Is “TPH“ always TPH?

or - What has your lab actually measured?

ELQF meeting
(9 March 2023)

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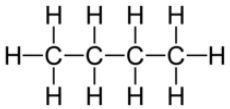
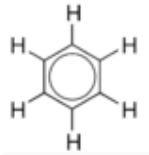
“TPH” is not always TPH

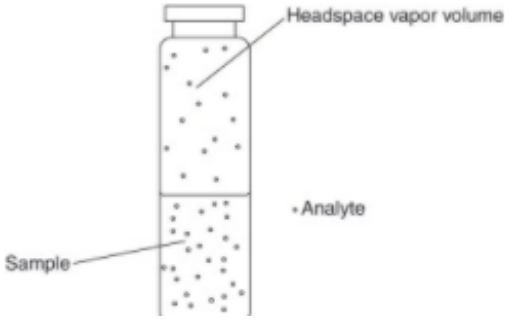
- What do you actually understand about your “TPH” test result ?
  - What is the difference between EPH, TPH, TPH1, …. ?
  - Is the methodology for TPH-CWG the same for all labs ?
  - Why is my WAC mineral oil result larger than the TPH-CWG result ?
  - How do (can) I compare “TPH” results from one lab to another ?
  - What’s this new test - GC-GC ?
  - Is a lab’s interpretation definitive ?
    - Is my “TPH” from petroleum hydrocarbons?
- To start answering these questions, we really have to:
  - Understand how hydrocarbons are measured
  - Consider other sources of hydrocarbons
  - Integrate with other information
- And not just process the” TPH” concentration

Lab Terminology

- Misunderstood and misused terms due to confusion relating to poor definitions and lack of transparency. **Generally;**
- "**TPH**" - Total Petroleum Hydrocarbons comprises hydrocarbons within the range ~C5-C44; includes the aliphatics  & the aromatics 
- "**EPH**" - Extractable Petroleum Hydrocarbons are the solvent extractable portion of all hydrocarbons in range ~C10-C40
- "**Cleaned-up EPH**" - Where take "EPH" extract and pass it through a silica gel or Florisil clean-up to remove **non-petroleum** hydrocarbons
  - e.g. humic acids, fatty acids
- "**DRO**" : Diesel Range Organics – simply covers the range ~C10-C25
- "**Mineral Oil**"
  - Mineral oil (~C10-C40) - should be same as "Cleaned-up EPH"

More “TPH”

- GRO : Gasoline Range Organics (~C5-C10)
  - Analysis of the volatiles found in the “headspace”
    - BTEX: benzene, toluene, ethyl benzene and xylene



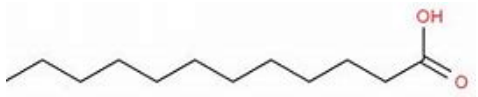
- TPH-CWG
  - TPH Criteria Working Group – analysis requires both GRO (C5-C10) and EPH where EPH is cleaned-up twice:
    - 1st into aliphatic fraction
    - 2nd into the aromatic fraction
  - Bandings are used for evaluating human health risks

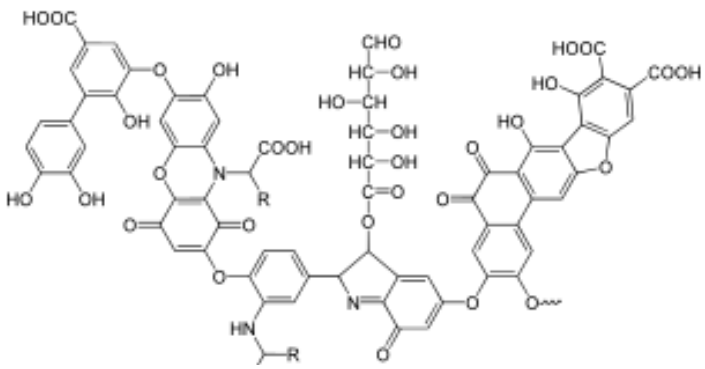
Aliphatic	Aromatic
>C5-C6	>C6-C7
>C6-C8	>C7-C8
>C8-C10	>C8-C10
>C10-C12	>C10-C12
>C12-C16	>C12-C16
>C16-C21	>C16-C21
>C21-C35	>C21-C35
>C35-C44	>C35-C44

- Note: In waste classification, you cannot use the individual bands, you must use total of the aromatic & aliphatic bands
  - **And** you need C6 to C40 (not C35)

Importance of the clean-up step

- Oils derived from the refining of crude oil comprise primarily C and H atoms
- In waste classification, the WM3 guidance describes how to assess soils contaminated by oil spills or by unknown oil(s) ➔ i.e. Refined Oils
- But soils can also contain other hydrocarbons - such as fatty acids and humic acids;
  - formed by the microbial degradation of dead plant & animal matter
  - humics are aromatic molecules
  - contain oxygen atoms

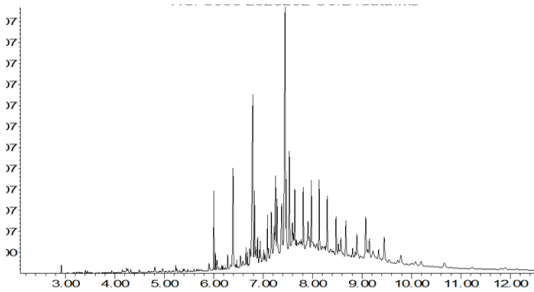




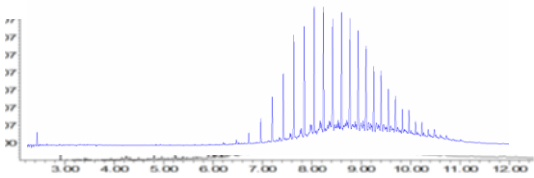
- The clean-up step attempts to remove these non-petroleum hydrocarbons
- & results in **lower** “TPH” concentrations

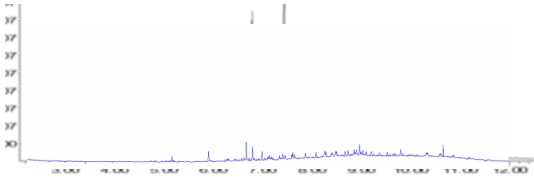
Let's understand basics of "TPH" testing first

- Preparation method same for both "EPH" and "TPH-CWG"
  - Solvent extraction using a solvent eg hexane/acetone
- "EPH"
  - Run extract straight through a GC-FID
  - Measures all extracted hydrocarbons



- "TPH-CWG" (has 2 **clean-up** steps)
  - Silica-alumina column
  1. Aliphatics eluted using a non-polar solvent – hexane
     - Aromatics remain bound to alumina in column
  2. Aromatics eluted using a polar solvent - DCM
  - Both elutes then passed separately through a GC-FID





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But how do you know what a lab has actually done?

- Terminology for naming “TPH” tests is not transparent or consistent
- From name alone, it is very difficult or impossible to tell what a lab has done
- Lab’s method statements (where included) are brief/unclear
- Terminology for same “TPH” test can vary between the term used in Quote, Schedule, PDF Report
- Also the same “TPH” name, used in both the Solids and WAC reports, can give very different results (because used different methods)

A selection of lab names
GRO >C5-C10
EPH Range >C10-C40
TPH1 (C10-C40)
TPH (C10-C40)
EPH(C5-C40)
Total Aliphatics & Aromatics >C10-C44
Total Aliphatics >C10-C44
Total Aromatics >C10-C44
Total Petroleum Hydrocarbons
Total Aliphatics & Aromatics >C10-C44
Mineral Oil (mg/kg)
Mineral Oil >C10-C40

To make “TPH” testing more transparent : The HWOL Acronym System

Acronym	Description
HS	Headspace analysis
MS	Mass Spectrometry
EH	Extractable hydrocarbons - i.e. everything extracted by the solvent
CU	Chemical clean-up - by florisil or silica gel
1D	GC - Single coil gas chromatography
Total	Aliphatics & Aromatic fractions
AL	Aliphatic fraction only
AR	Aromatic fraction only
2D	GC-GC - Double coil gas chromatography
#1	Mathematical clean-up for the humics (GC-GC)
+	Operator to join tests together e.g. GRO C5-C10 and EPH C10-C40

Adding the HWOL Acronyms

#	Labels used in Lab PDF Reports	Actual Analysis
1	“GRO >C5-C10”	HS_1D_Total
2	“EPH Range >C10-C40”	EH_1D_Total
3	“TPH1 (C10-C40)”	EH_1D_Total
4	“TPH (C10-C40)”	EH_CU_1D_Total
5	“EPH(C5-C40)”	EH_CU+HS_1D_Total
6	“Total Aliphatics & Aromatics >C10-C44”	EH_CU_1D_Total
7	“Total Aliphatics >C10-C44”	EH_CU_1D_AL
8	“Total Aromatics >C10-C44”	EH_CU_1D_AR
9	“Total Petroleum Hydrocarbons”	EH_2D_Total
10	“Total Aliphatics & Aromatics >C10-C44”	EH_2D_Total_#1
11	“Mineral Oil (mg/kg)”	EH_1D_Total
12	“Mineral Oil >C10-C40”	EH_CU_1D_AL

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Report Example

EPH (>C10 to C40) (EH_1D_Total)	(mg/kg)	MCERTS	2700
EPH cleaned-up (>C10 to C40) (EH_CU_1D_Total)	(mg/kg)	u	1500
Aliphatics			
> C5 to C6 (HS_MS_1D_AL)	(mg/kg)	u	<0.1
> C6 to C8 (HS_MS_1D_AL)	(mg/kg)	u	< 0.1
> C8 to C10 (HS_MS_1D_AL)	(mg/kg)	u	< 0.1
> C10 to C12 (EH_CU_1D_AL)	(mg/kg)	u	0.5
> C12 to C16 (EH_CU_1D_AL)	(mg/kg)	u	3.0
> C16 to C21 (EH_CU_1D_AL)	(mg/kg)	u	28
> C21 to C35 (EH_CU_1D_AL)	(mg/kg)	u	190
> C35 to C40 (EH_CU_1D_AL)	(mg/kg)	u	75
Aromatics			
> C5 to C7 (HS_MS_1D_AR)	(mg/kg)	u	< 0.1
> C7 to C8 (HS_MS_1D_AR)	(mg/kg)	u	< 0.1
> C8 to C10 (HS_MS_1D_AR)	(mg/kg)	u	0.3
> C10 to C12 (EH_CU_1D_AR)	(mg/kg)	u	1.0
> C12 to C16 (EH_CU_1D_AR)	(mg/kg)	u	5.8
> C16 to C21 (EH_CU_1D_AR)	(mg/kg)	u	86
> C21 to C35 (EH_CU_1D_AR)	(mg/kg)	u	300
> C35 to C40 (EH_CU_1D_AR)	(mg/kg)	u	170
Total			
> C5 to C40 (EH_CU+HS_1D_Total)	(mg/kg)	u	860

- And mineral oil in the WAC report

Solid Analysis			
Total Organic Carbon	%	MCERTS	4.4
Loss on Ignition	%	UKAS	41
BTEX	(mg/kg)	MCERTS	< 0.30
PCB's (7 Congeners)	(mg/kg)	u	< 0.056
Mineral Oil (> C10 to C40) (EH_1D_Total)	(mg/kg)	u	2700
PAH	(mg/kg)	u	< 0.34
pH	units	MCERTS	8.9

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So what is Gas Chromatography

How does it work?

