Derwentside Environmental Testing Services

The Analysis of Total Petroleum Hydrocarbons

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Petroleum Hydrocarbons

- Composition
- Common refinery products
- VPH/EPH methods
- Example chromatograms
- Forensic analysis

Characteristics of Petroleum Hydrocarbons

- Thousands of compounds derived from crude oil
- Varying in appearance from pale yellow condensates to black tars, with SG of <1 (0.7 – 0.95)
- Toxicity, mobility and environmental persistence of compounds is highly variable
- Crude oil: predominantly C + H, plus N, S + O

Properties of Petroleum Products (1)

Generally with increasing molecular size (usually recorded as ‘carbon number’) there is:

- increase in boiling and melting points
- lower vapour pressure
- increase in density
- decrease in water solubility
- stronger adhesion to soils and therefore less mobility in subsurface conditions

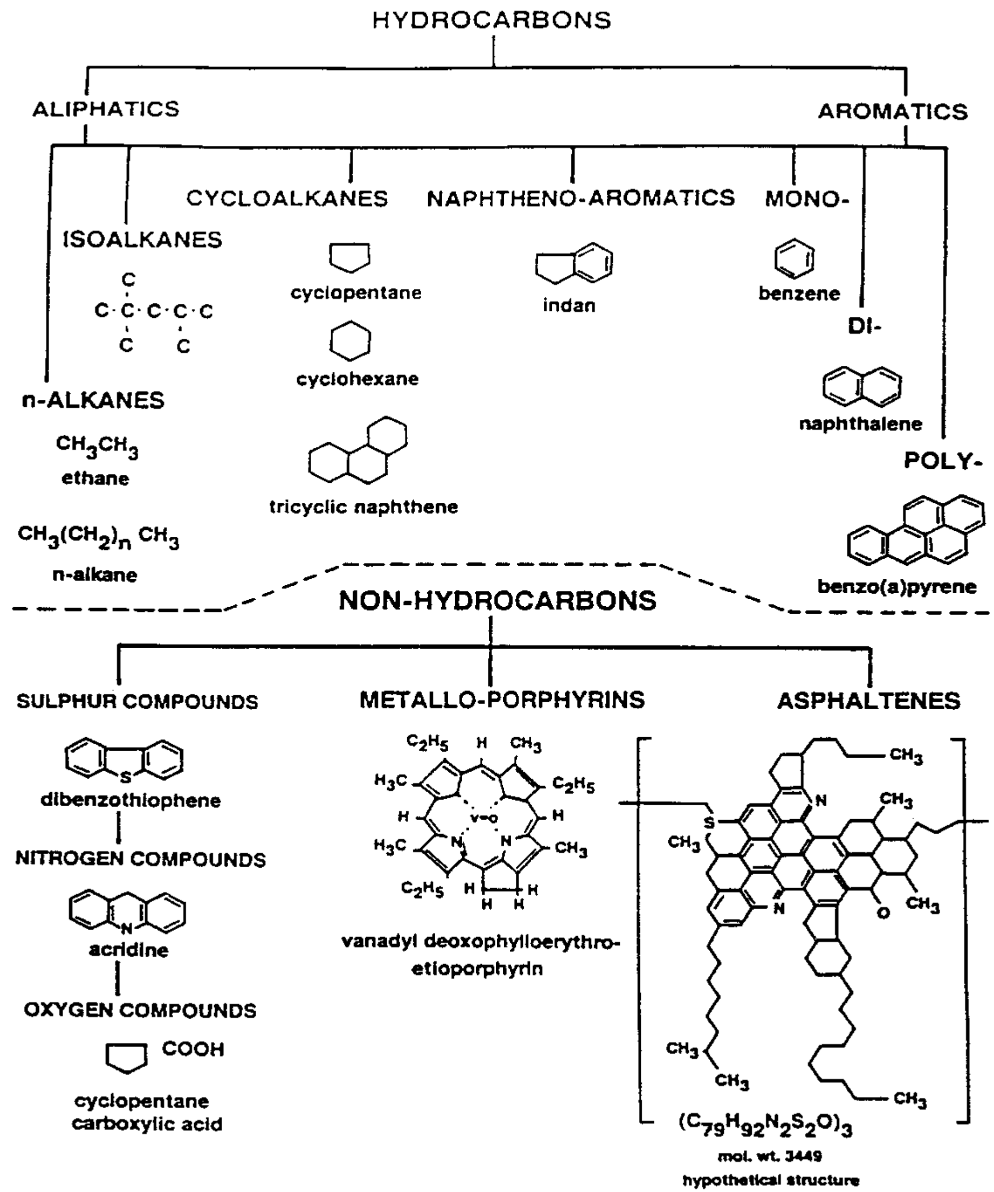
Properties of Petroleum Products (2)

Oil Type	C Range	Boiling Pt.	Sol. in H_2O	Density	% Arom.
Gasoline	C_4-C_{10}	25-215^{O}C	Moderate	0.74	10 - 25
Kerosene & Jet Fuel	C_{10}-C_{15}	160-400^{O}C	Moderate/ Low	0.81	<15
Diesel Fuel & Light Fuel Oils	C_{12}-C_{28}	160-400^{O}C	Low	0.86	15 - 20
Heavy Fuel Oils	C_{19}-C_{35}	315-540^{O}C	V. low	0.88	15 - 35
Motor Oils & Lube Oils	C_{20}-C_{44}	425-540^{O}C	V. low	0.90	< 15
Bitumen	> C $_{35}$	> 500^{o}C	Insol.	1.0	30 - 50

Hydrocarbon Structures

PIANO

- parafins
- isoalkanes
- aromatics
- naphthenes
- olefines



Methods of Analysis

- **Infra red (IR) – limited use**
- **Gas Chromatography – Flame Ionisation Detector (GC- FID)**
- **GCMS – PAHs and biomarkers**

TPH - Gas Chromatography

What is chromatography?
'The separation of a complex mixture of compounds by partitioning between a stationary phase (the column), and a mobile phase (gas or liquid)'

- **GRO (VPH) by headspace**
- **EPH by extract analysis**
- **Modified US EPA methods**
- **Detection limits:**
    - **Soil : 10 mg/kg**
    - **Water : 0.01 mg/l**

Chromatography Theory

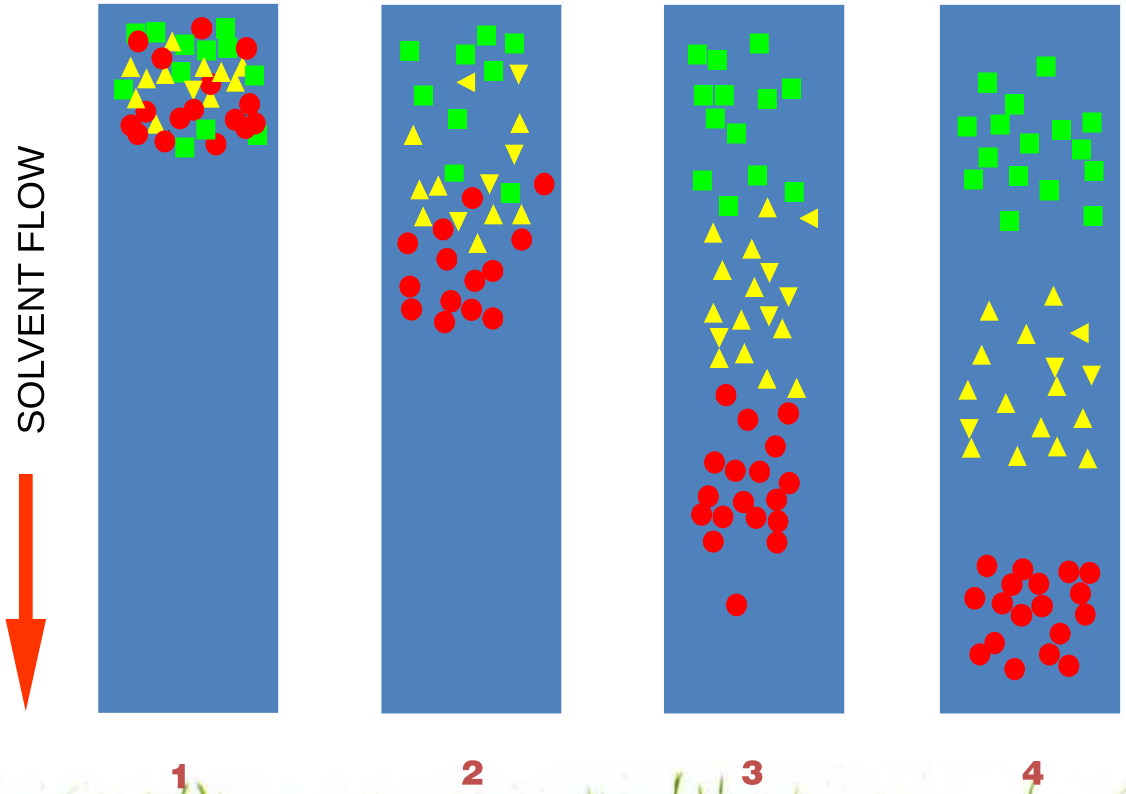
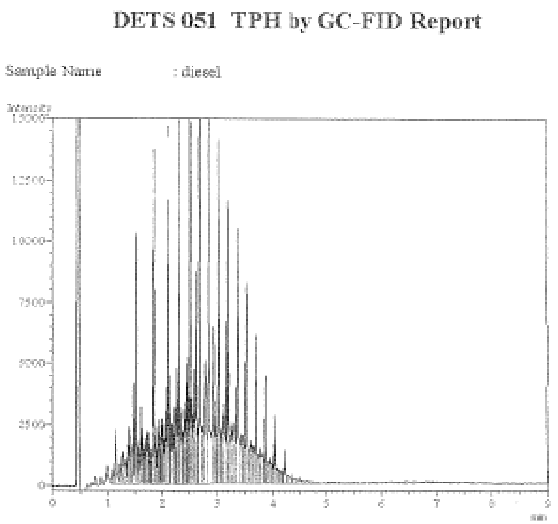


