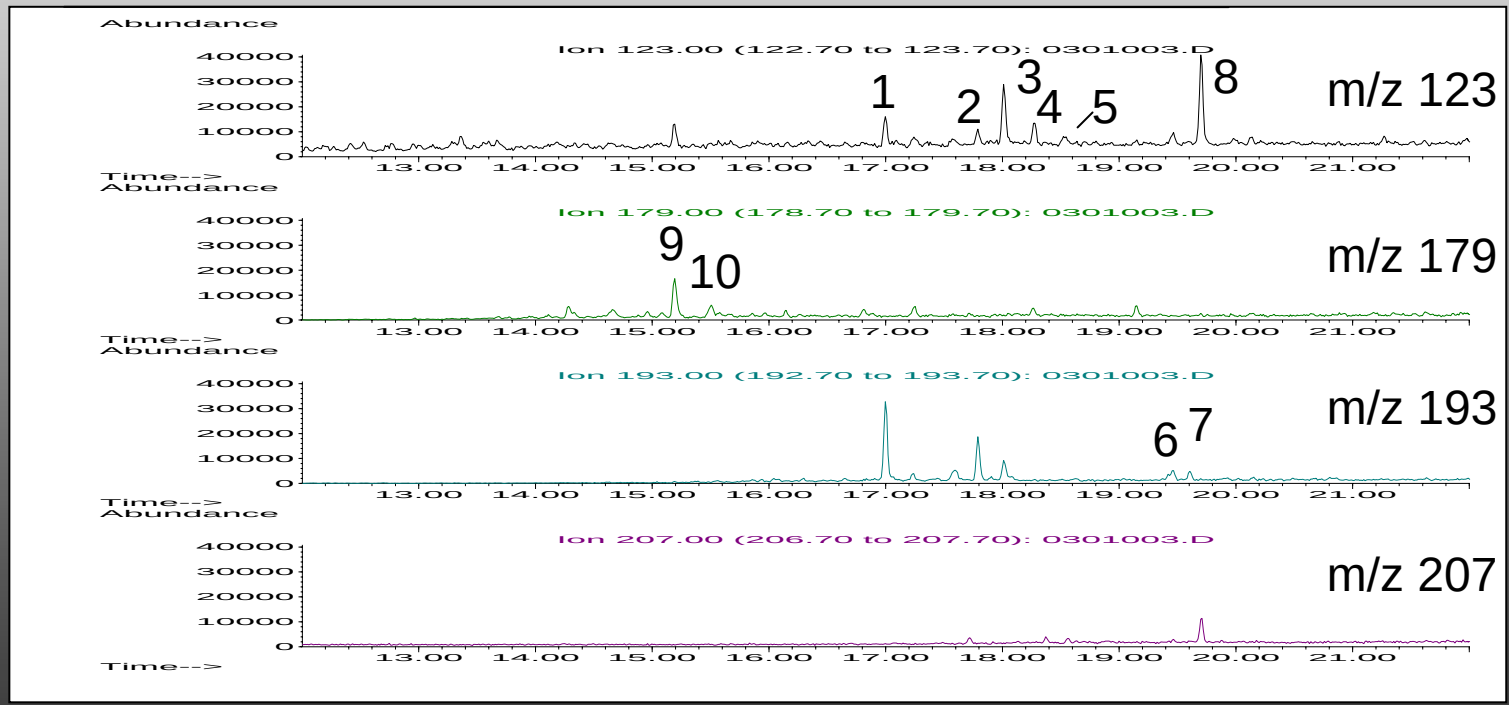
Gasoline/Heavy Naphtha
Kerosene/Jet A /Diesel 1
Diesel 2 / Fuel 2
Bunker C
Lube Oil
Crude Oil

Not limited with full scan MS
Can look for them all.

Digging in

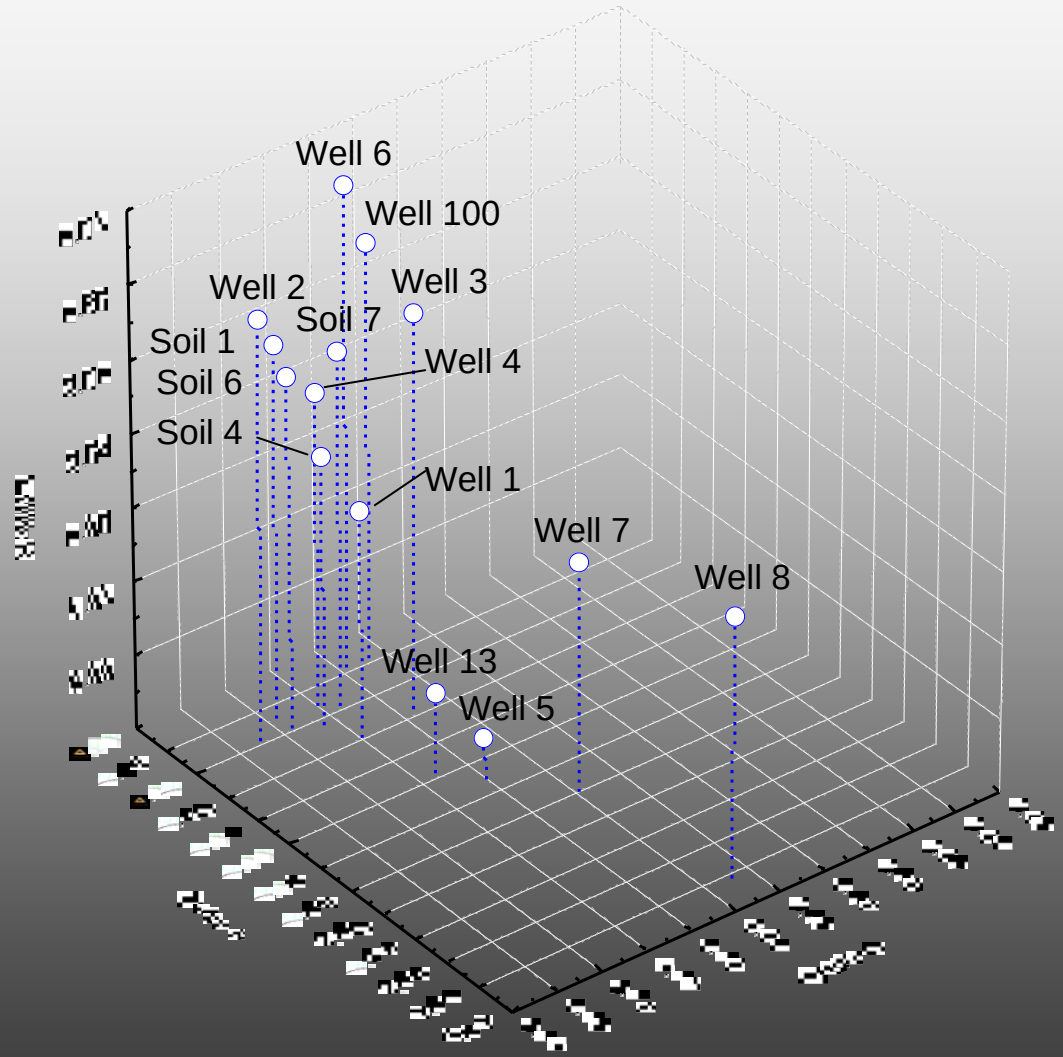
- Using bicyclic sesquiterpane biomarkers to aid in source identification
- Pull out ions specific to this family of biomarkers
- Using raw abundances to calculate ratios