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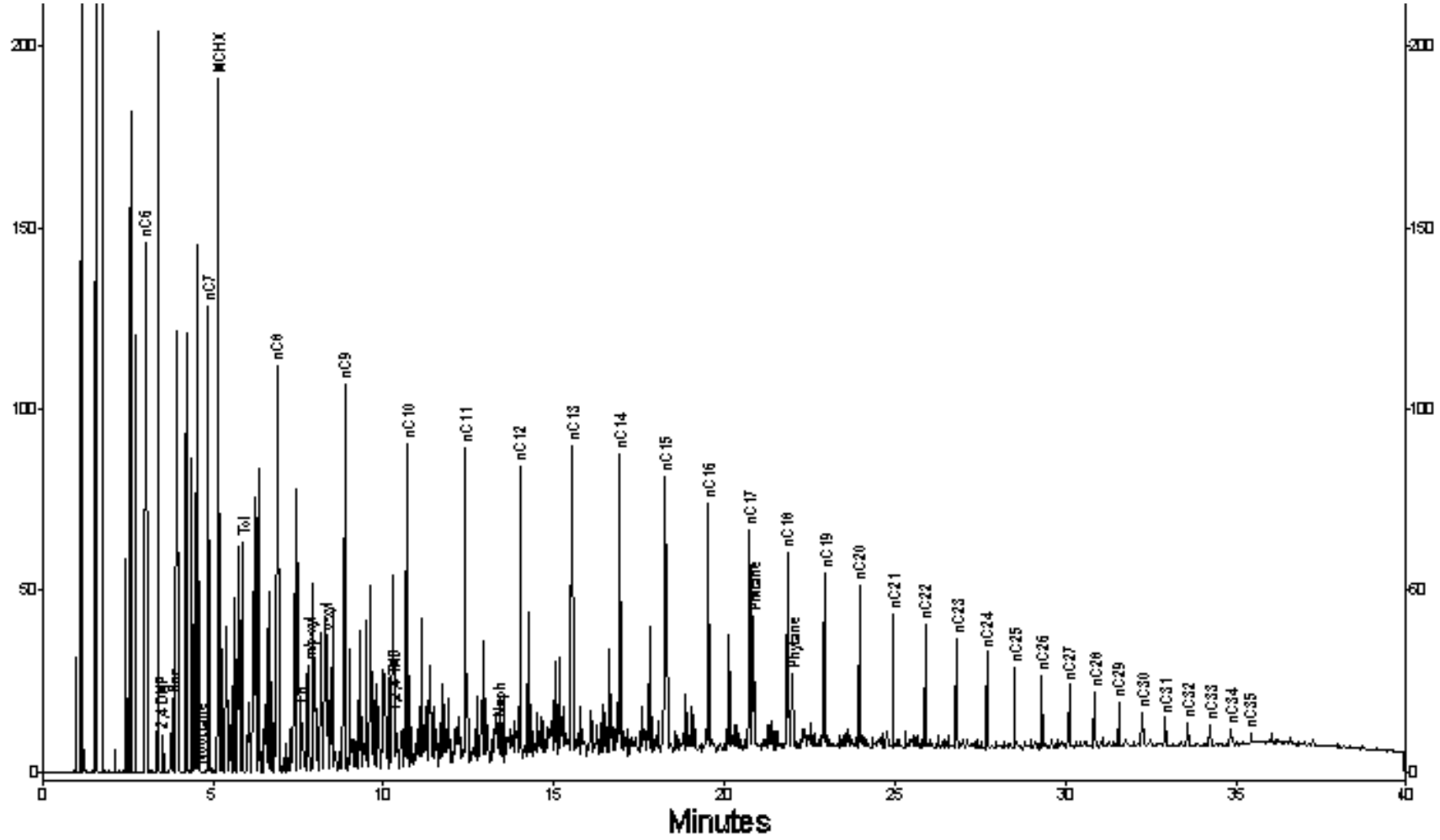
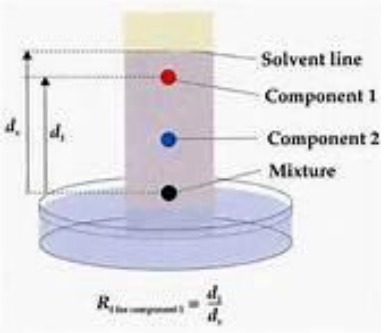
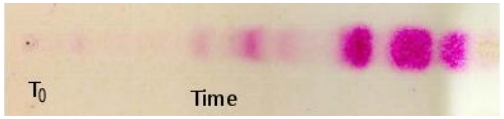
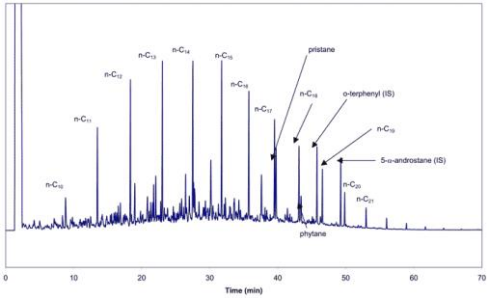
Oil “spectrum”



Analytical Chromatography







- Family of techniques for the separation and analysis of complex mixtures. Typically comprises:
  - Thin layer of silica gel coated on to a plate (layer is called the stationary phase)
  - Sample added to one end of the plate
  - Solvent (the mobile phase) is drawn up the plate via capillary action
  - Because different analytes (molecules) ascend the plate at different rates, separation is achieved
  - At end of plate, a different machine measures the intensity of the analytes against time (called the retention time)

Laboratories and analysis of volatiles

Lab method names			Detector
GC-FID	1D GC-FID	1D Gas Chromatography	Flame Ionization Detector
GC-MS		1D Gas Chromatography	Mass Spectrometer
GC-GC	2D GC-FID	2D Gas Chromatography	Flame Ionization Detector
GC-GC-MS		2D Gas Chromatography	Mass Spectrometer

- GC used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition (i.e. the volatiles)
- Mobile phase is a gas e.g. nitrogen or helium
- Stationary phase (viscous liquid or polymer) is coated on an inert material inside a glass or metal column

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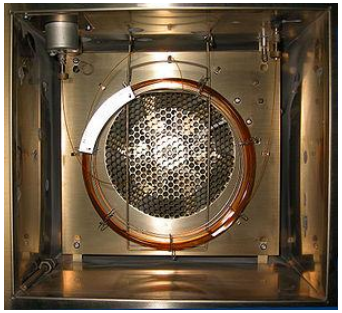
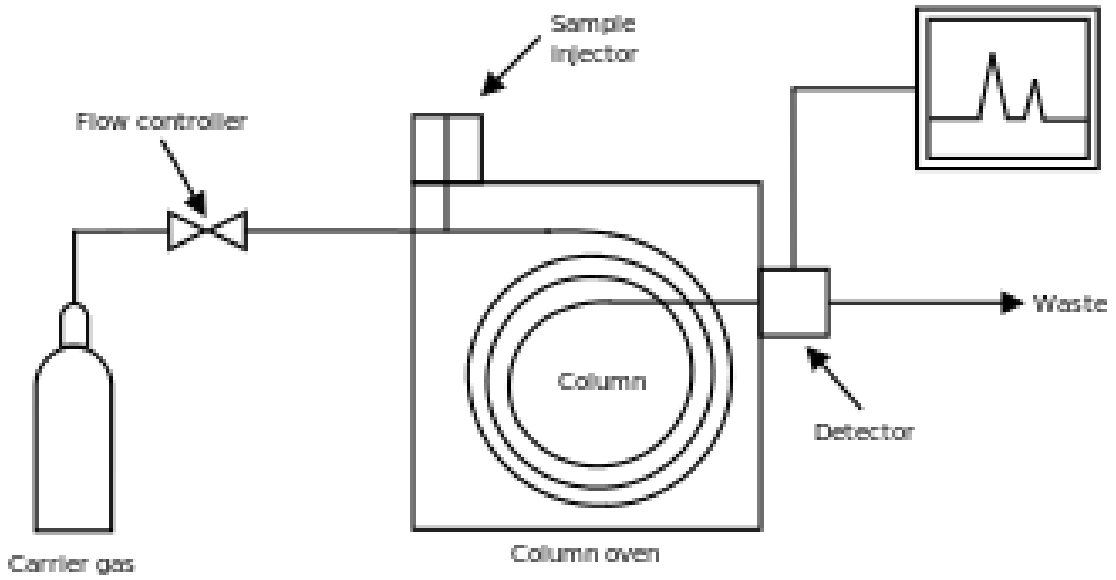
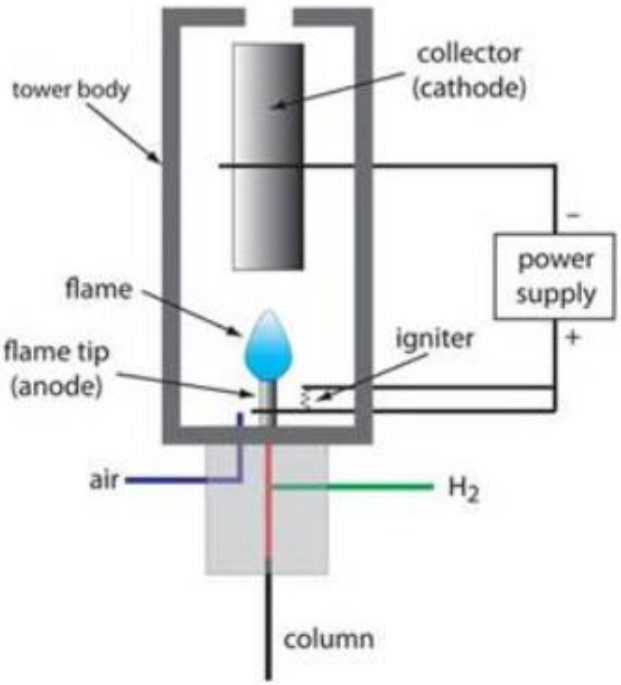
1D Gas Chromatography