Image by ALcontrol Laboratories

Polarity

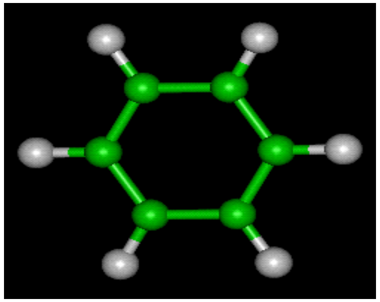
Reactivity of compounds, due to electronic charge. Non-polar compounds will elute with the solvent front from a column

- **Non-polar – alkanes, aliphatics, mineral oil, saturates, paraffins**
- **Moderately polar – polyaromatics**
- **Very polar – NSOs (nitrogen, sulphur and oxygen containing organics)**



BTEX by GC-FID

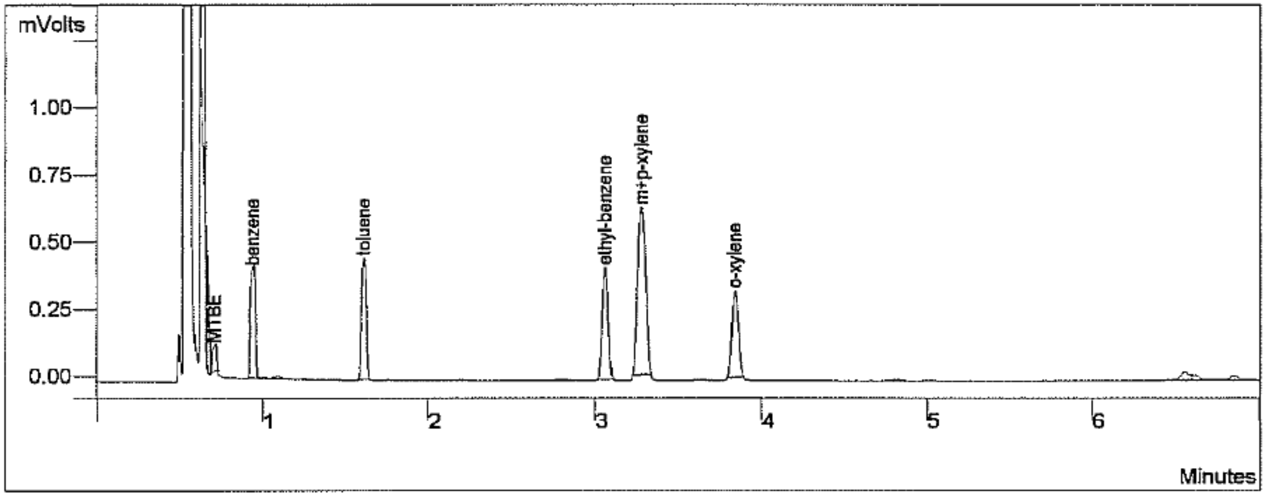
DETS 062 - BTEX by GC-FID



Benzene ring

Sample ID: **qcw**

Instrument (Inj): DETS ORG 016
Injection Method: c:\star\methods_016\btex\btex_06.mth
Data File: d:\data_016\btex\2006\07jul\21jul2006qcw.run
Operator (Inj): ms Operator (Calc): ms
Injection Date: 07/21/06 09:47:22

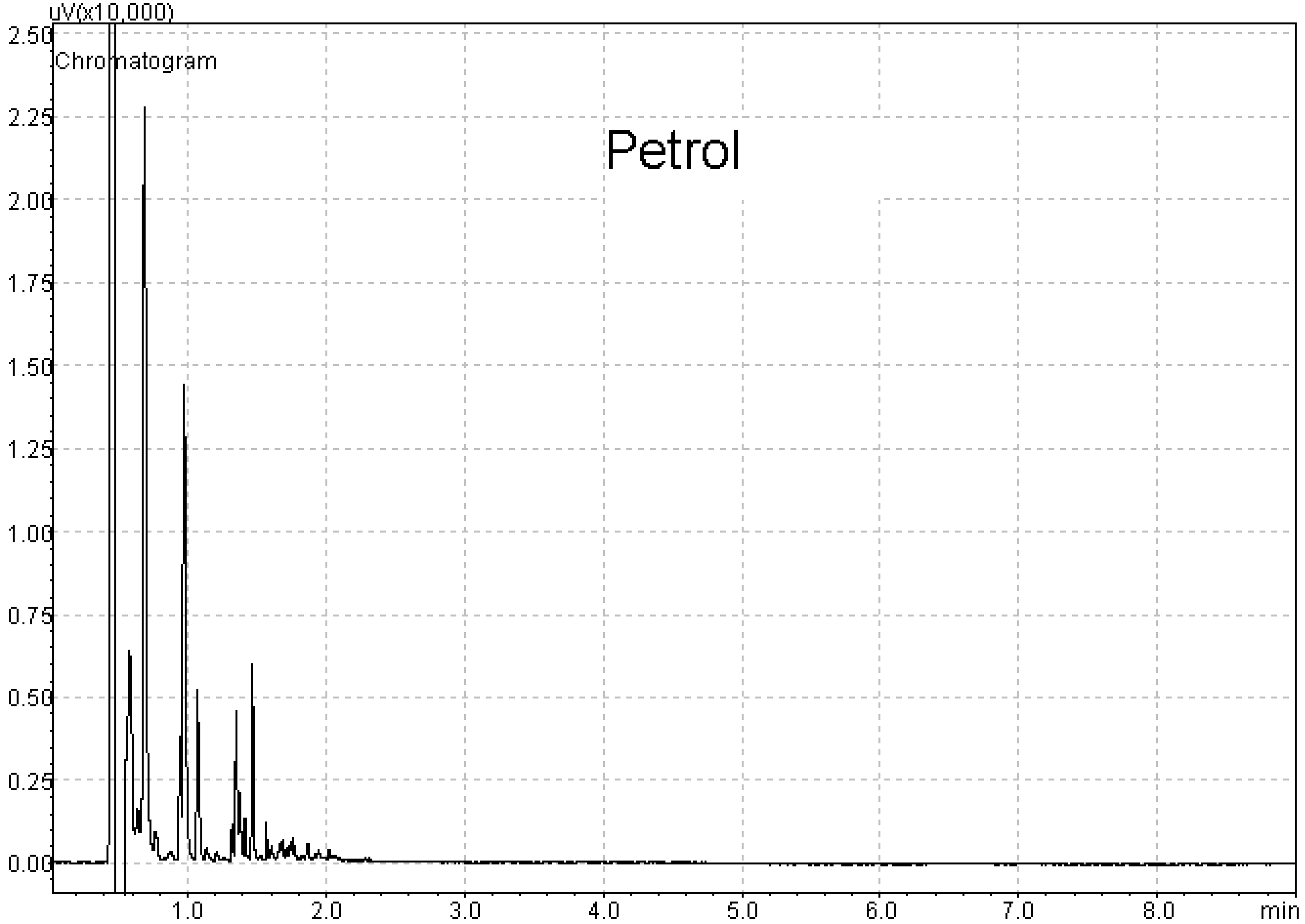


Gasoline Range Organics (GRO)

- Also known as petrol range organics (PRO) or volatile petroleum hydrocarbons (VPH)
- Carbon range C_5- C_{10}, typically up to 400 compounds
- Includes n- and iso-alkanes, e.g. pentane, dimethylpentane, octane; and naphthenes (cycloparaffins)
- Includes mono-aromatics, e.g. benzene, toluene, ethyl benzene, xylenes
- Can include methyl tertiary butyl ether (MTBE), but GCMS is the preferred method for greater certainty of identification

GRO - GCFID

- Headspace method
- Rapid turnaround
- Minimal sample handling
- Inexpensive
- Detection to 10 ppb
- Total volatiles (C_5- C_{12})
 + BTEX + banding


uV(x10,000)
Chromatogram
Petrol
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
min

Extractable Petroleum Hydrocarbons (EPH)

- Requires solvent extraction
- Carbon range C_{10}- C_{40} with speciation
- Includes aliphatics, aromatics and hetero-compounds
- Includes internal standards
- Identification of diesel, kerosene, lube oil, plus degree of weathering
- Detection limit :
  - Soils 10 mg/kg
  - Waters 0.01 mg/l