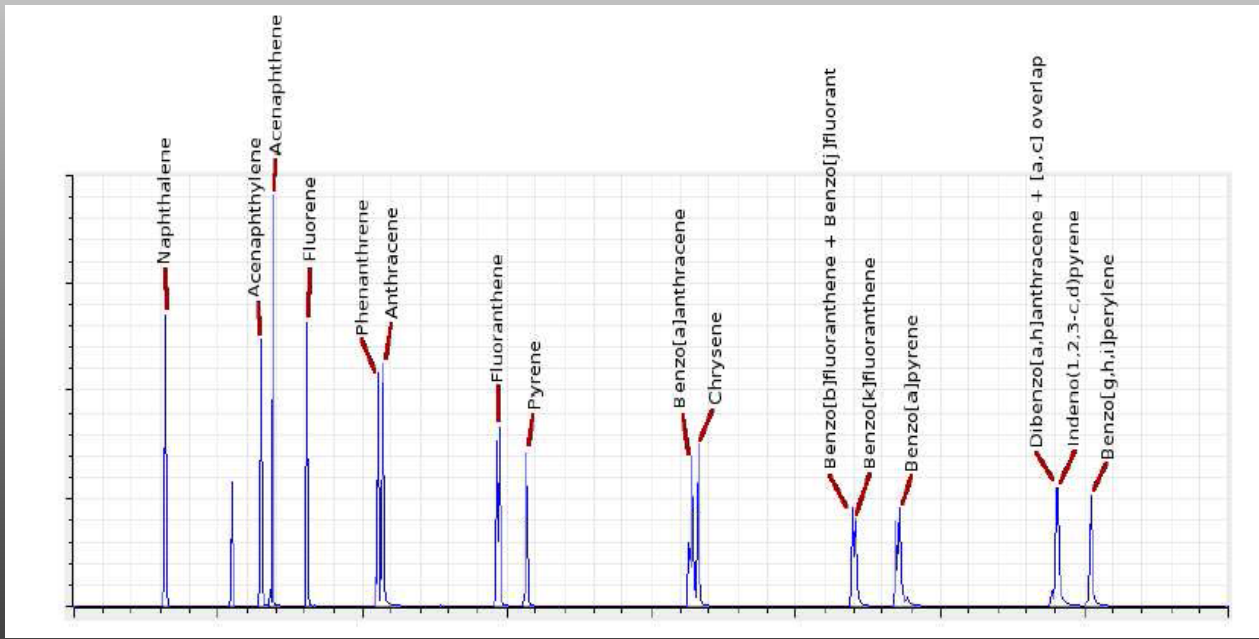
3D Ratio Plots of Biomarkers

- Used the established peak area ratios from literature
- Demonstrates difference in chemical composition between sources
- Sesquiterpanes are not in lube oils



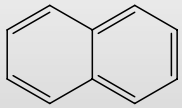
Targeted GC-MS (SIM)

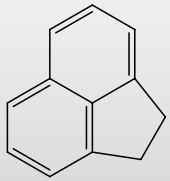
- Cost – moderate to high
- Interpretation – easy
- Time – fast
- Blinded by what you are looking for
- Generic – PAHs
- Usually quantitative based on isotope dilution or surrogate standards
- Can also be qualitative – presence/absence

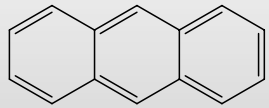


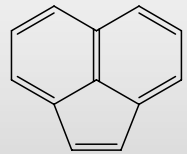
US EPA "Priority Pollutant" PAH Compounds

LMW


naphthalene


acenaphthene


anthracene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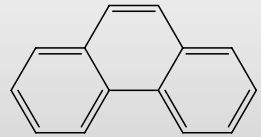
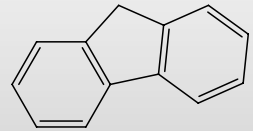
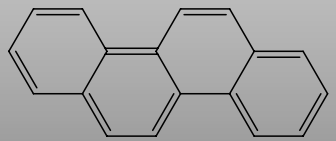
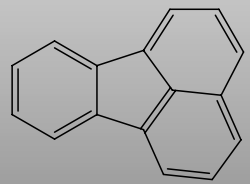

phenanthrene

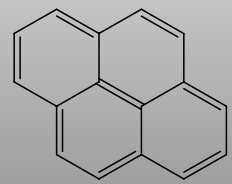

fluorene

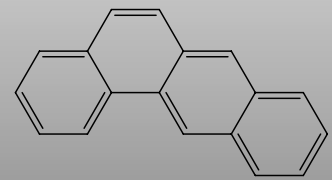
2-ring

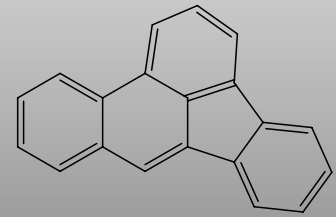
3-ring


chrysene


fluoranthene

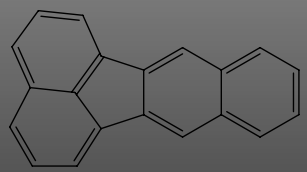

pyrene

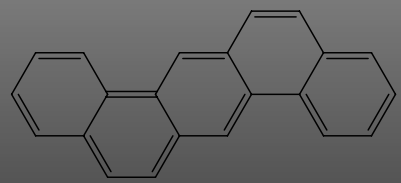

benzo[a]anthracene

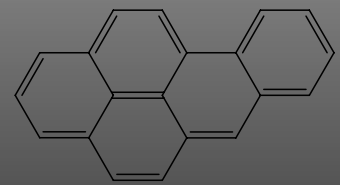

benzo[b]fluoranthene

HMW

4-ring


benzo[k]fluoranthene


dibenz[a,h]anthracene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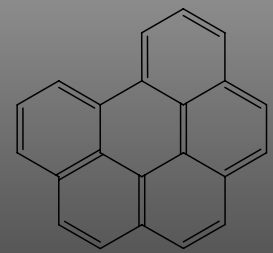
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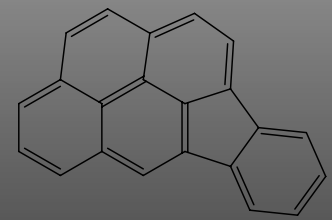
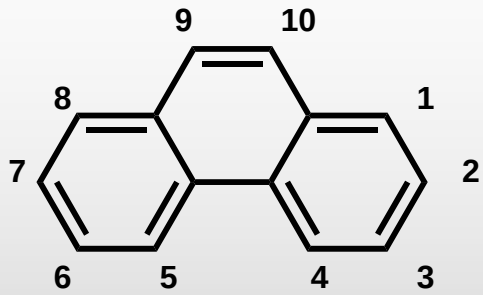