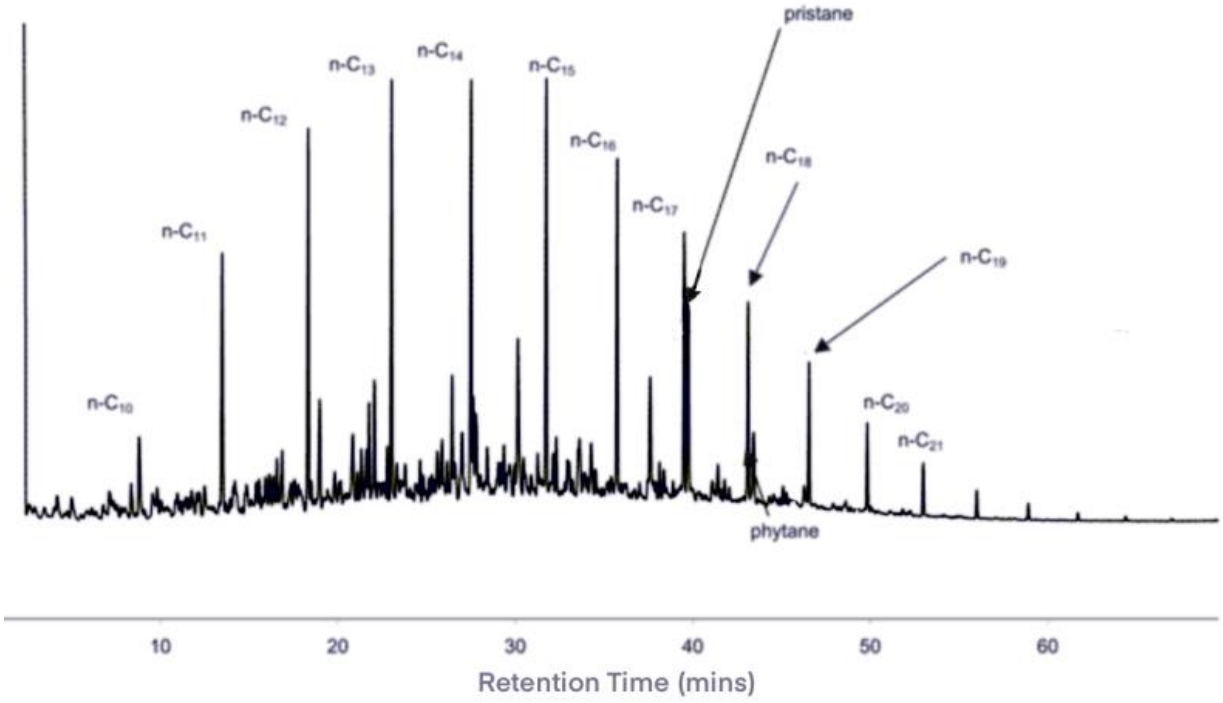
- Oven temperature ramped up in steps
- Detector result is plotted against time

FID - Flame Ionization Detector



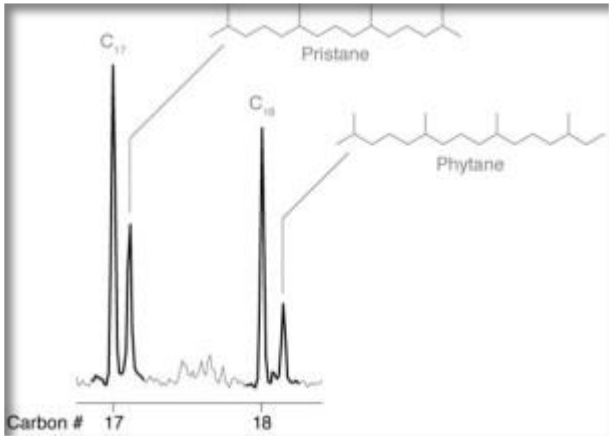
- FID measures concentrations of organic species in a gas stream
  - The flame ionization detector passes sample and carrier gas from the column through a hydrogen-air flame.
  - While the hydrogen-air flame creates a few ions, when an organic compound is burned there is an increase in ions produced.
  - A polarizing voltage attracts these ions to a collector located near the flame.
  - The current produced is proportional to the amount of compound being burned.
  - This current is sensed by an electrometer, converted to digital form, and sent to an output device.

How does a lab identify a diesel



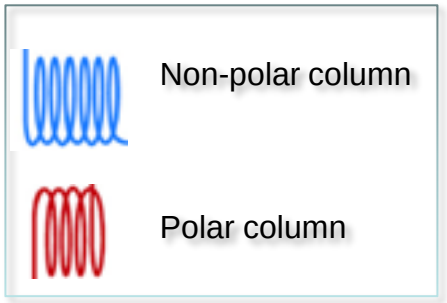
Marker compounds

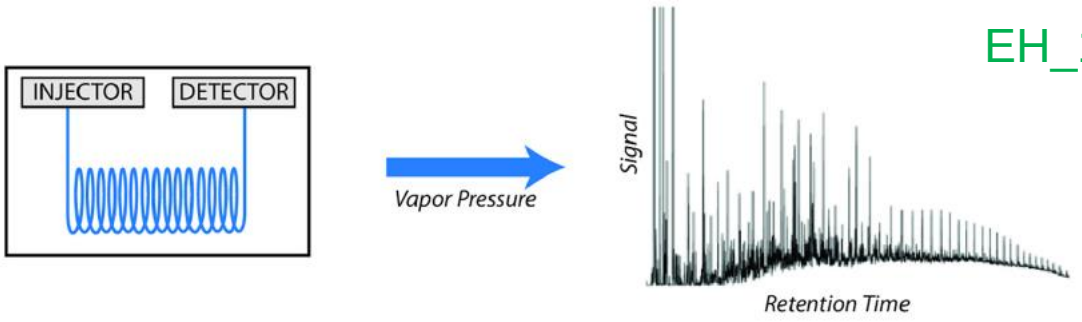
- *C_{-17} / pristane*
- *C_{-18} / phytane*