Extraction Solvent

- Ideally, the solvent should solubilize the target analytes but not the sample matrix
- Solvent polarity should match the target analytes (i.e. like dissolves like)
- Sample matrix may affect efficiency

Overall, due to the range of possible contaminants, an almost impossible decision…

Solvent Comparison

HEXANE/ACETONE DCM/METHANOL DCM/PENTANE CYCLOHEXANE FREON 112

Image by ALcontrol Laboratories

SCA TPH Working Group

- Round robin trials
- Samples provided by Shell
- As received soil is preferable
- Comparison of solvents
- Analysis by GCFID, not IR
- Standard in draft format pending completion

Extraction of Waters

- **Liquid/liquid extraction**
- **Stir bar liquid/liquid**
- **Solid Phase Extraction (SPE)**
- **DNAPLs and LNAPLs**

Issues to consider:

- **Solubility in water – generally low**
- **Dissolved, colloidal, or product layer?**
- **To filter or not to filter?**

Gas Chromatography

Identification

- Known Sample
- Retention Time

Quantification

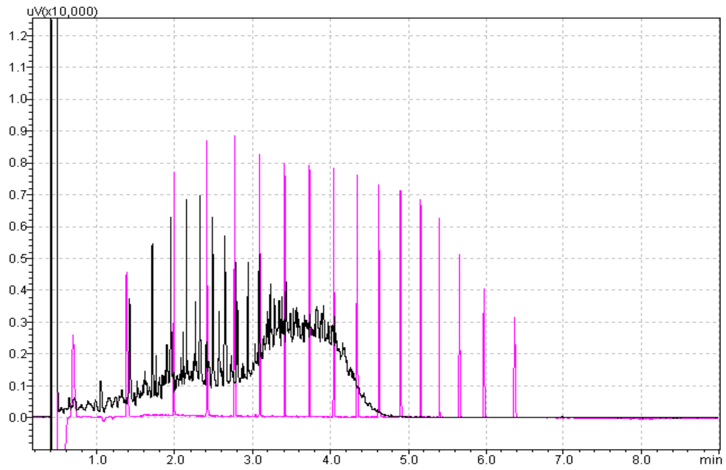
- Calibration Standards

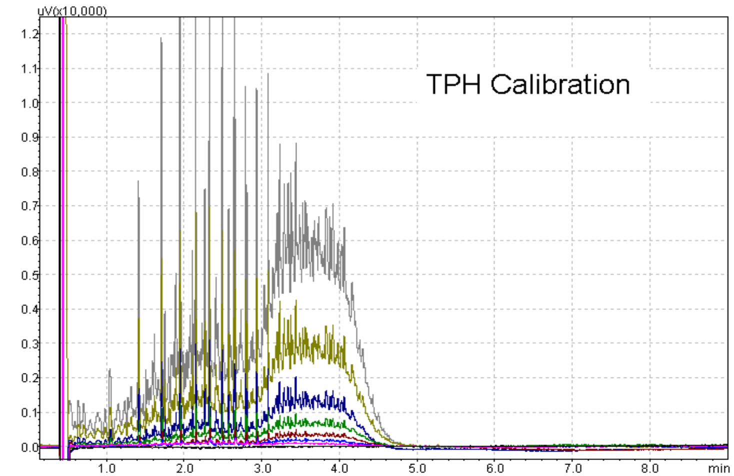
Banding

- Retention Time

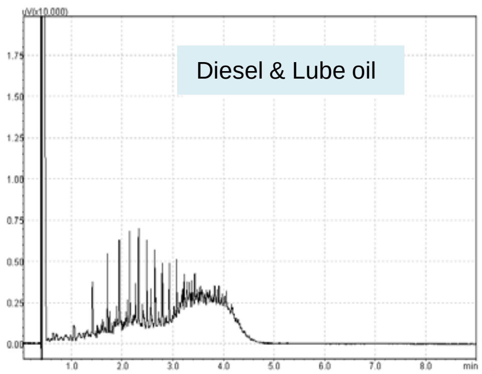
Quality

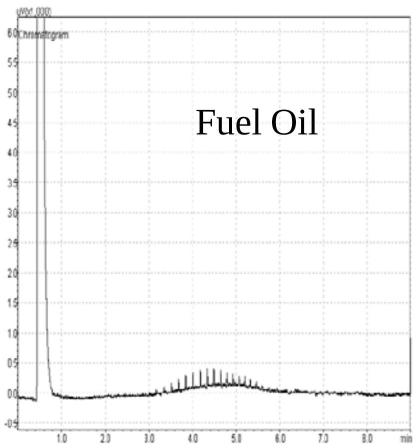
- QC
- Blanks
- Duplicates
- Calibration Checks
- Proficiency Testing

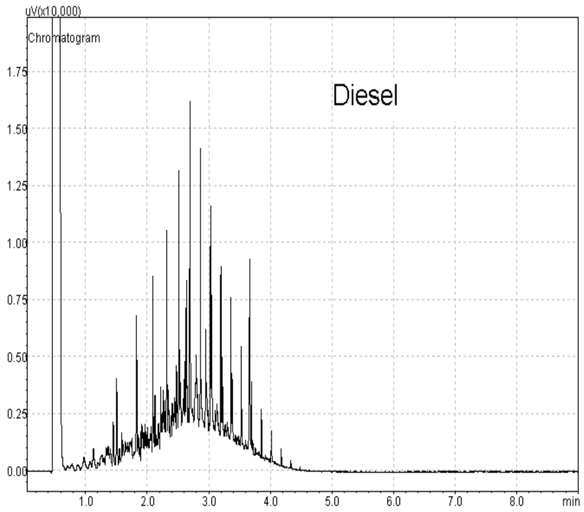


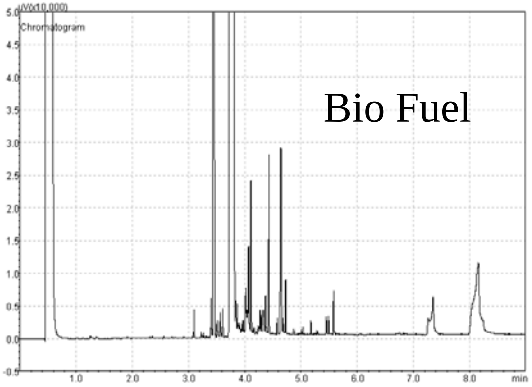


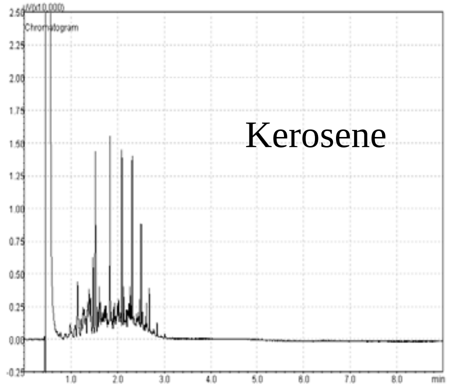
Chromatograms

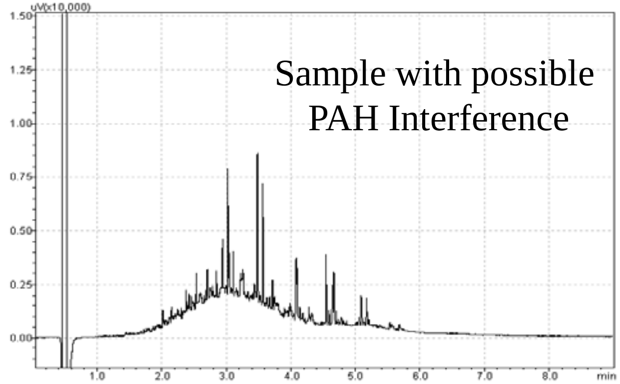












Possible Interferences in TPH analysis

- Polar hydrocarbons
- Oxygenated fuels
- Non-Petroleum compounds
  - Biogenic material
  - Plant oils and waxes
  - Coal material
  - Fats

Cleaned up EPH and Mineral Oil

ISO Definition of mineral oil (drinking water):

Compounds in the range C_{10}- C_{40} which are not retained by a silica column, using a non-polar solvent. Chemically, this consists of aliphatics (n-alkanes, iso-alkanes and cyclo-alkanes) only.