indeno[1,2,3-cd]pyrene

5-ring

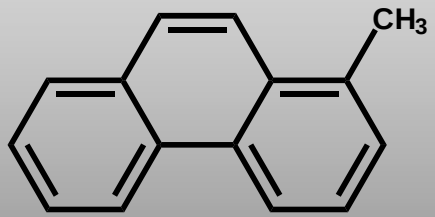
6-ring

Substituted PAHs



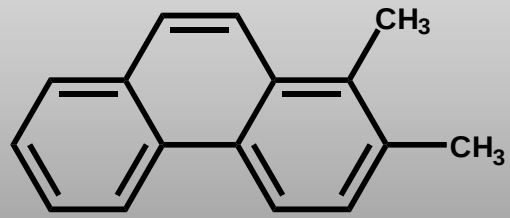
Phenanthrene

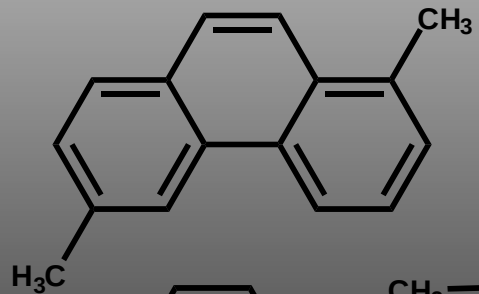
C1-Phenanthrenes

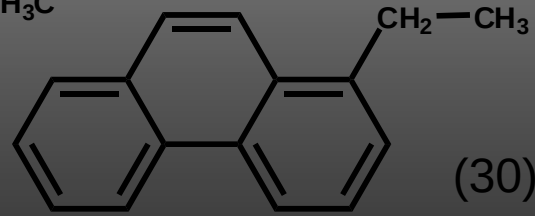


(5)

C2-Phenanthrenes

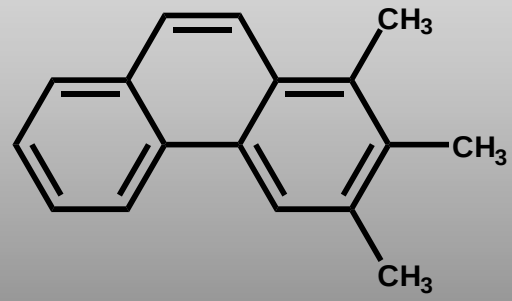


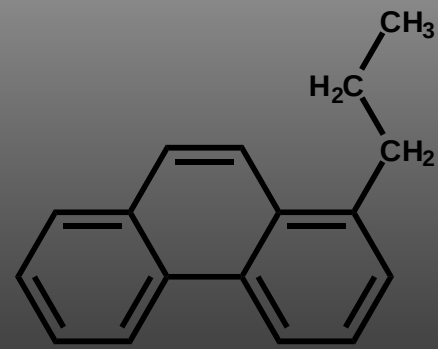




(30)

C3-Phenanthrenes





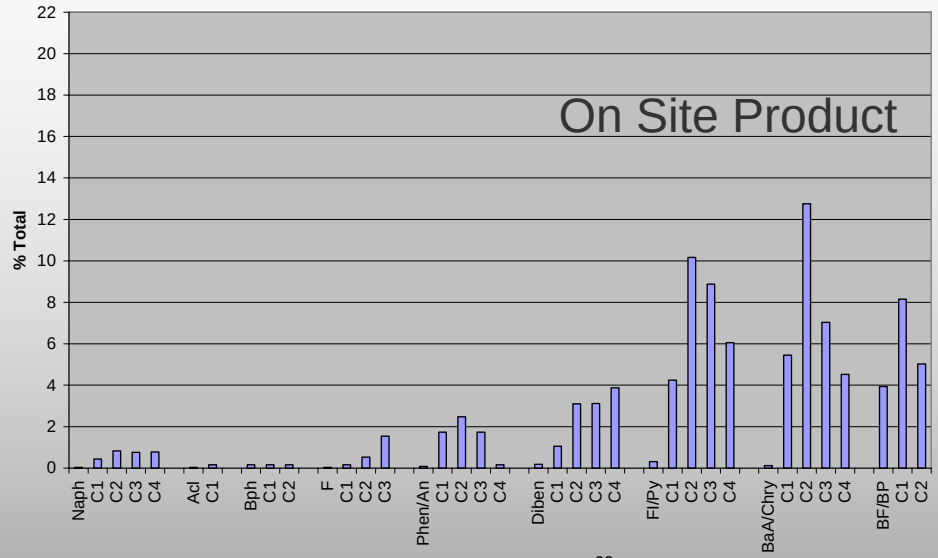
(?)

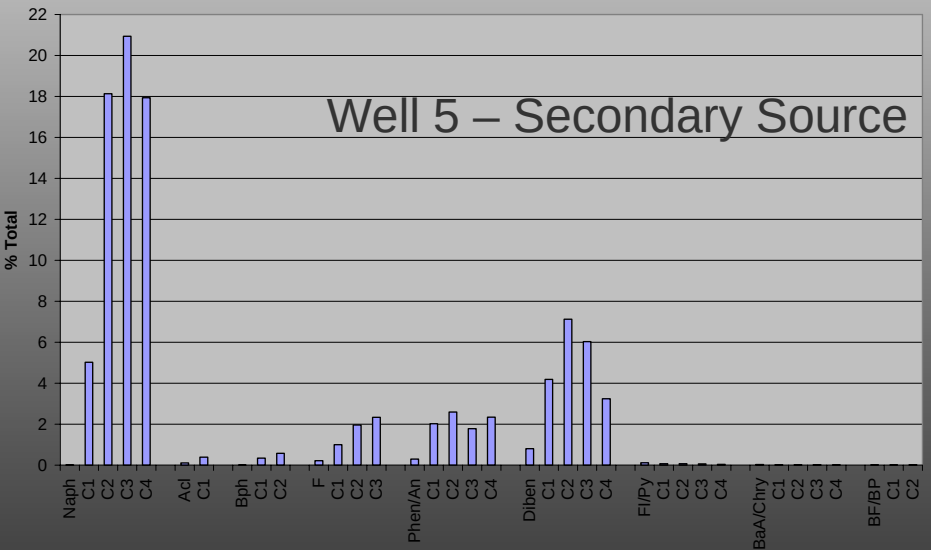
C4-Phenanthrenes…

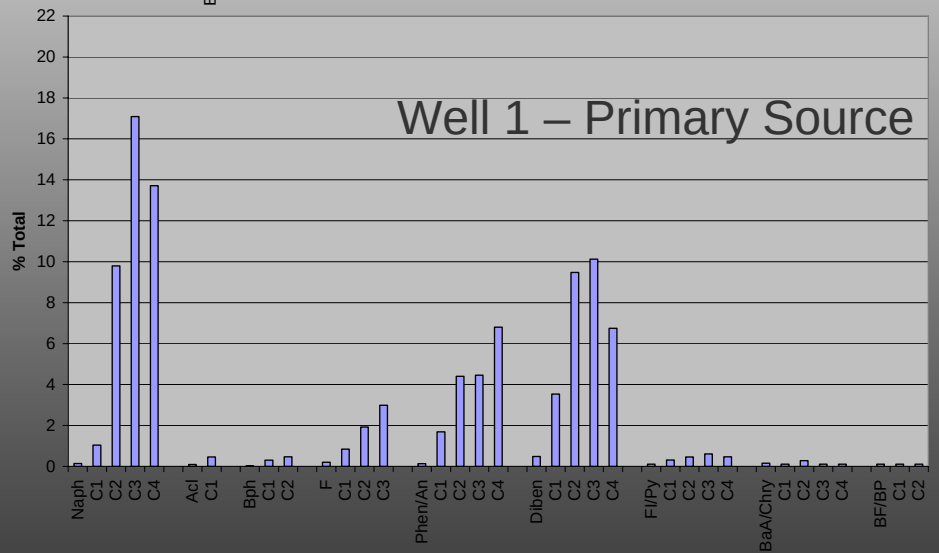
PAHs

- Methods vary from lab to lab
- Quantification
  - Semi-quantitative methods with surrogates
  - Quantitative methods with labeled internal standards
- Analytes measured
  - Routine EPA
  - Routine EPA+
  - "Deluxe" Method includes EPA compounds with substituted PAHs (up to 63 compounds)