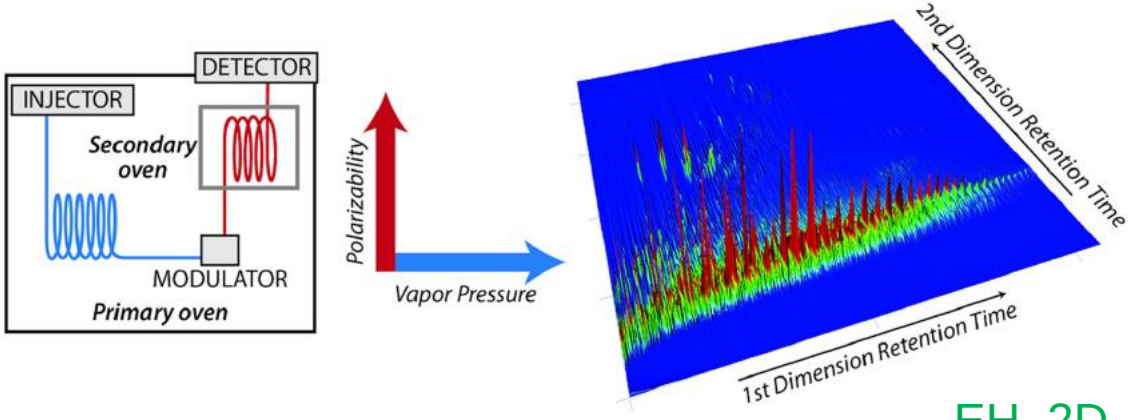
New - GC-GC

- Synonyms: GCxGC; 2D GCFID



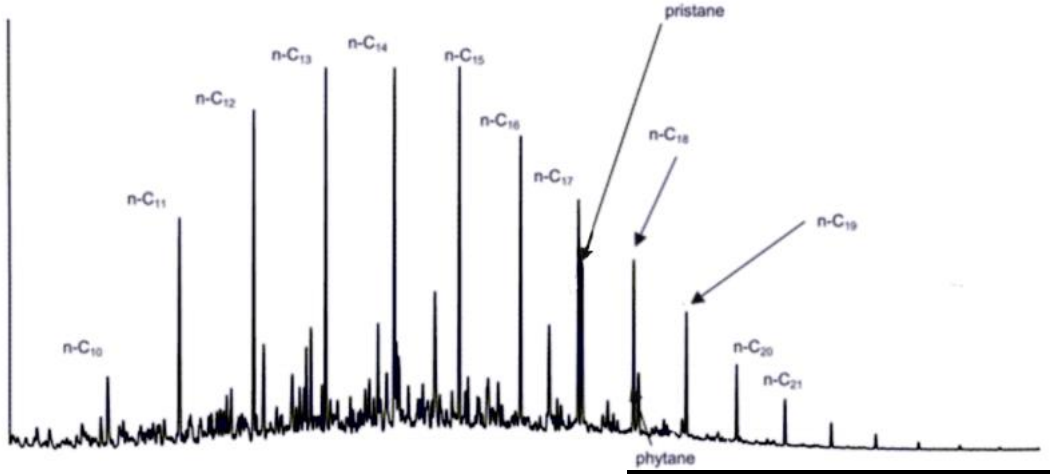


EH_1D_Total

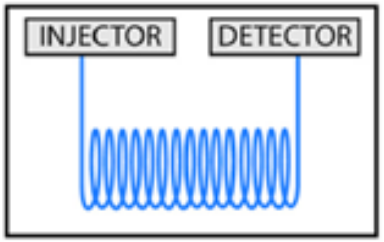


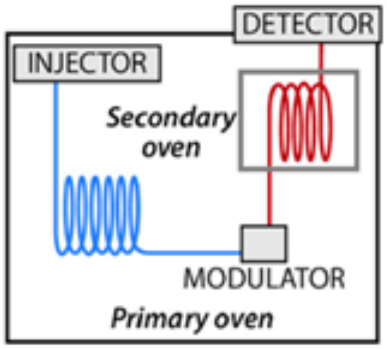
EH_2D_Total

Example: Diesel

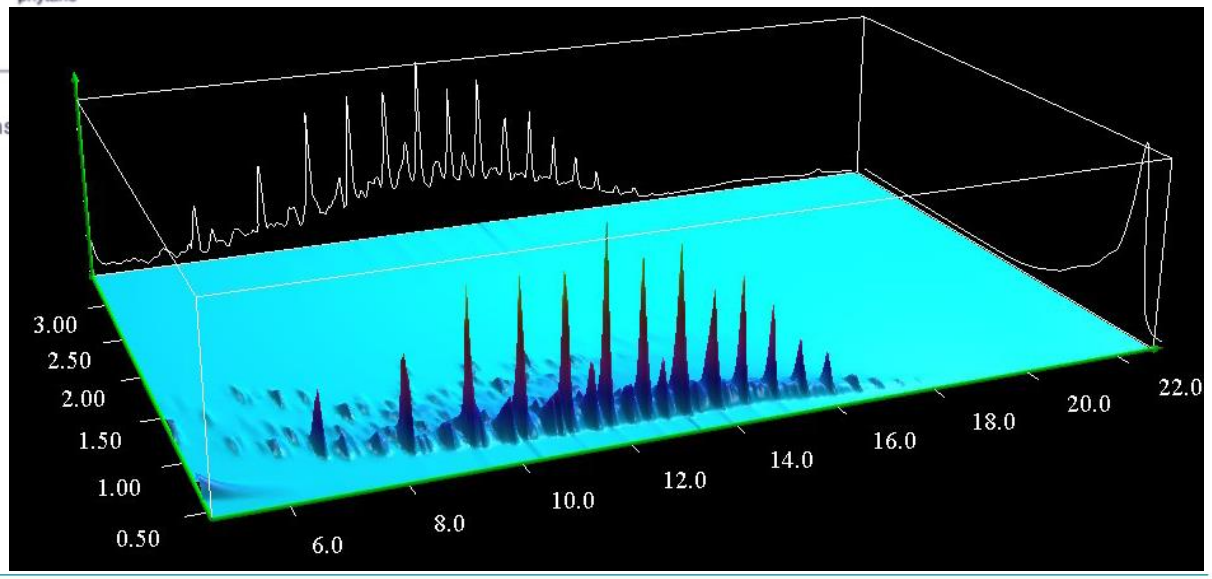


1D GC-FID



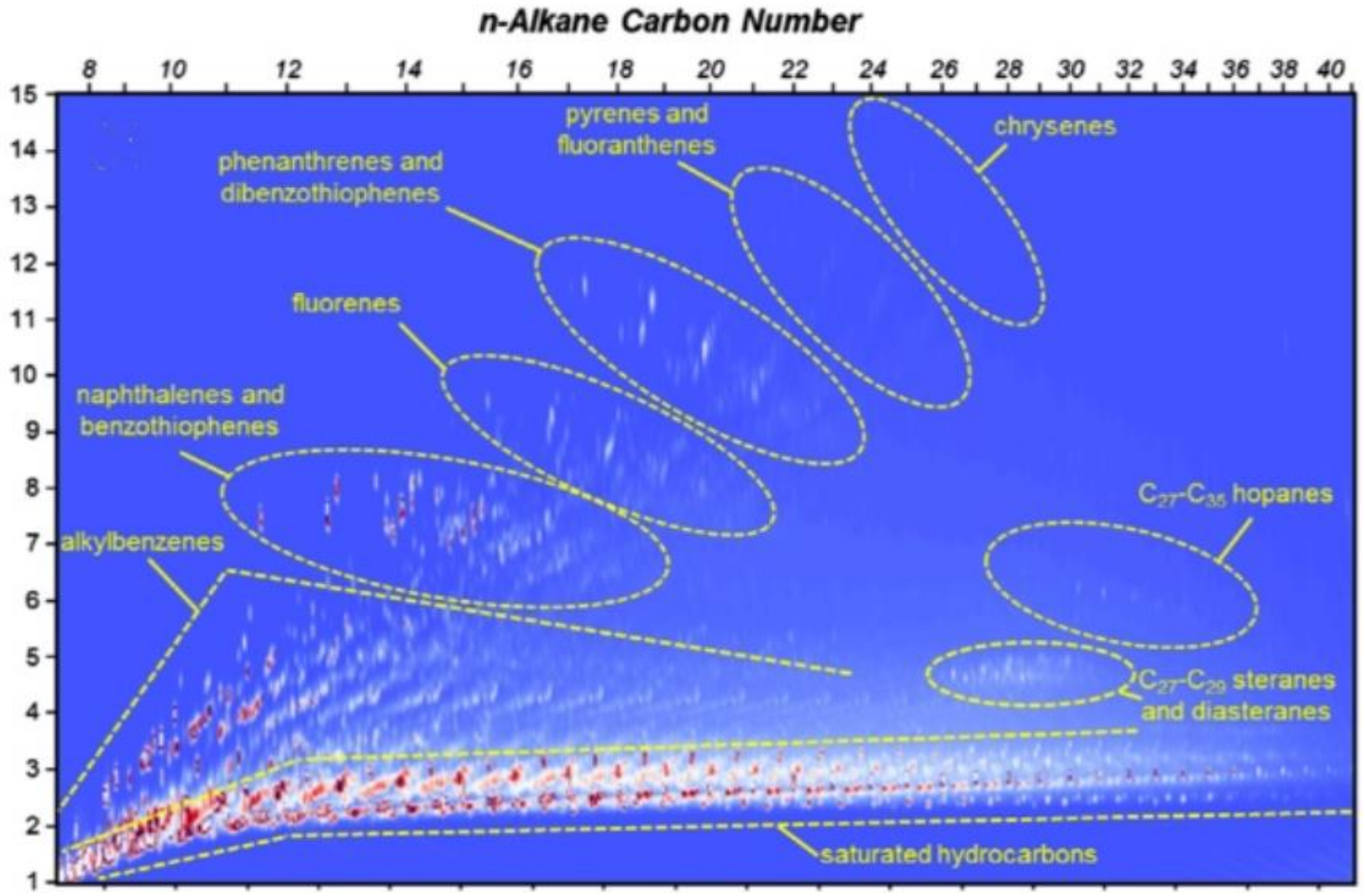


2D GC-FID



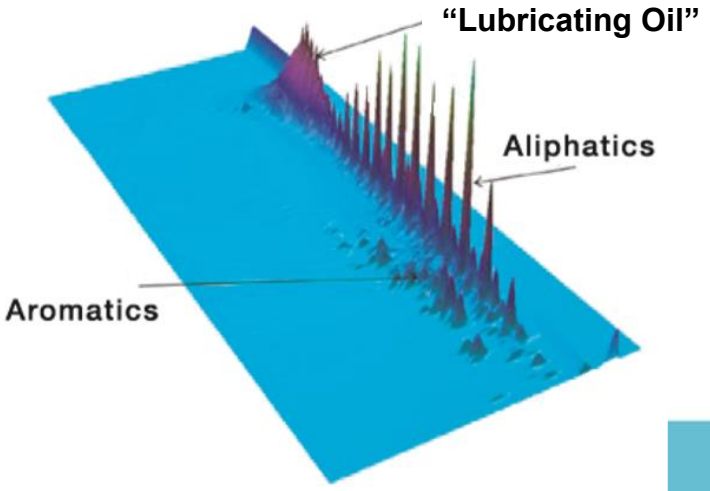
Looking at GC-GC plot in plan view

Aromatics (# rings)
benzene (1)
naphthalene (2)
flourene (3)
phenanthrene (3)
pyrene (4)
fluoranthene (4)
Chrysene (4)



Reddy et al 2011
Gulf oil spill

Calculation of concentrations



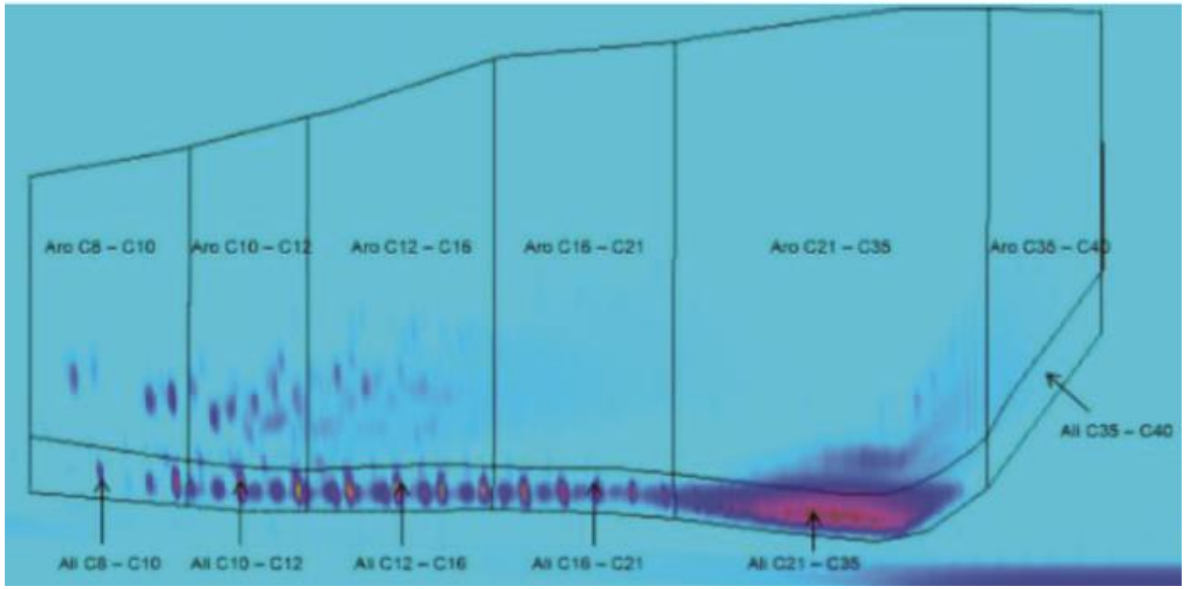
& with HWOL Acronyms:

- Aliphatics C21-C35 etc EH_2D_AL
- Aromatics C21-C35 etc EH_2D_AR

And

- Total C8-C40 EH_2D_Total

- Calculation grids called stencils or positioning grids



Source: agilent.com datasheet 2015

Lab comparisons – "TPH-CWG"

- Preliminary findings (2020)

	Element	ALS	Chemtest	Envirolab
Technology	**GC-FID**	**GCxGC-FID**		
Lab Name	TPH-CWG	TPH CWG GC (S)	TPH Criteria Working Group (soils)	TPH UKCWG
Extraction	hexane/acetone	hexane/acetone	DCM	pentane/acetone
Standards	Mod. EPA 5021 Mod. EPA 8015B	-	-	-
Method Ref.	TM36/PM12 TM5/PM8/PM16	TM089 TM414	2680	A-T-022s A-T-055s
Clean-up	silica gel n-hexane & DCM	Mathematical #1=Estimate of humics	On Request (florisil)	On Request (silica gel)
Band nomenclature	Aliphatics >C5-C44 Aromatics >EC5-EC44	Aliphatics > C5-C44 Aromatics >EC5-EC44	Aliphatic TPH >C5-C44 Aromatic TPH >C5-C44	Ali >C5-C44 Aro >C5-C44
Total: HWOL Acronym Sys.	EH_CU+HS_1D_Total	EH_2D_Total_#1+ HS_1D_Total	EH_2D_Total (EH_CU_2D_Total?)	EH+HS_2D_Total (EH_CU+HS_2D_Total?)

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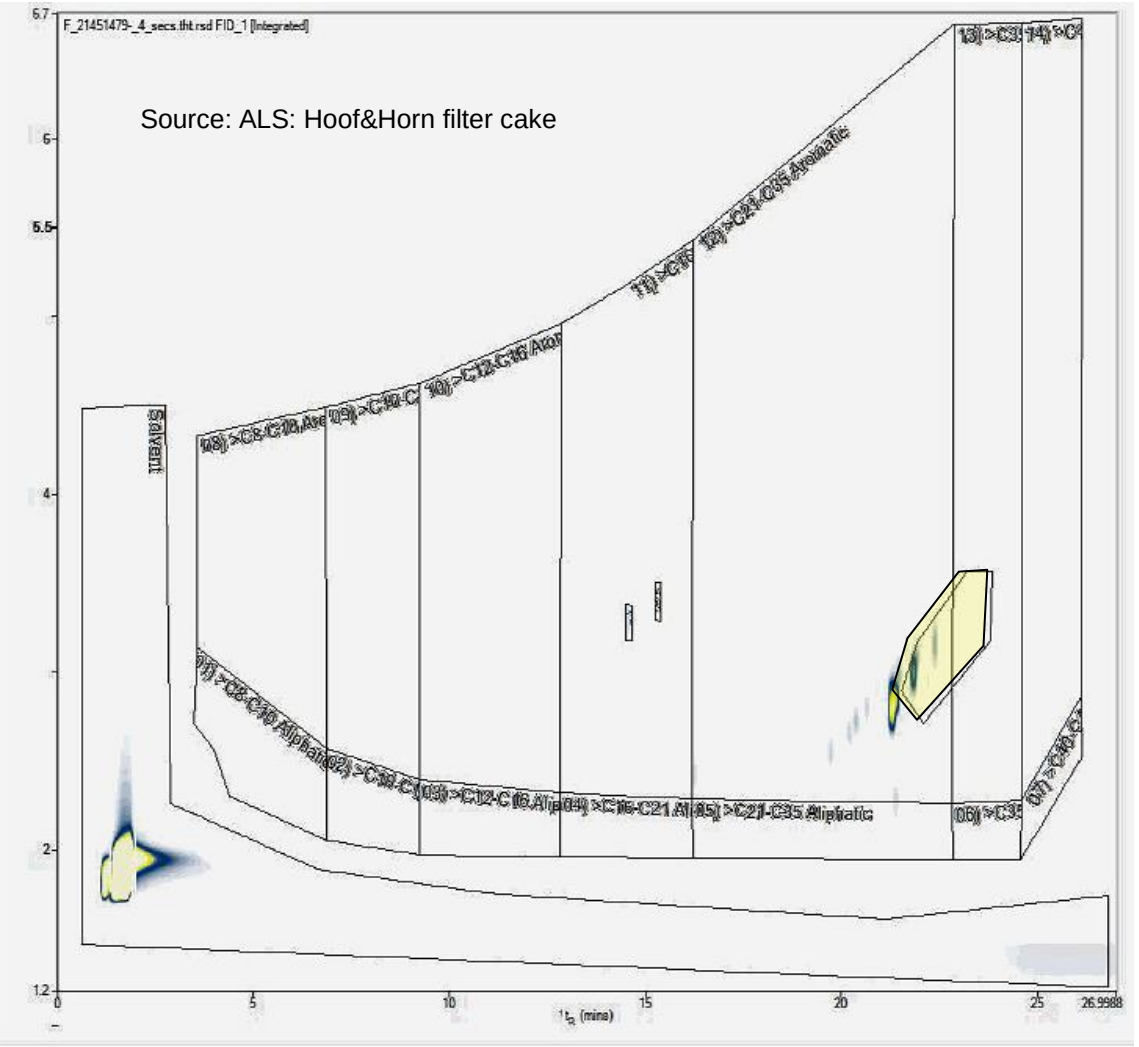
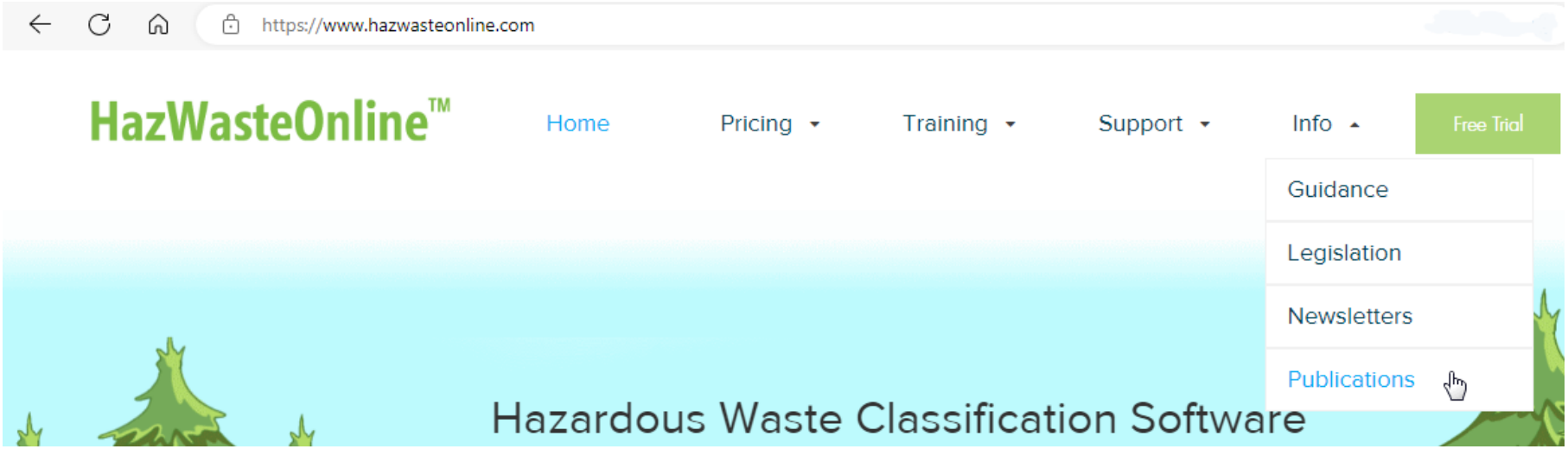
Mathematical clean-up - ALS

- One lab subtracts the humics
  - EH_2D_Total_#1
- But is only attempting to correct for humics
- Other labs can do a chemical clean-up..
- But only if you ask for it



White Paper

www.hazwasteonline.com/wp-content/uploads/2021/04/HWOL-Acronym-System.pdf



Guide to understanding "TPH" tests
using the
The HWOL Acronym System

Next Important Question

Is “TPH” always “TPH”?