A 'cleaned up' EPH requires both a non-polar solvent and an aromatic solvent for elution – only the polar NSO compounds will be retained on the column

Speciation

- Breakdown of TPH into narrow carbon band ranges (CWG)
- Includes GRO and EPH
- Includes aliphatics & aromatics
- Used in risk assessment packages such as RBCA

Separation

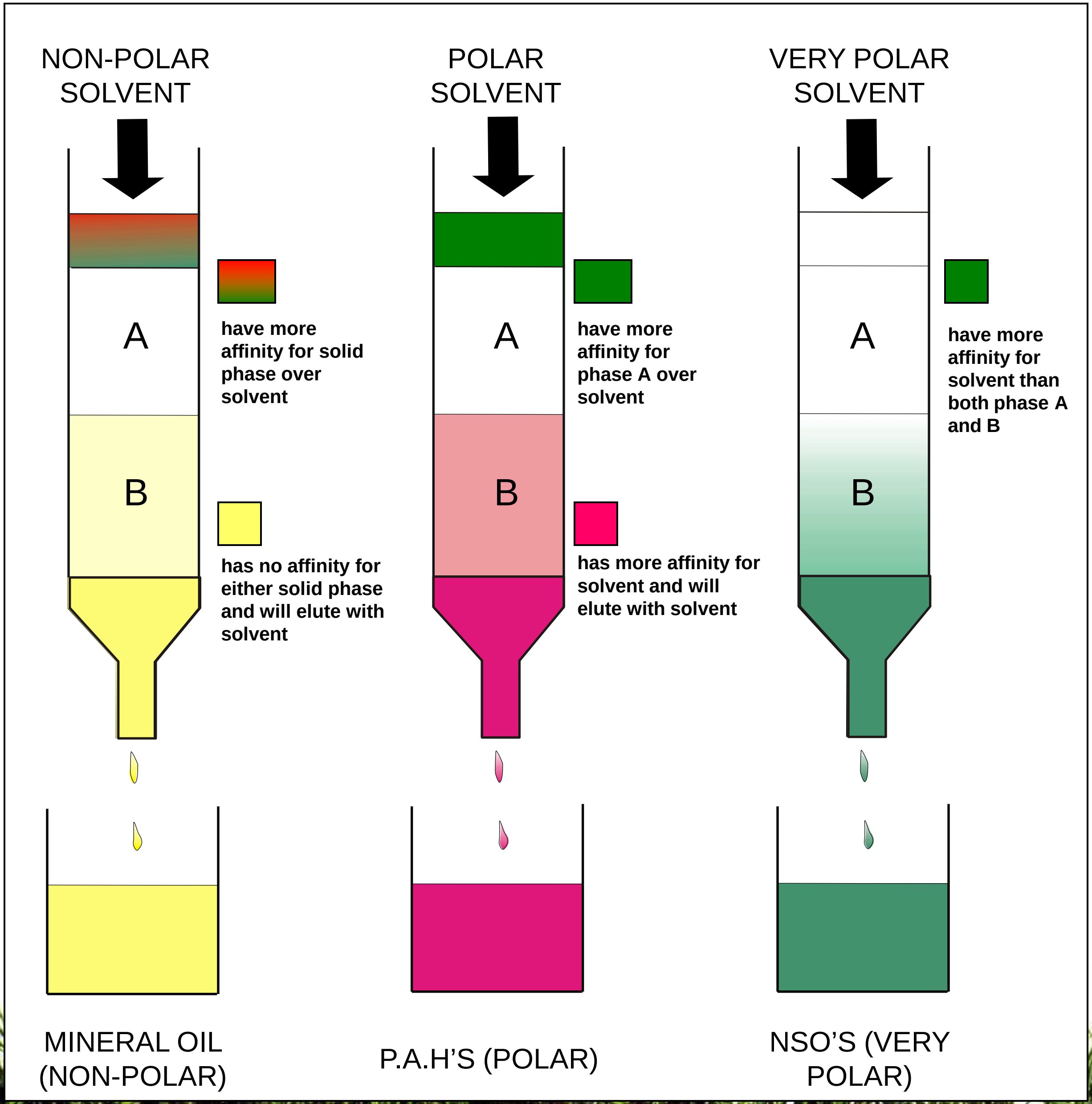
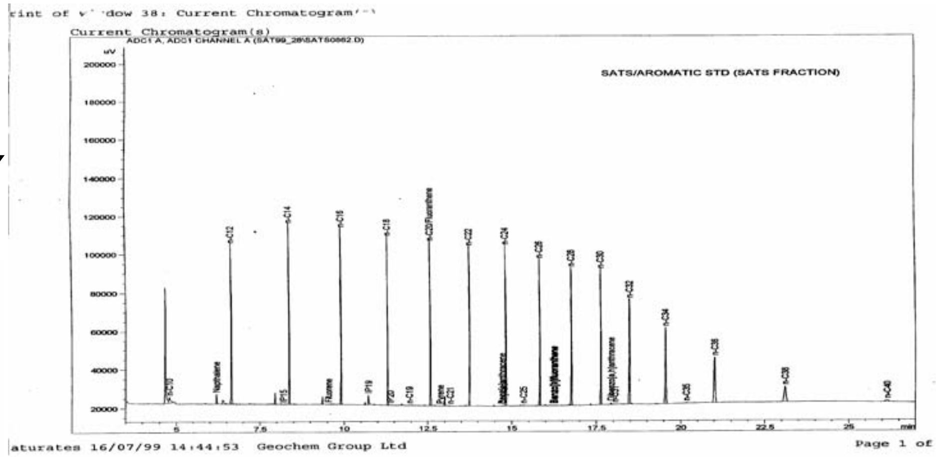
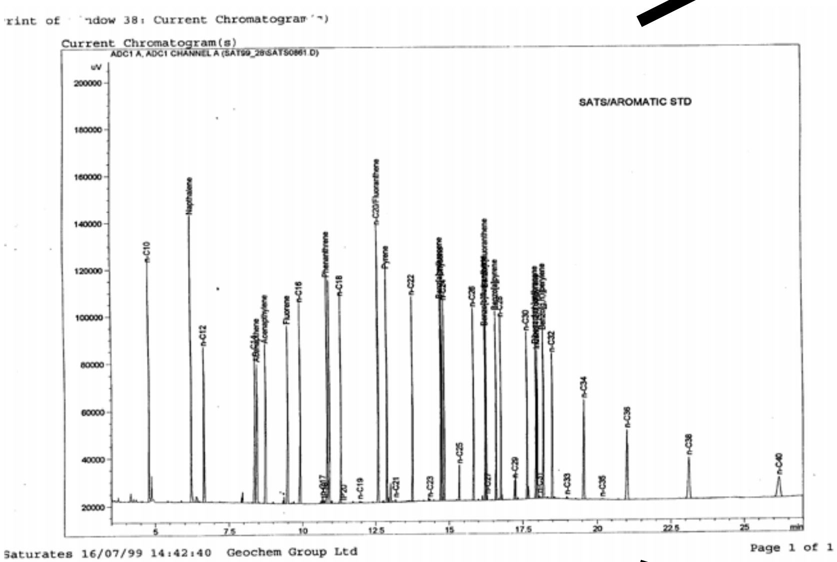


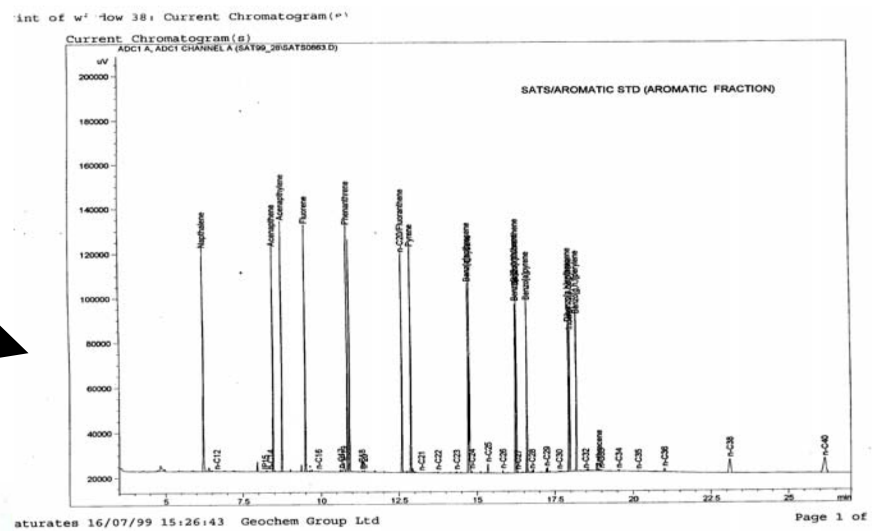
Image by ALcontrol Laboratories

Aliphatic Fraction





Aromatic Fraction



Combined Aliphatic and Aromatic Standard

Images by ALcontrol Laboratories

TPH Screen by Rapid GC ($C_6 - C_{40}$)

- **Advantages**
  - Rapid analysis
  - GRO & EPH in one run
  - Lower costs
- **Disadvantages**
  - Incomplete resolution of all peaks
  - Higher detection limits
  - Suitable for soils only

GCFID Methods

Advantages

- Covers the full TPH range
- Good sensitivity (10 ug/l for components)
- Carbon chain speciation
- Provides a fingerprint
- Identify individual analytes i.e. BTEX
- Identifies different products
- Identifies degree of weathering
- Good recovery efficiency

Disadvantages

- Slower, and slightly more expensive

TPH Method Summary

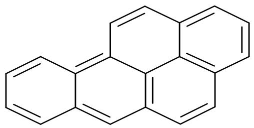
- VPH by headspace GC-FID – for gasoline range organics (C_5 – C_{10})
- EPH by GC-FID for diesel and lube oil range organics (C_{10} – C_{40})
- Cleaned up EPH to remove polars
- Speciated TPHCWG for aliphatic and aromatic banding (C_5 – C_{44})
- TPH screen for VPH and EPH combined (C_6 – C_{40})

TPH – Forensics analysis

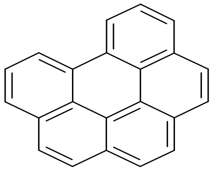
Four main questions:

- What is it?
- What was the source?
- When did it happen?
- Who was responsible?