PAH Patterns







Summary

- Conventional chromatograms – demonstrated differences in products
- GC-MS – determined the differences and number of sources
  - PAHs could not distinguish between multiple sources
  - Biomarkers differentiated the sources

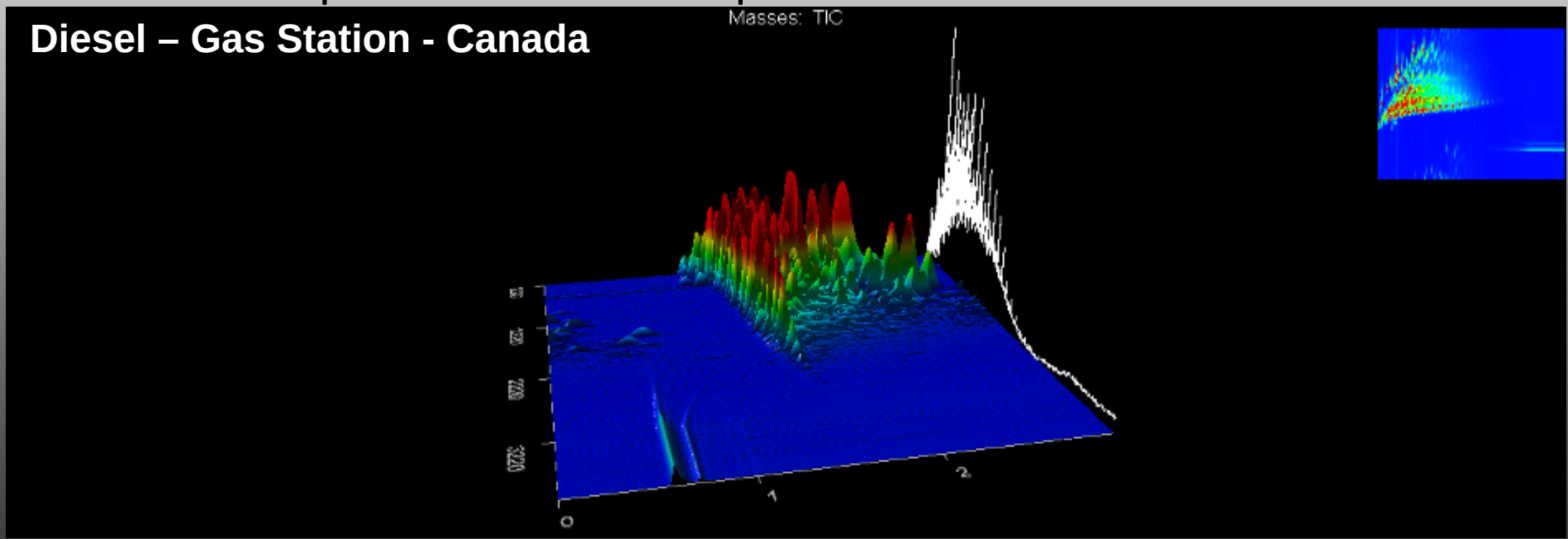
- Important to know methods that are available for forensic samples
- Next step – preparing for court and testimony

What is next for environmental forensics?

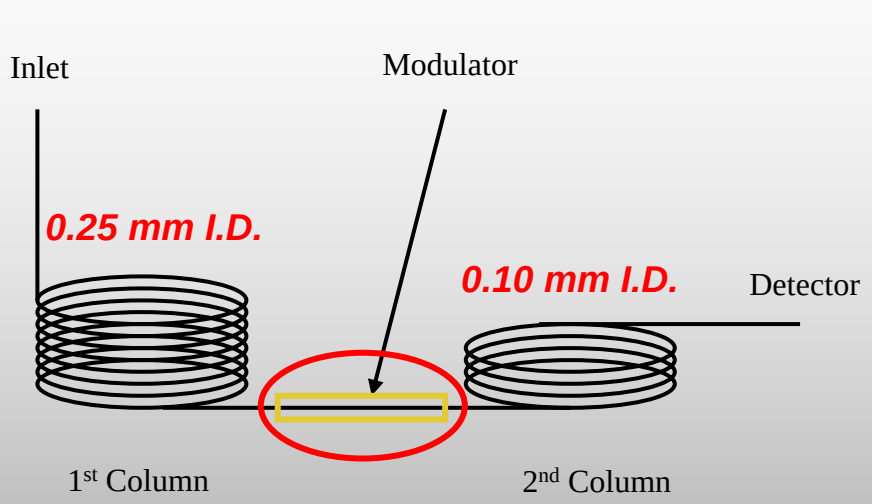
Advanced – 2D-GC-TOF-MS

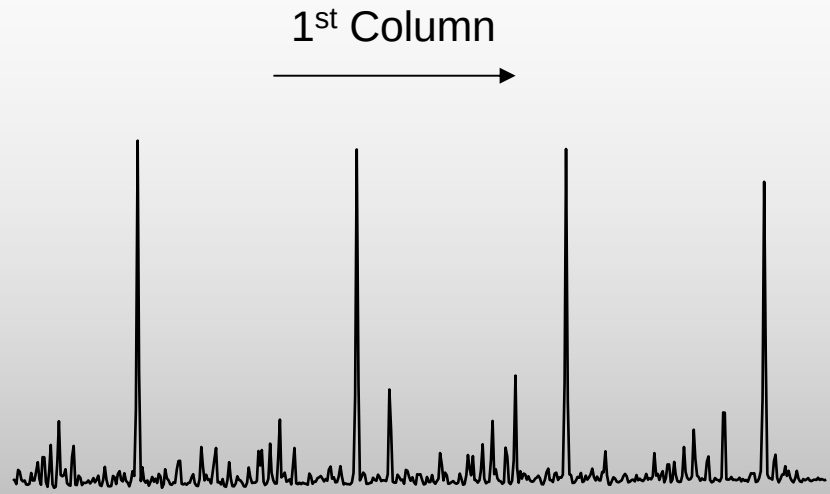
- Cost – Highest
- Interpretation – Difficult
- Time – slow
- Can look for anything
- Advantage – separation + mass spectra id + sensitivity
- Can be qualitative or semi-quantitative