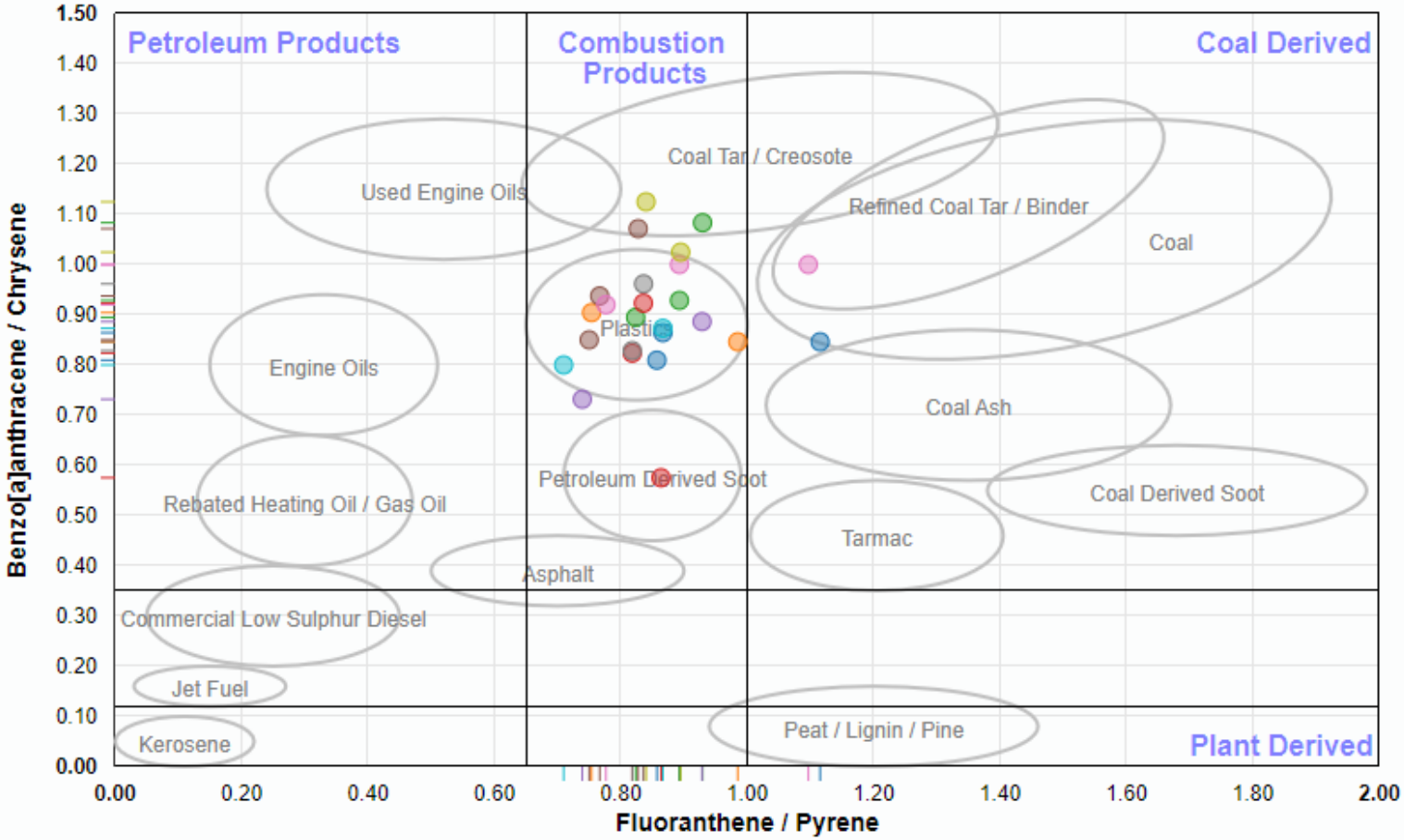
March 3, 2023

Is “TPH” always “TPH” ?

- WM3’s unknown oil is referring to **Petroleum** Hydrocarbons generated from the refining of crude oil
- But a lab’s “TPH” result can include molecules from not just petroleum products but also:
  - Combustion of petroleum derived
  - Coal derived
  - Plant and/or animal derived
- How can we tell? Clues from:
  - Site history e.g. coal gasification, railway yard
  - Observation, smell
  - PAH double plot ratios
  - Lab interpretation & use of chemical marker compounds
  - TPH forensics: TPH-CWG; EPH; SVOC & TICS

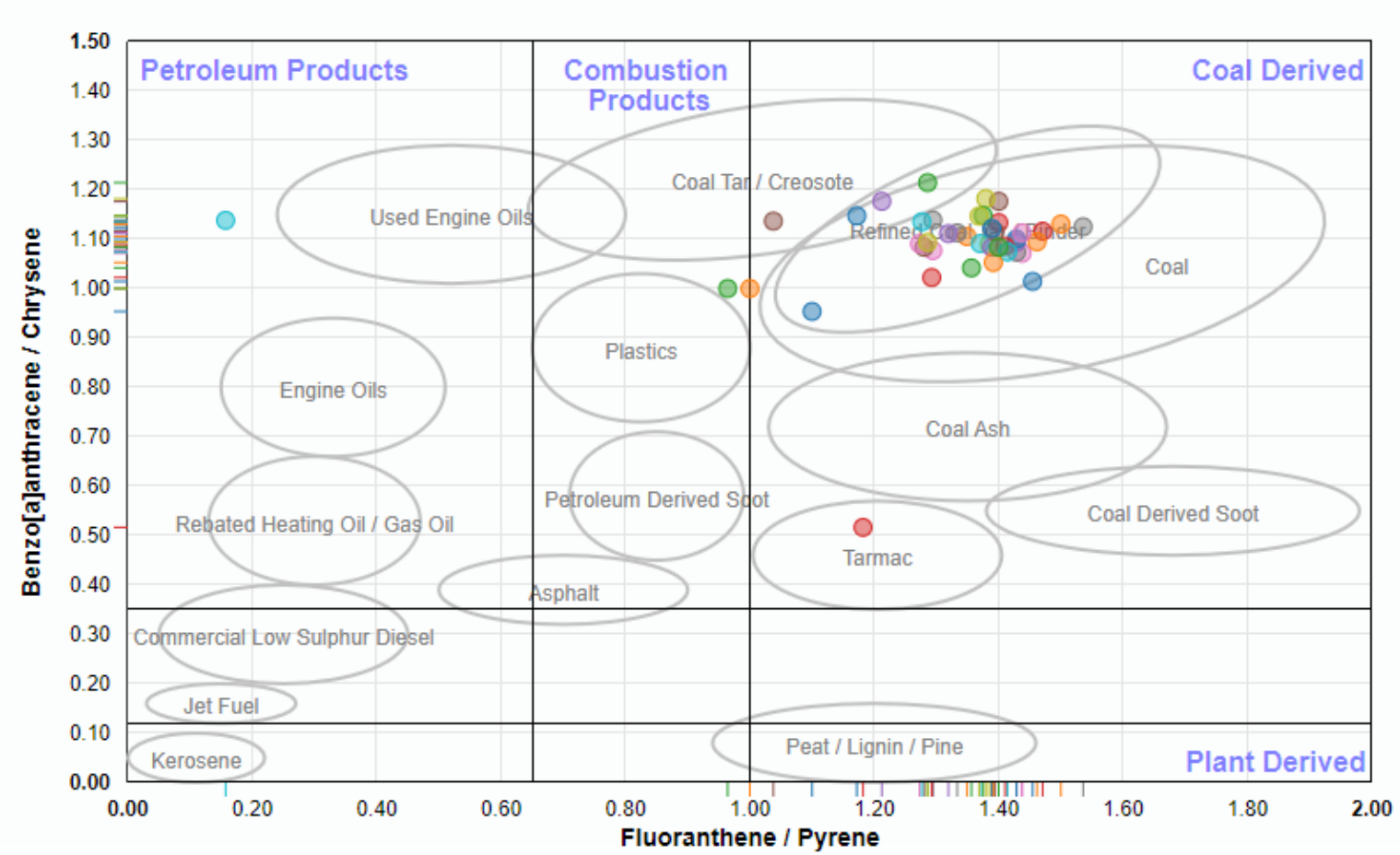
PAH double ratio plots

Cyclone ash from the pyrolysis & incineration of municipal waste



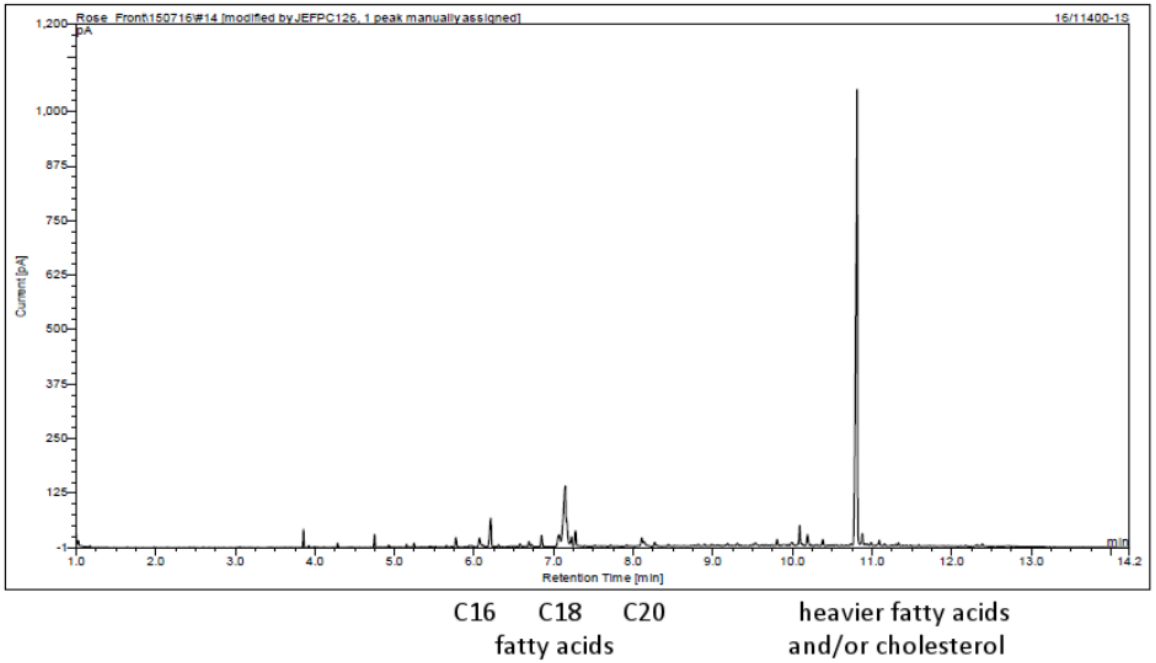
PAH double ratio plots

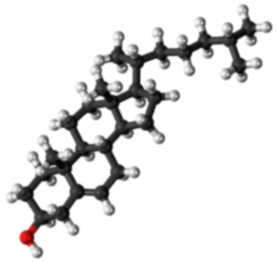
Road paving materials – refined coal tars