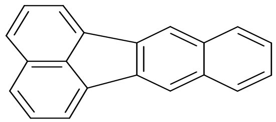
Polyaromatic Hydrocarbons



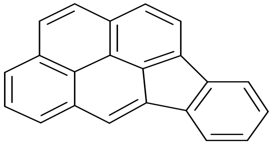
Benzo(a)pyrene



Benzo(ghi)perylene



Benzo(k)fluoranthene



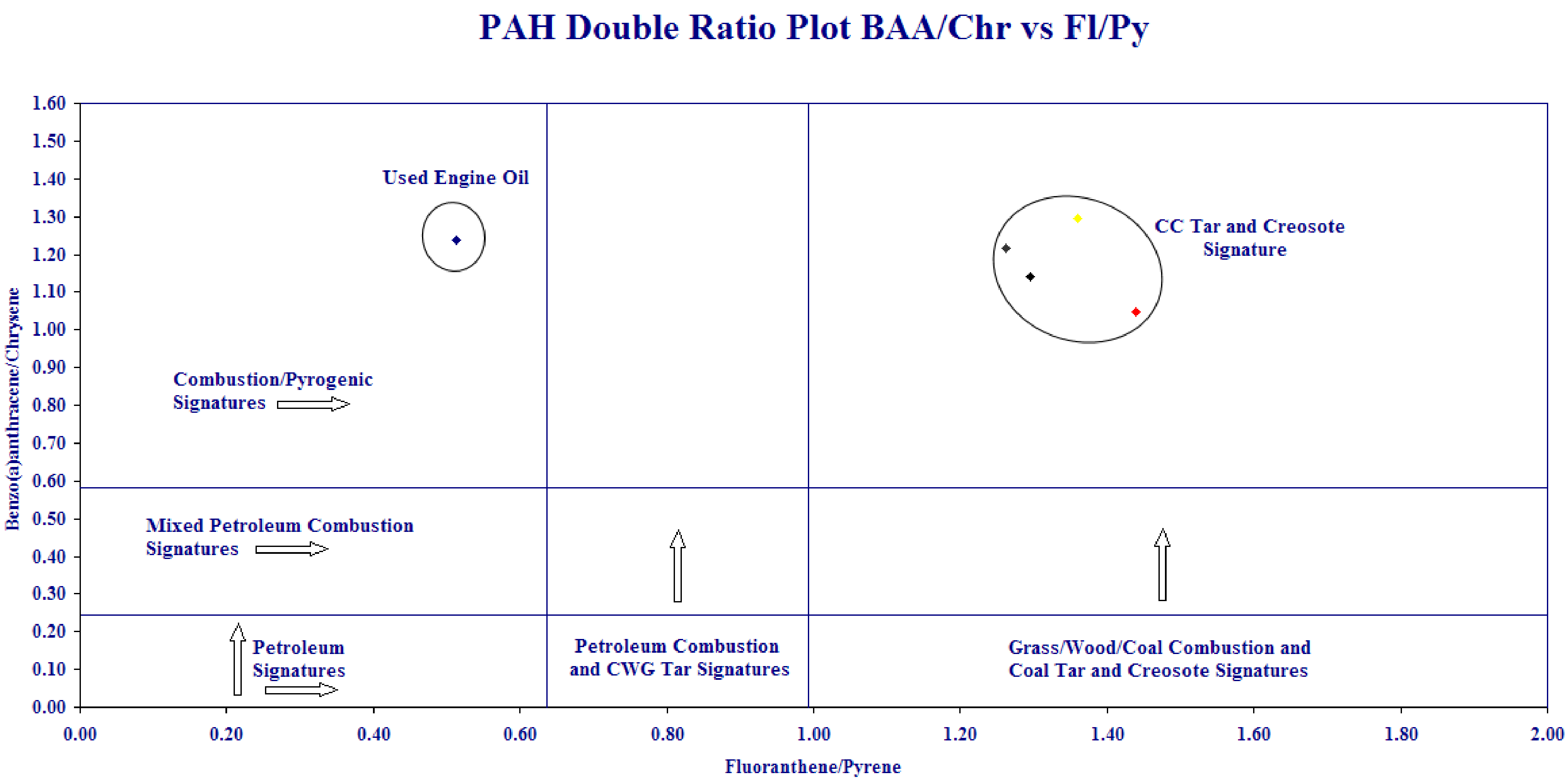
Indeno(c,d 1,2,3)pyrene

- **Group of compounds composed of two or more fused aromatic ring structures**
- **USEPA 16 priority PAHs represent approx. 80% of the PAHs found in the USA. Plus coronene in the WAC suite**
- **Some of the 4, 5 & 6 ring PAHs are considered probable or possible carcinogens, particularly benzo(a)pyrene**
- **A product of natural & fossil fuel combustion**
- **Gas works, wood preserving, landfill sites**

PAH double plots

- PAH double plots can be used for a number of forensic type analyses
- Typically fluoranthene:pyrene is plotted against benzo(a)anthracene:chrysene
- This provides a guide to the source of the original contamination in the soil
- When used for several samples, it can be possible to identify if a site has more than a single contamination source