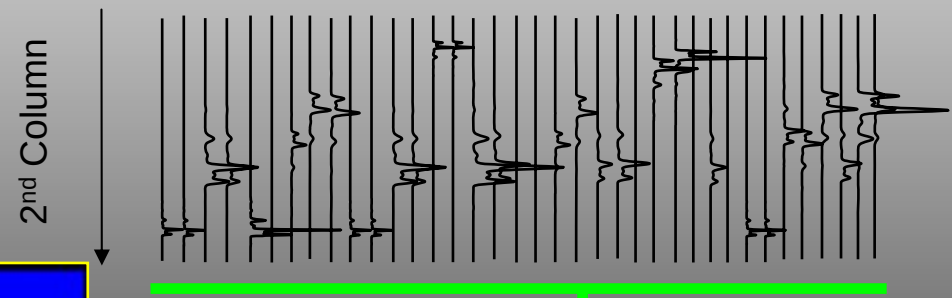
Diesel – Gas Station - Canada

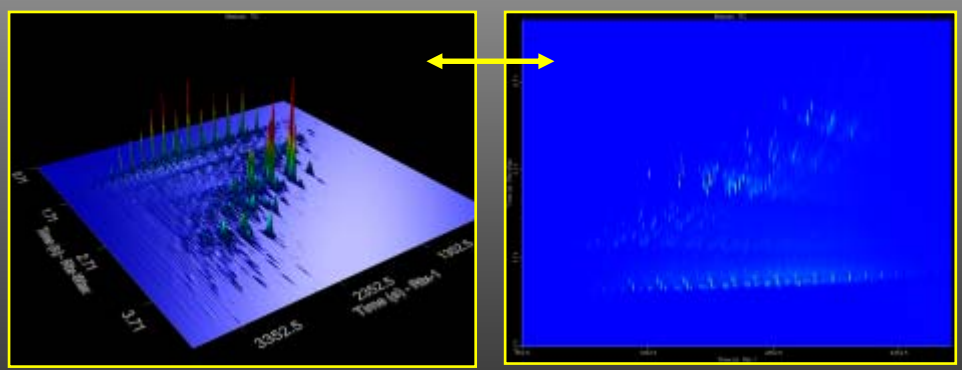


MODULATION IN GCXGC

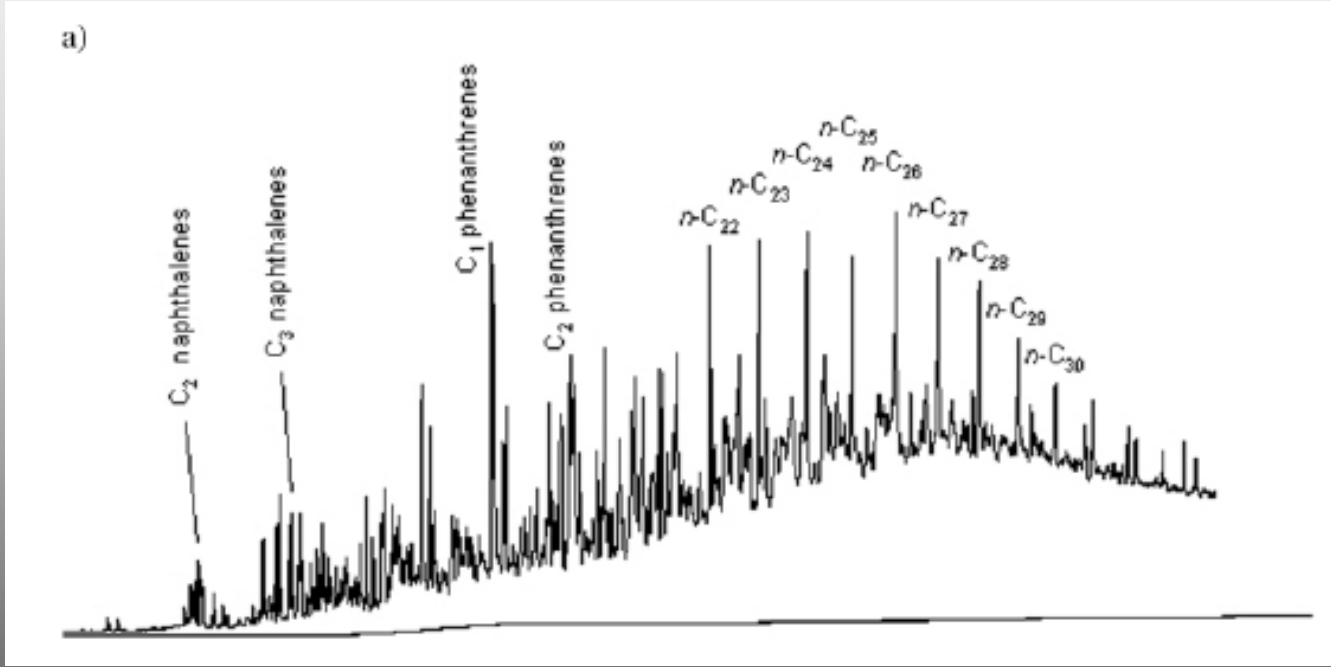






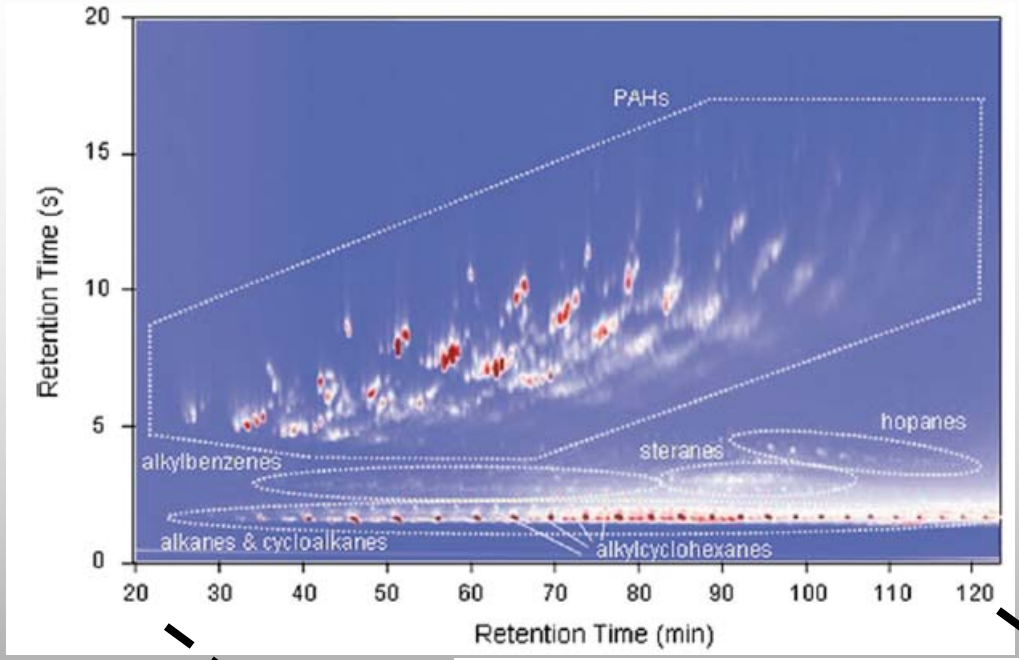


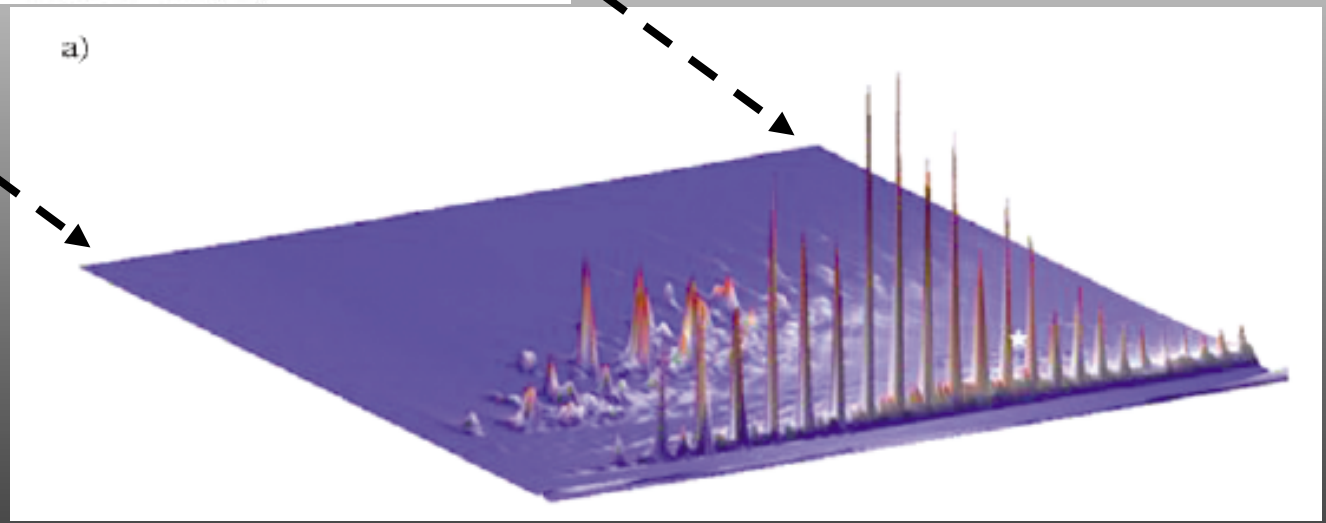
Conventional GC Analysis



Nelson et al. Environmental Forensics, 7:33–44, 2006

2D-GC-TOF