Tentatively Identified Compounds (TICS)

- SVOC = only a list of ~250 **pre-defined** organic compounds
- “TPH” = total concentration for all hydrocarbons in a given range
- A chromatogram shows you peaks for many organic compounds
- TICS can tell you which compound each peaks represents:

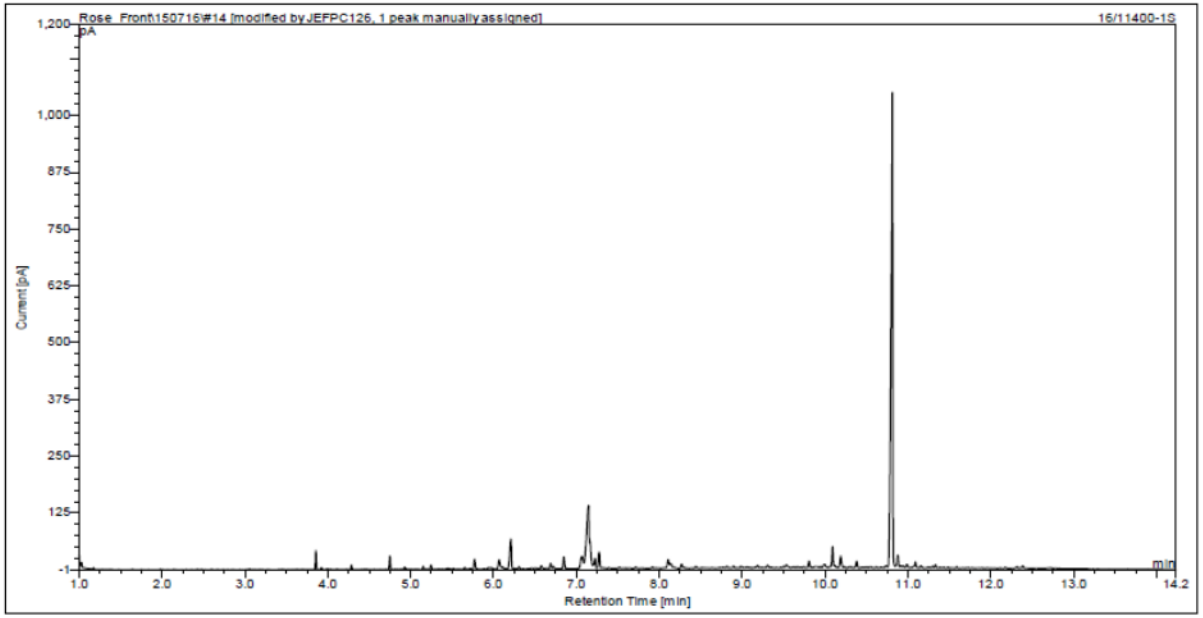




Lab Interpretations depend on “TPH” test

- **EPH** 20,000 mg/kg

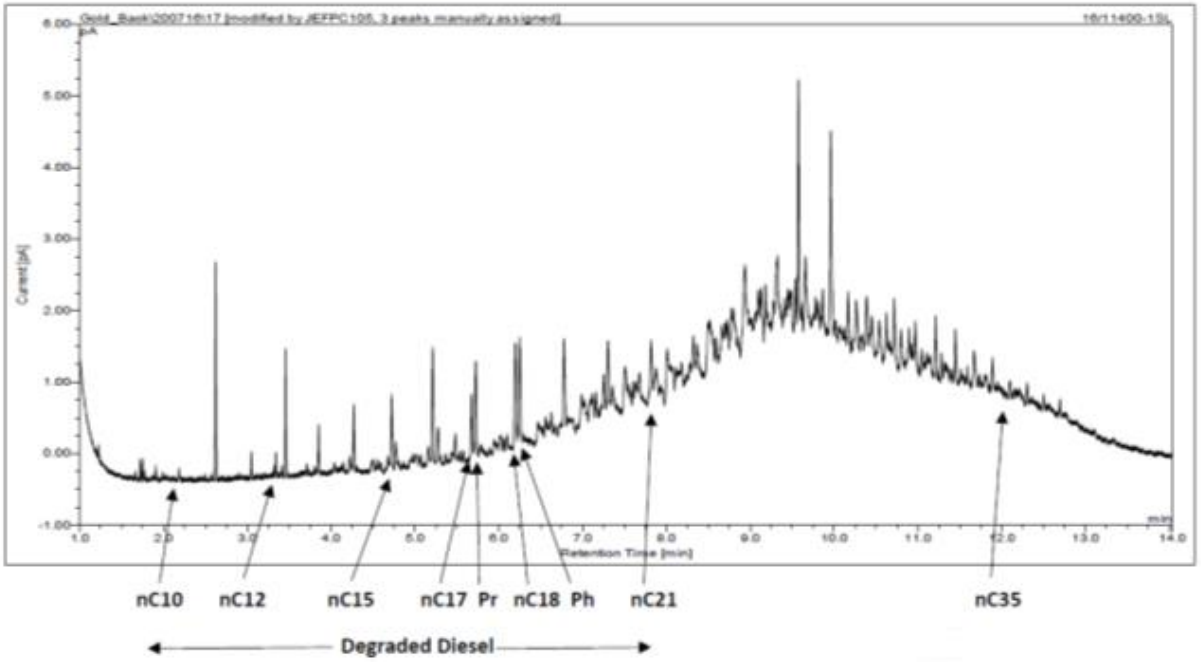
16/11400	1	Filter Cake A	1	Fatty acids and naturally occurring compounds
16/11400	1	Filter Cake B	2	Fatty acids and naturally occurring compounds



Then do the clean-up steps

- **TPH-CWG** – aliphatics 1,000 mg/kg

16/11400	1	Filter Cake A		1	Degraded diesel, lube oil and possible naturally occurring compounds
16/11400	1	Filter Cake B		2	Degraded diesel, lube oil and possible naturally occurring compounds



Misleading chromatogram

Wood dust from waste wood preparation

Petroleum Hydrocarbons

TPH-CWG - Aliphatic >EC5 - EC6 $_{HS\_1D\_AL}$	mg/kg	0.001	MCERTS	< 0.001
TPH-CWG - Aliphatic >EC6 - EC8 $_{HS\_1D\_AL}$	mg/kg	0.001	MCERTS	< 0.001
TPH-CWG - Aliphatic >EC8 - EC10 $_{HS\_1D\_AL}$	mg/kg	0.001	MCERTS	< 0.001
TPH-CWG - Aliphatic >EC10 - EC12 $_{EH\_CU\_1D\_AL}$	mg/kg	1	MCERTS	< 1.0
TPH-CWG - Aliphatic >EC12 - EC16 $_{EH\_CU\_1D\_AL}$	mg/kg	2	MCERTS	< 2.0
TPH-CWG - Aliphatic >EC16 - EC21 $_{EH\_CU\_1D\_AL}$	mg/kg	8	MCERTS	110
TPH-CWG - Aliphatic >EC21 - EC35 $_{EH\_CU\_1D\_AL}$	mg/kg	8	MCERTS	1700
TPH-CWG - Aliphatic > EC35 - EC44 $_{EH\_CU\_1D\_AL}$	mg/kg	8.4	NONE	620
TPH-CWG - Aliphatic (EC5 - EC35) $_{EH\_CU+HS\_1D\_AL}$	mg/kg	10	MCERTS	1800
TPH-CWG - Aliphatic (EC5 - EC44) $_{EH\_CU+HS\_1D\_AL}$	mg/kg	10	NONE	2400

TPH-CWG - Aromatic >EC5 - EC7 $_{HS\_1D\_AR}$	mg/kg	0.001	MCERTS	< 0.001
TPH-CWG - Aromatic >EC7 - EC8 $_{HS\_1D\_AR}$	mg/kg	0.001	MCERTS	0.076
TPH-CWG - Aromatic >EC8 - EC10 $_{HS\_1D\_AR}$	mg/kg	0.001	MCERTS	< 0.001
TPH-CWG - Aromatic >EC10 - EC12 $_{EH\_CU\_1D\_AR}$	mg/kg	1	MCERTS	< 1.0
TPH-CWG - Aromatic >EC12 - EC16 $_{EH\_CU\_1D\_AR}$	mg/kg	2	MCERTS	< 2.0
TPH-CWG - Aromatic >EC16 - EC21 $_{EH\_CU\_1D\_AR}$	mg/kg	10	MCERTS	< 10
TPH-CWG - Aromatic >EC21 - EC35 $_{EH\_CU\_1D\_AR}$	mg/kg	10	MCERTS	< 10
TPH-CWG - Aromatic > EC35 - EC44 $_{EH\_CU\_1D\_AR}$	mg/kg	8.4	NONE	< 8.4
TPH-CWG - Aromatic (EC5 - EC35) $_{EH\_CU+HS\_1D\_AR}$	mg/kg	10	MCERTS	< 10
TPH-CWG - Aromatic (EC5 - EC44) $_{EH\_CU+HS\_1D\_AR}$	mg/kg	10	NONE	< 10

- But lab report only contained one chromatogram
- There should be two chromatograms