PAH double plot



Ageing of petroleum products

Ageing =

weathering + biodegradation

Most Affected

- C_{10}-C_{20} n-alkanes
- Alkylated aromatics
- 2 and 3 ring aromatics

Least Affected

- C_{20+} alkanes
- Cyclo naphthenes
- C_4-C_6 ring aromatics

Most affected

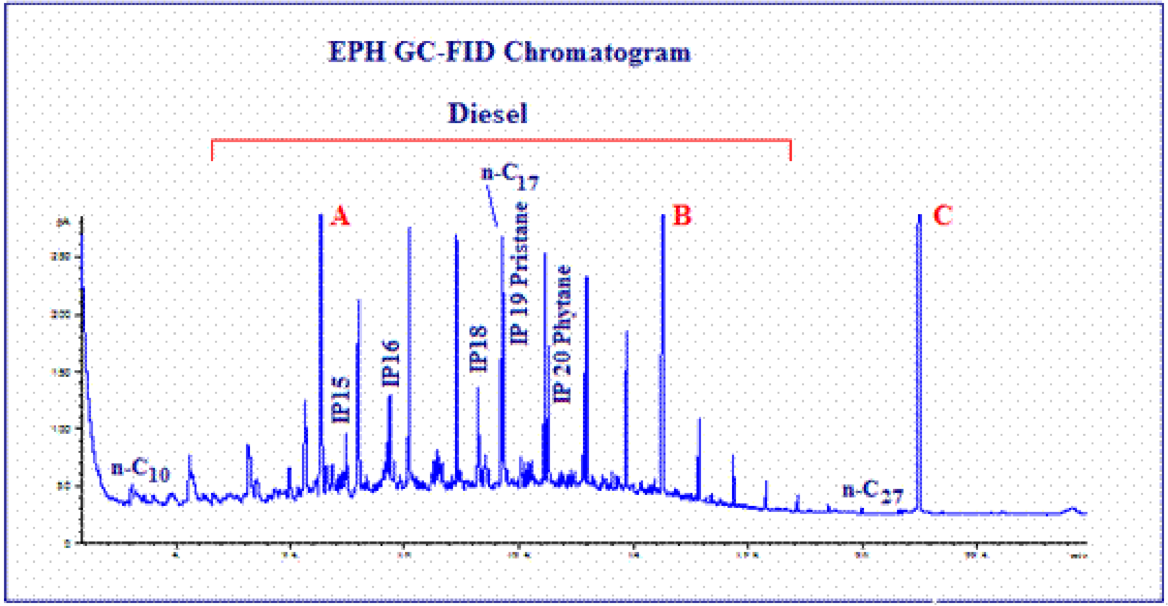
- C_{35}-C_{10} alkanes

Least affected

- Iso-prenoids
- Pristane
- Phytane
- C_6-C_2 ring aromatics

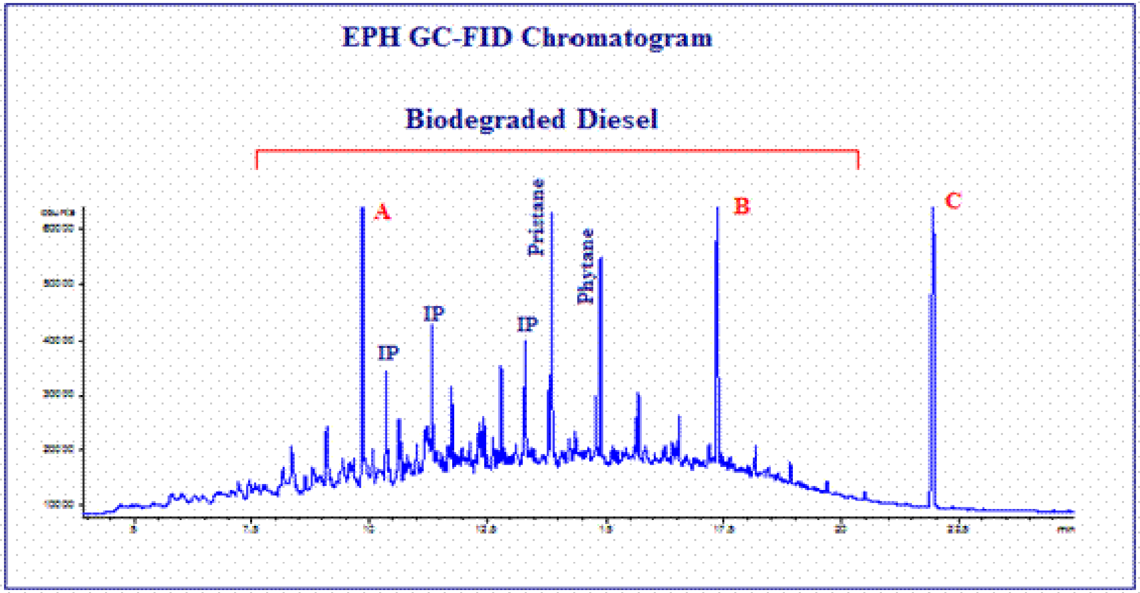
Ageing of petroleum products

Diesel – fresh and degraded



Most commonly used ratios:

- nC_{17}/Pristane
- nC_{18}/Phytane
- Pristane/Phytane



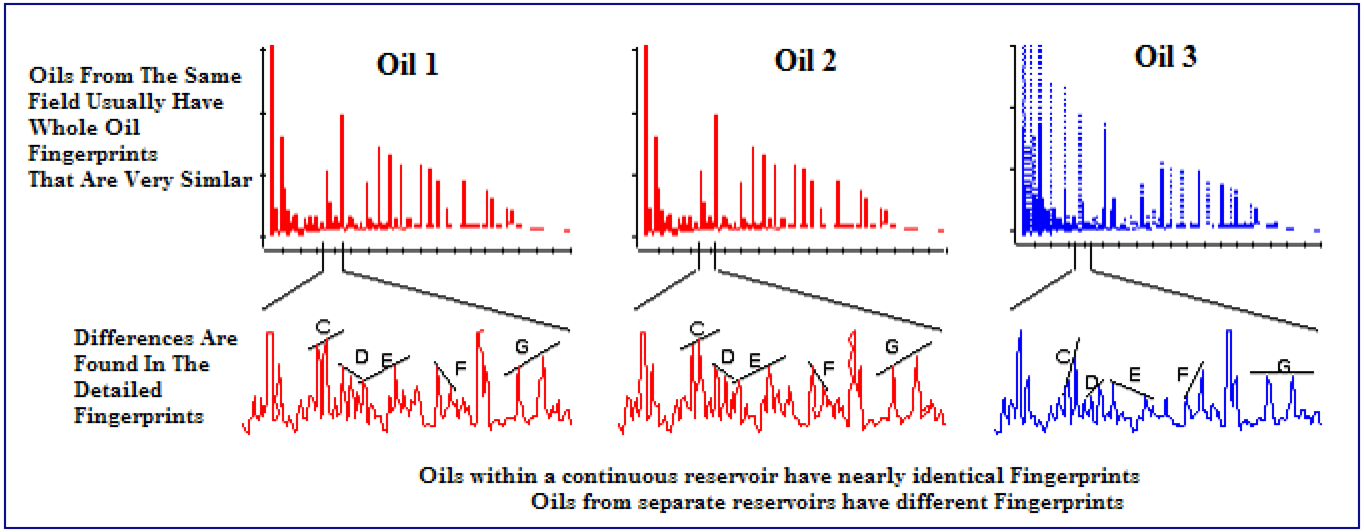
Images by ALcontrol Laboratories

Ageing

In the subsoil, several processes may change the composition of diesel.

- Evaporation - results in loss of volatiles
- Leaching - removal of the more water soluble components
- Microbial action - results in transformation of components with specific configurations, e.g unbranched alkanes
- Environment – particle size, matrix, pH

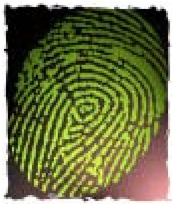
Oils From the Same Source or Not ??



Slide courtesy of Ken Scally, Jones Forencics

Ken.Scally@Alcontrol.ie

Compound Ratio Analysis Technique (CORAT)



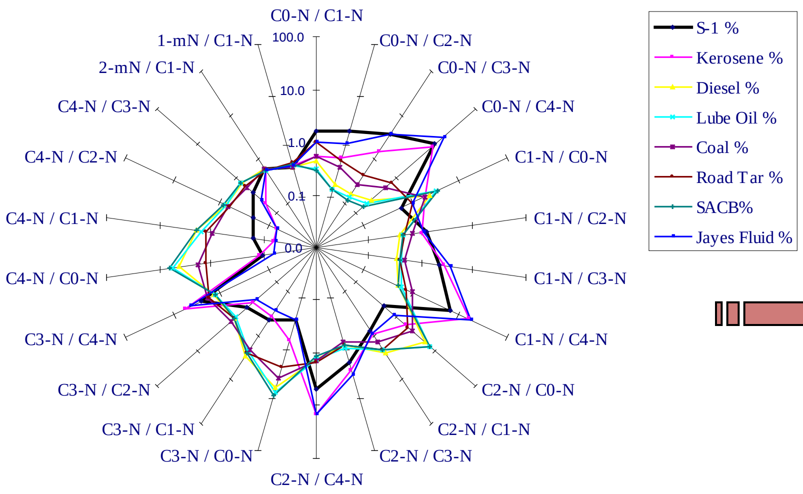
Compound Ratio Analysis Technique (CORAT) is a combination of analytical and interpretive techniques that utilises "fingerprint" chromatogram of crude oil samples used in the petroleum geochemistry industry. This technique, is also called "Reservoir Oil Fingerprinting" (ROF) this was originally developed by scientists at Chevron in the USA for crude oil comparisons.

Slide courtesy of Ken.Scally, Jones Forensics

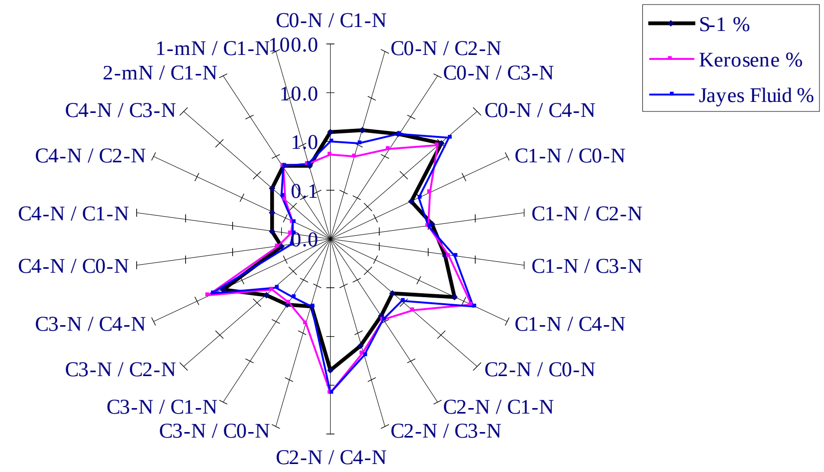
Source: Internet

Naphthalene Alkylated Series

Combined CORAT



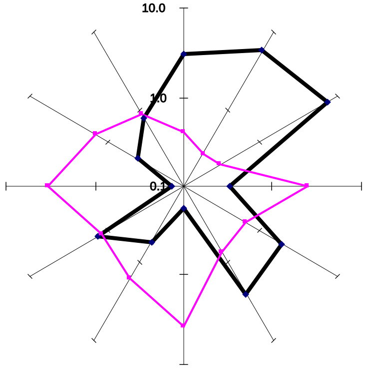
Best Fit



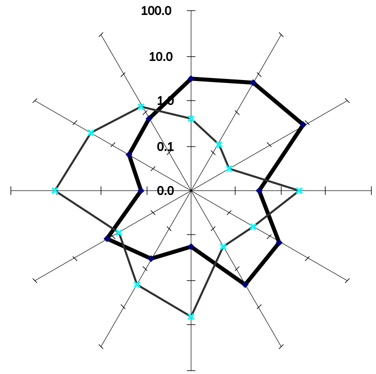
Alkylated Isomer	S-1	Kerosene	Diesel	Lube Oil	Coal	Road Tar	SACB	Jeyes Fluid
Naphthalene (N)								
C_0-Naphthalene	40	18	5	4	9	13	4	31
C_1-Naphthalene	25	35	12	14	17	13	13	31
2-methylnaphthalene	15	20	7	8	10	7	7	19
1-methylnaphthalene	10	14	4	6	7	6	6	13
C_2-Naphthalene	20	32	29	29	24	26	27	27
C_3-Naphthalene	11	12	32	30	33	31	32	8
C_4-Naphthalene	4	2	22	23	17	18	25	2