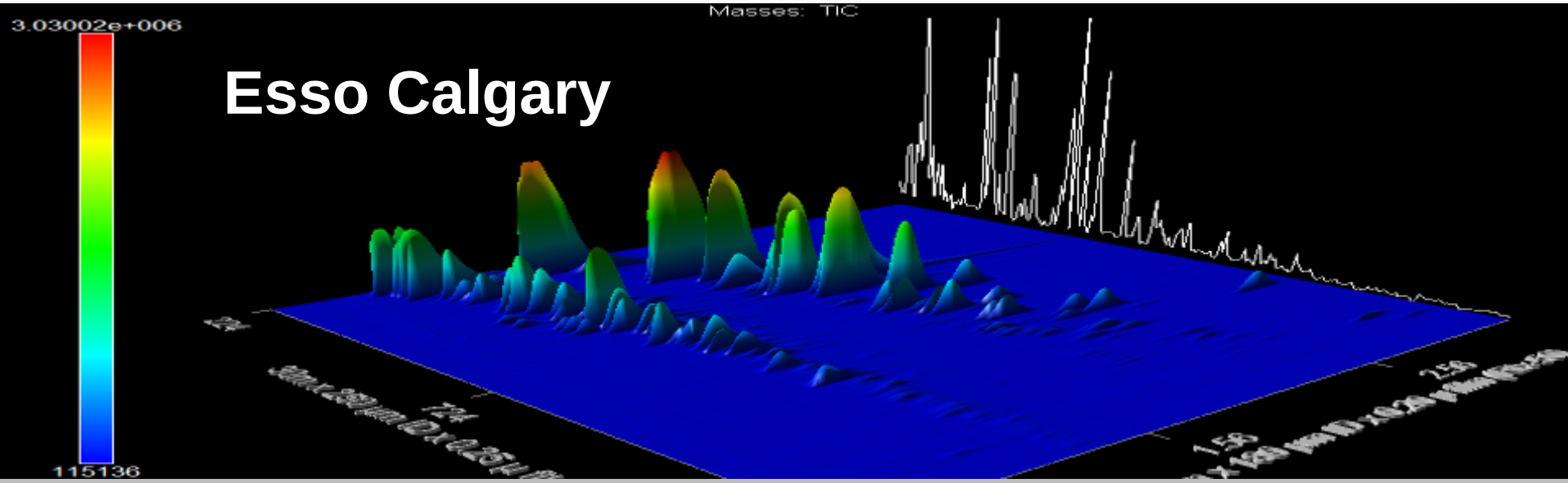


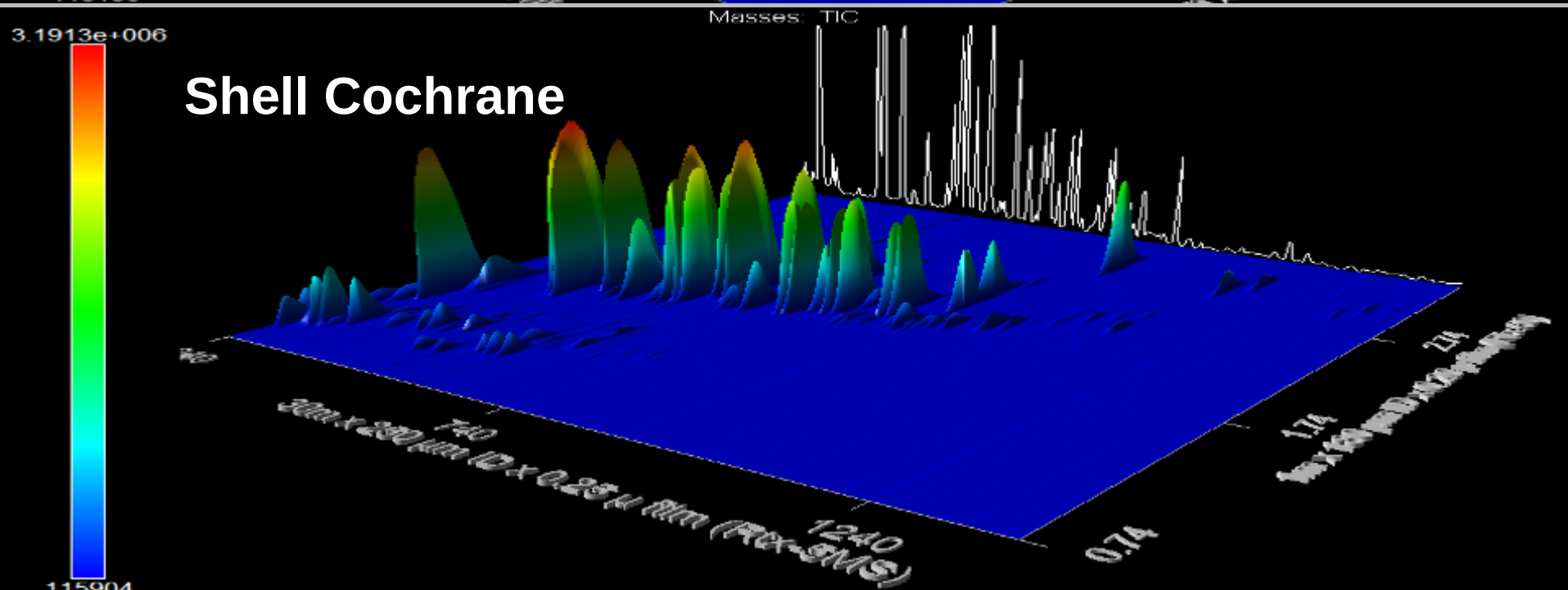


Nelson et al. Environmental Forensics, 7:33–44, 2006

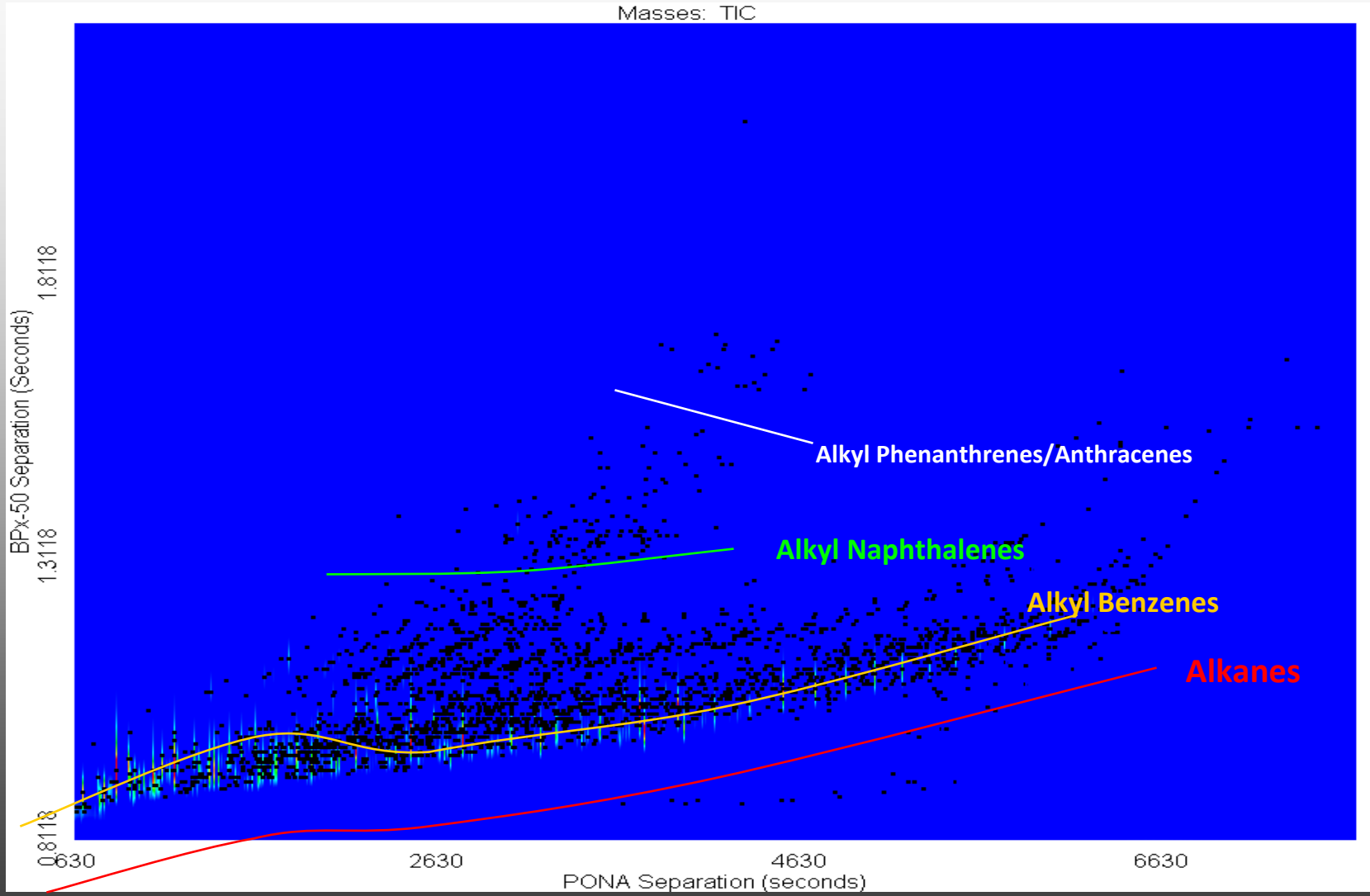
COMPARISON OF GASOLINES

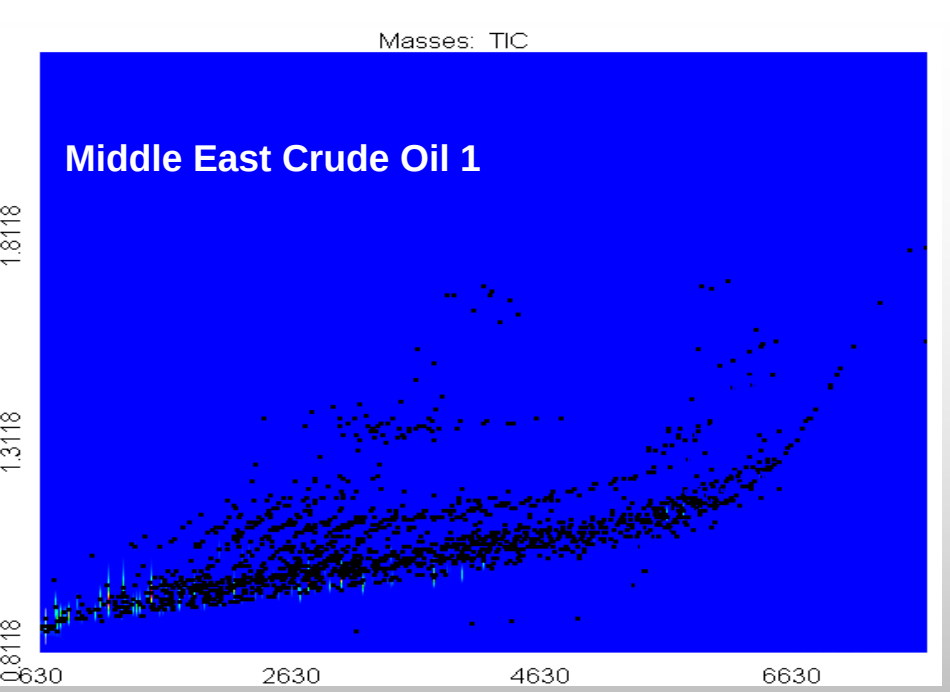
TRIUM

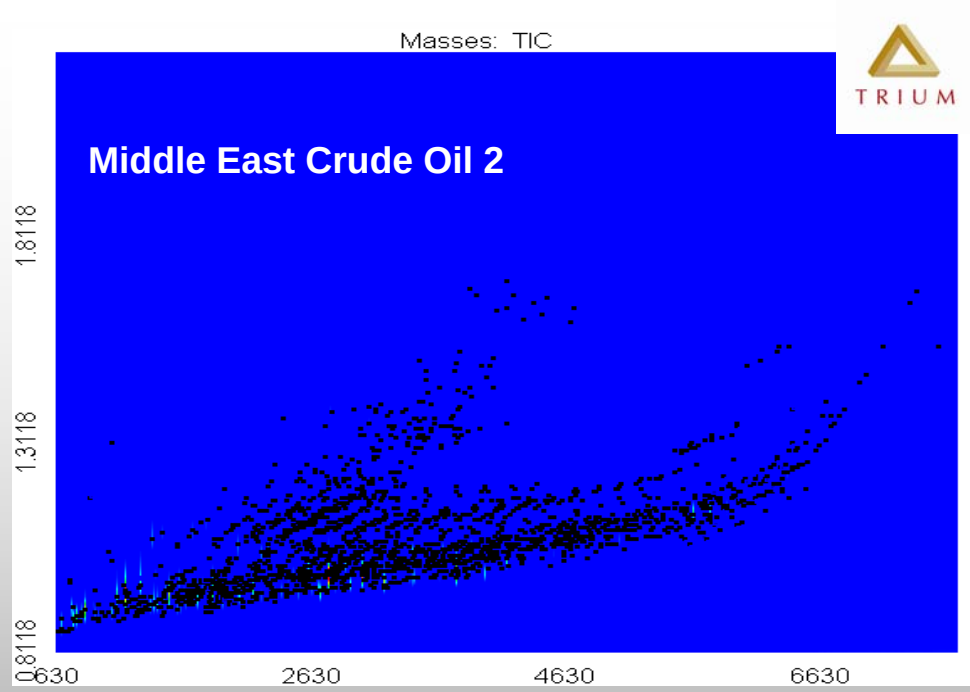


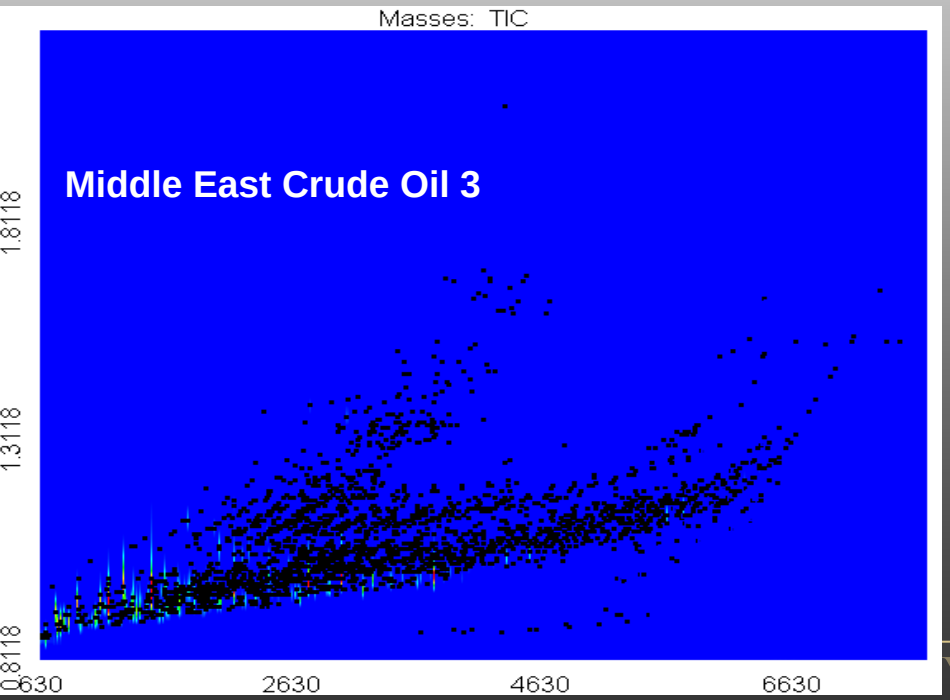


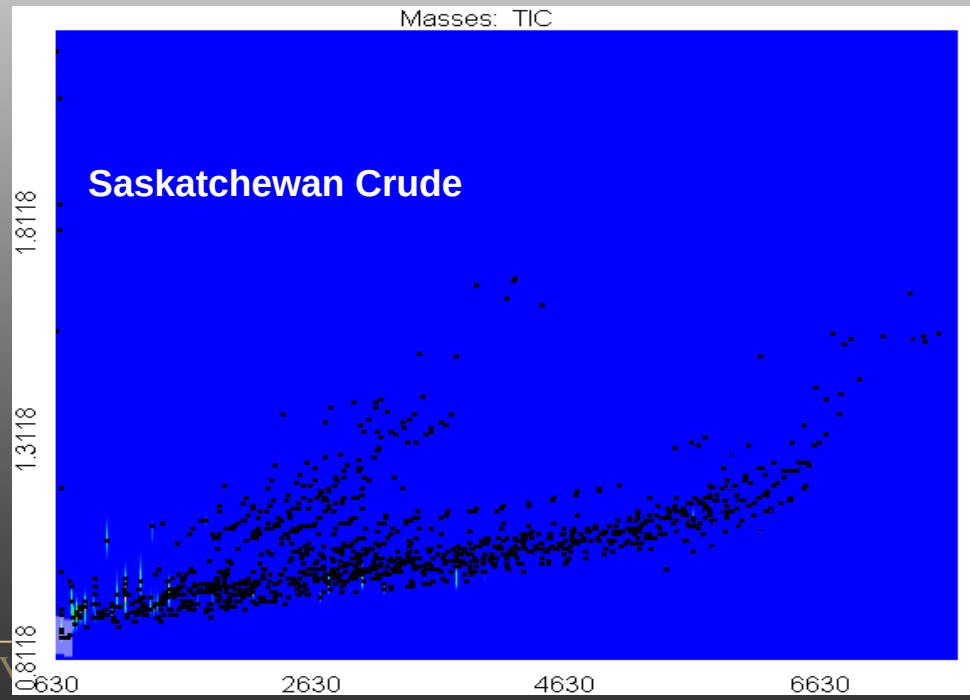
Middle East Crude Oil Investigation




Masses: TIC
Middle East Crude Oil 1
1.8118
1.3118
0.8118
630
2630
4630
6630


Masses: TIC
Middle East Crude Oil 2
1.8118
1.3118
0.8118
630
2630
4630
6630


Masses: TIC
Middle East Crude Oil 3
1.8118
1.3118
0.8118
630
2630
4630
6630


Masses: TIC
Saskatchewan Crude
1.8118
1.3118
0.8118
630
2630
4630
6630

Future Work

- Complete chemical fingerprinting can now be accomplished with a single analysis
- Fingerprint archiving for future reference
- Problems exist in dealing with the amount of data
- Visual side of data can be quite convincing

Questions?

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http://environmental-qaqc.blogspot.com/

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