Slide courtesy of Ken Scally, Jones Forensics

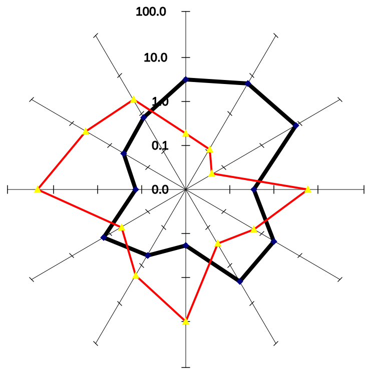
CORAT 2



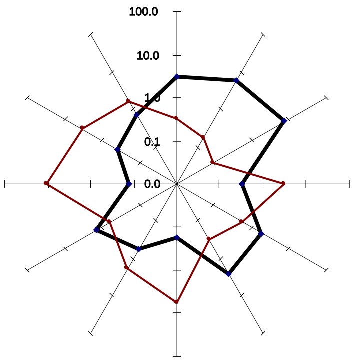
Diesel



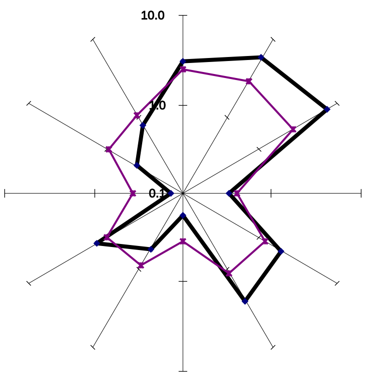
Coal



Lubrication Oil



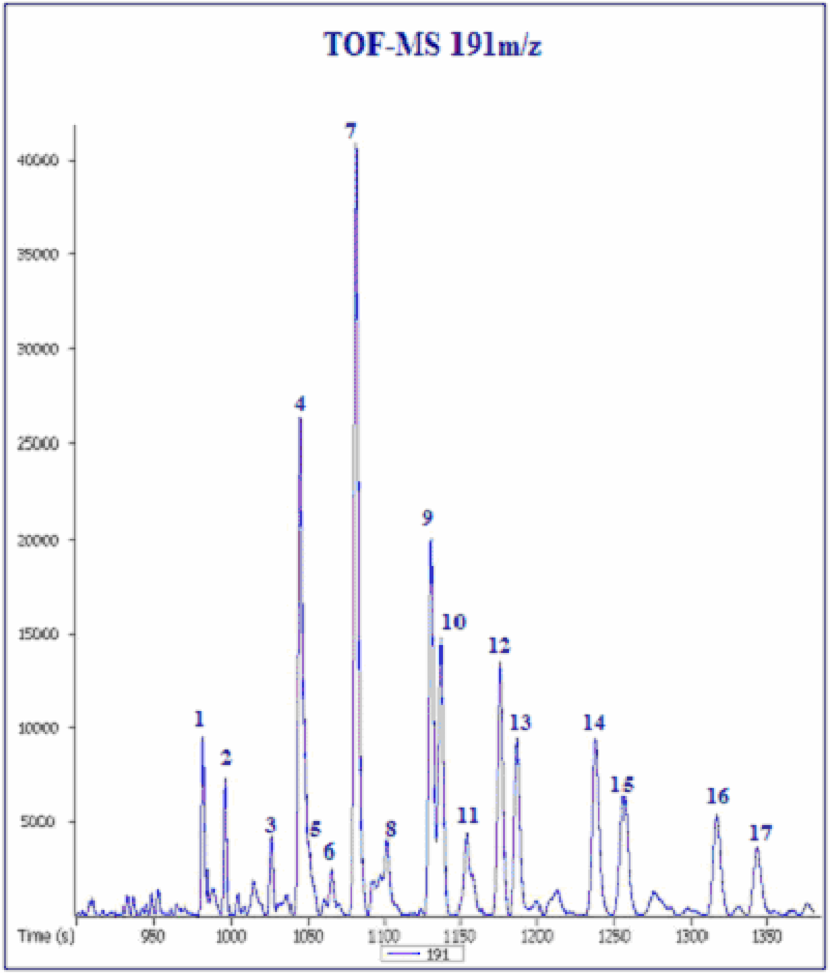
SACB

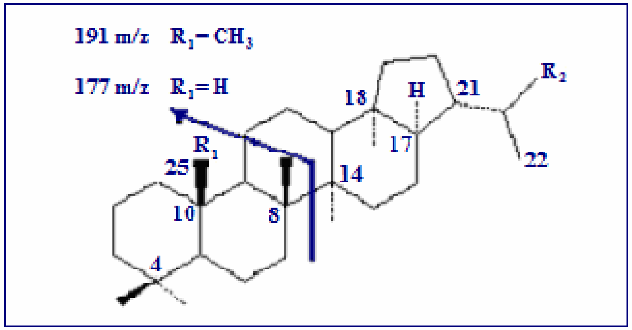


Road Tar

Slide courtesy of Ken Scally, Jones Forensics

Hopane Biomarkers

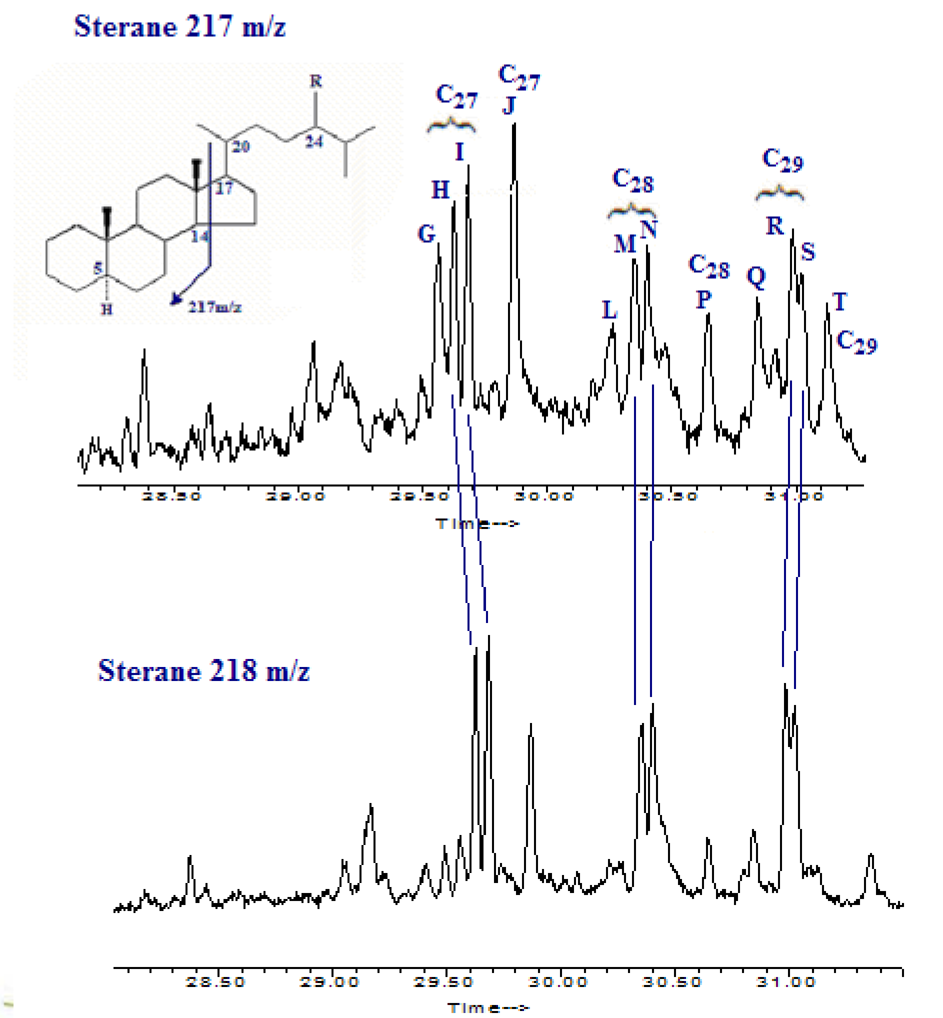




TOF-MS Peak	Carbon Number	Hopanes and Moretanes
1	n-C_{27}	18α(H)-22,29,30-trisnorneohopane (Ts)
2	n-C_{27}	17α(H)-22,29,30-trisnorhopane (Tm)
3	n-C_{28}	17α(H),21β(H)-28,30-bisnorhopane
4	n-C_{29}	17α(H),21β(H)-30-norhopane
5	n-C_{29}	18α(H),21β(H)-29-norneohopane (C_{29} Ts)
6	n-C_{29}	17β(H),21α(H)-30-normoretane
7	n-C_{30}	17α(H),21β(H)-hopane
8	n-C_{30}	17β(H),21α(H)-moretane
9	n-C_{31}	(22S)-17α(H),21β(H)-homohopane
10	n-C_{31}	(22R)-17α(H),21β(H)-homohopane
11	n-C_{31}	(22S + R)-17β(H),21α(H)-homomoretane
12	n-C_{32}	(22S)-17α(H),21β(H)-bishomohopane
13	n-C_{32}	(22R)-17α(H),21β(H)-bishomohopane
14	n-C_{33}	(22S)-17α(H),21β(H)-trishomohopane
15	n-C_{33}	(22R)-17α(H),21β(H)-trishomohopane
16	n-C_{34}	(22S)-17α(H),21β(H)-tetrakishomohopane
17	n-C_{34}	(22R)-17α(H),21β(H)-tetrakishomohopane

Slide courtesy of Ken Scally, Jones Forensics

Sterane Biomarkers



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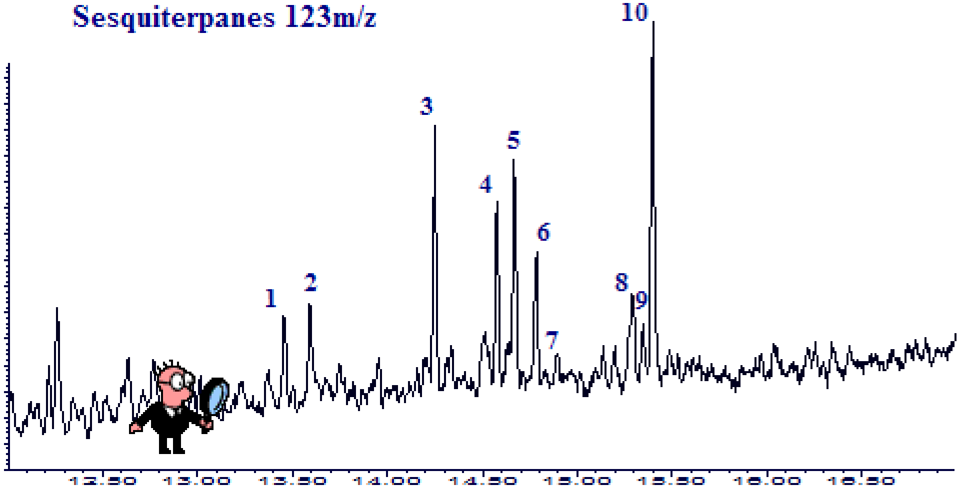
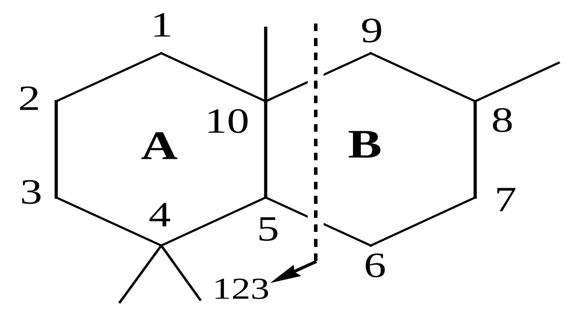
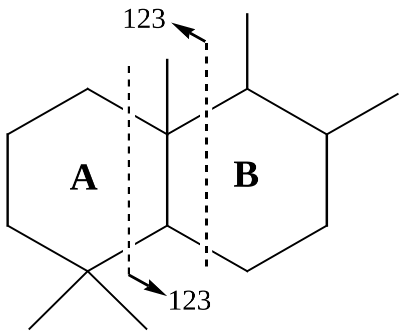
Bicyclic Sesquiterpanes

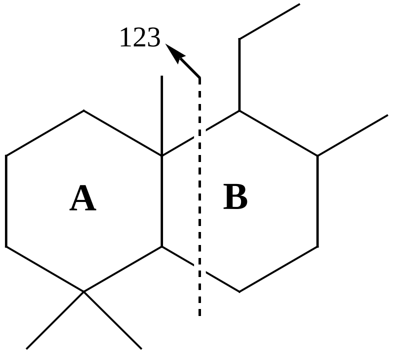




C_{14}: C_4-decalin (peak 1)



C_{15}: 8β(H)-drimane (peak 5)



C_{16}: 8β(H)-homodrimane (peak 10)

Slide courtesy of Ken Scally, Jones Forensics

Ken.Scally@Alcontrol.ie

Reference: Zhendi Wang (2005)

Exxon Valdez – We are leaking some oil

"25 – 32 million US gallons of crude oil"

"250,000 birds, their feathers soaked in oil, were found either dead or dying…"

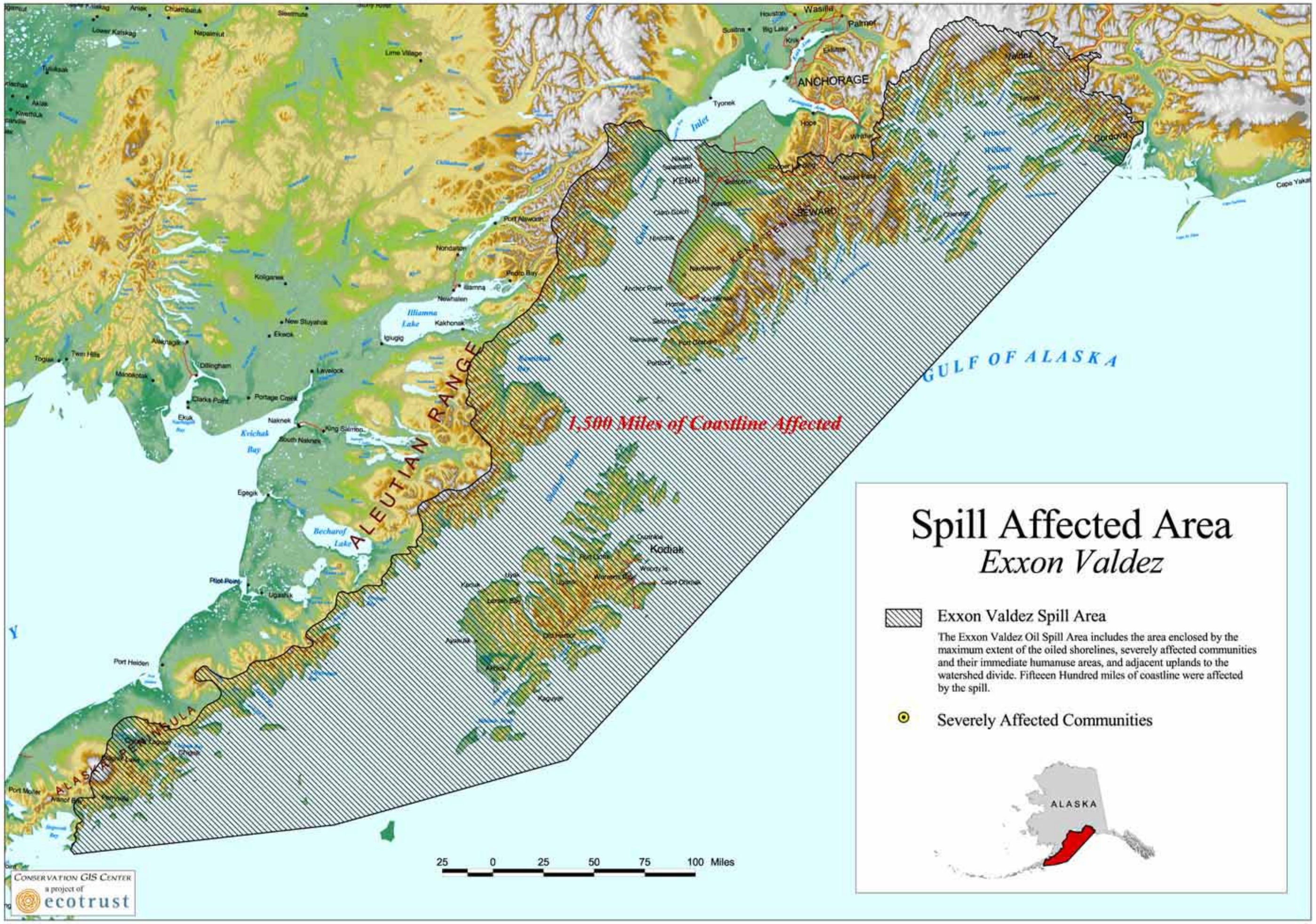
"300 seals, 247 Bald Eagles, 22 orcas, 2,800 sea otters"

"Each Sea Otter saved would cost Exxon forty thousand dollars …"

"Billions of salmon and herring eggs….

Slide courtesy of Jones Environmental

Source: http://www.solarnavigator.net/images/exxon_valdez.jpg



Slide courtesy of Jones Environmental

$287 Million Actual Damages
$5 Billion Punitive Damages

$2 Billion to clean up the spill

Slide courtesy of Jones Environmental

http://www.channel6.dk/native/Grabs%20full/AK4-078V.jpg http://gcaptain.com/maritime/blog/wp-content/uploads/2007/05/exxon-valdez.jpg http://whyfiles.org/168oil_spill/images/valdez_duck.jpg
http://marinebio.org/upload/74/11-5.jpg http://www.savewithclick.com/english/pictures/alaska3.jpg
http://www.our-energy.com/pictures/static_content/energy_and_ecology/oiled_bird_in_exxon_valdez_spill.png

The Analysis of Total Petroleum Hydrocarbons

Thank you

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