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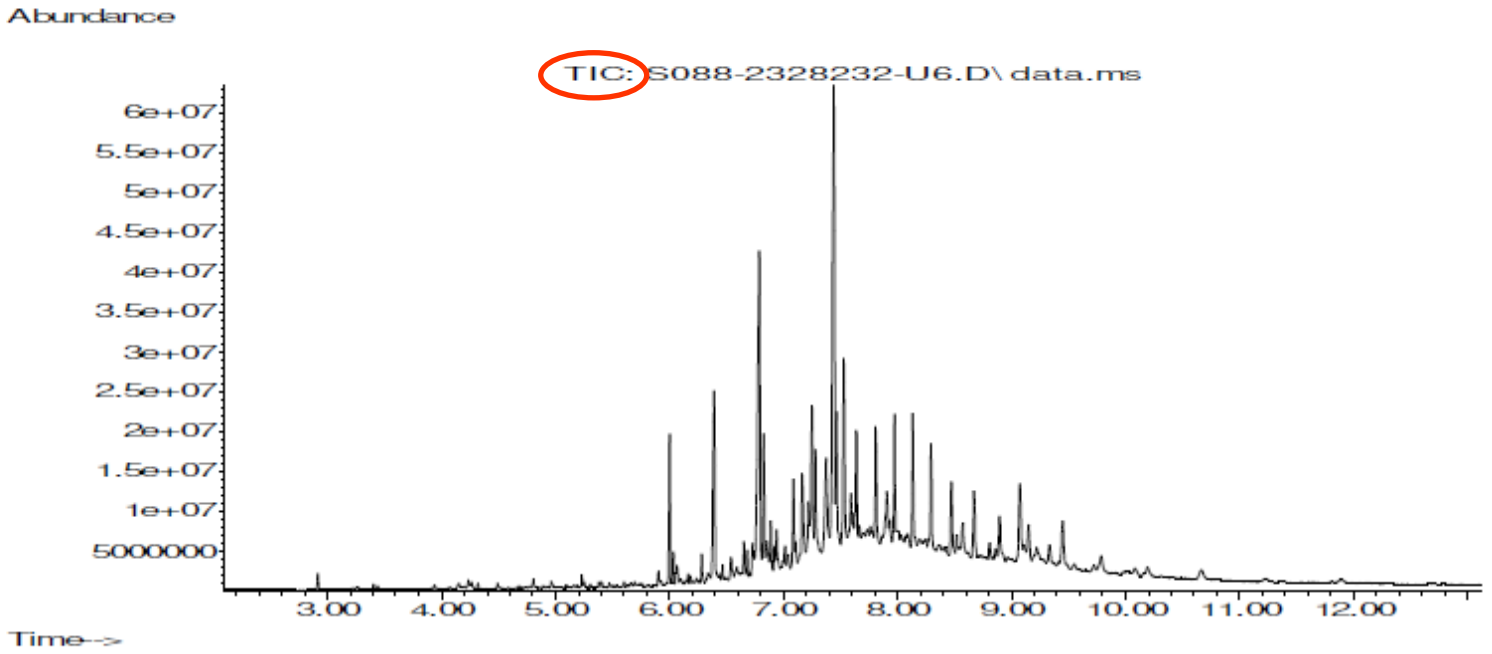
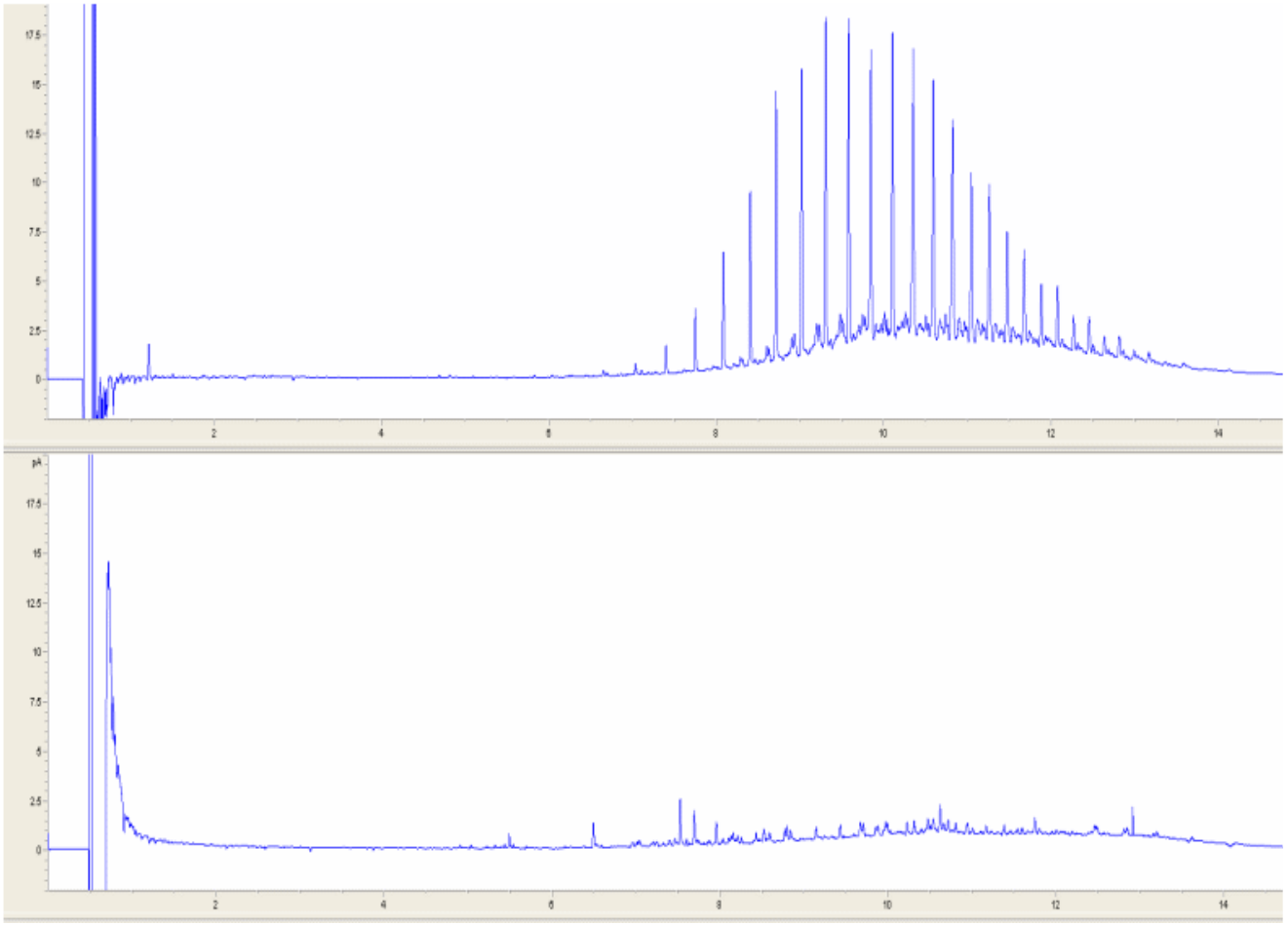
Supplied chromatogram for TPH-CWG?



- Chromatogram was not for TPH-CWG (EH_CU_1D_Total)
- It was “EPH” from the mass spectrometer (EH_1D_MS_Total)
  - Called a Total Ion Count chromatogram

Correct TPH-CWG chromatograms

- Aliphatics
- Aromatics



Using TICS to help understand EH_1D_Total

- Dust extraction system above waste wood processing plant
- > 30 compounds identified on the TIC report including:

CAS no.	Name	Retention time	% Match	Conc. mg/kg	Description
80-56-8	Alpha-Pinene	4.34	97	6.5	Found in oils of many species of coniferous trees, notably pinus sp.
1740-19-8	Dehydroabietic acid	13.05	99	104.2	Occurs widely in trees, primary irritant in pine wood, main components of pine resin
514-10-3	Abietic acid	13.31	99	31.9	
121-33-5	Vanillin	7.95	96	4.3	Found in plants; (& extract from vanilla bean)
458-36-6	2-propanol-1-chloro phosphate	9.85	95	29.08	Flame retardant used in polyurethane, foam, PVC, and epoxy resin
112-95-8	Eicosane	15.37	98	72.85	C20 alkane, a wax
57-11-4	Octadecanoic acid	11.79	99	14.09	C18 fatty acid

Putting it all together - TPH Forensics

- Glass Recycling – Filter cake
- Lab's TPH interpretation:
  - EPH chromatogram typical of waxes/fatty acids
  - Lab states that no diesel or gasoline is in the FC
- TICs identified fatty acids including
  - hexadecanoic acid (C16 fatty acid)
  - oleic acid (C18 fatty acid)
  - octadecanoic acid (C18 fatty acid)
- Also found
  - caffeine, ibuprofen, cholesterol

Example of a clean up

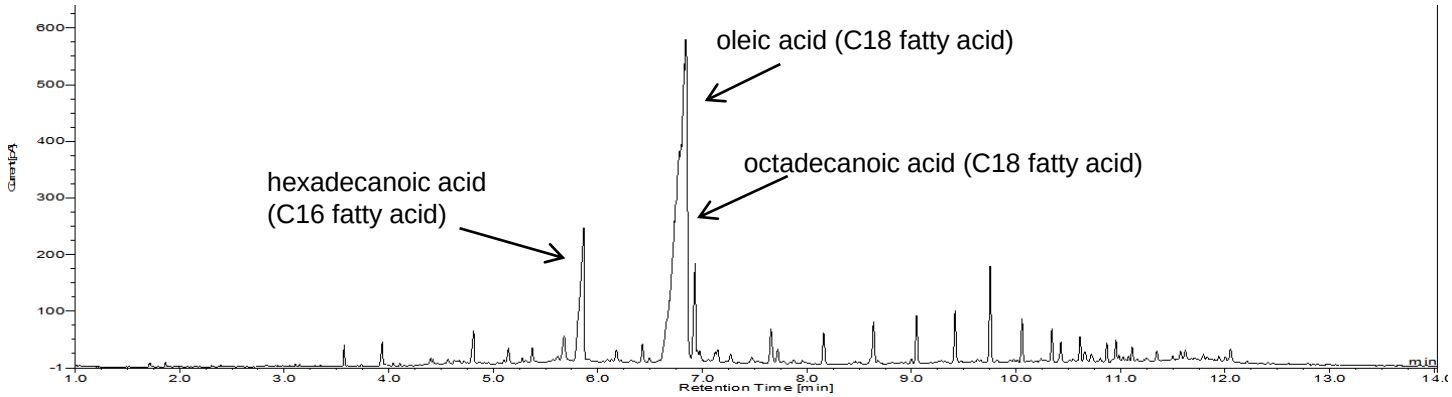
Filter cake from glass recycling

EPH

20,000 mg/kg

(i.e. everything)

EH_1D_Total



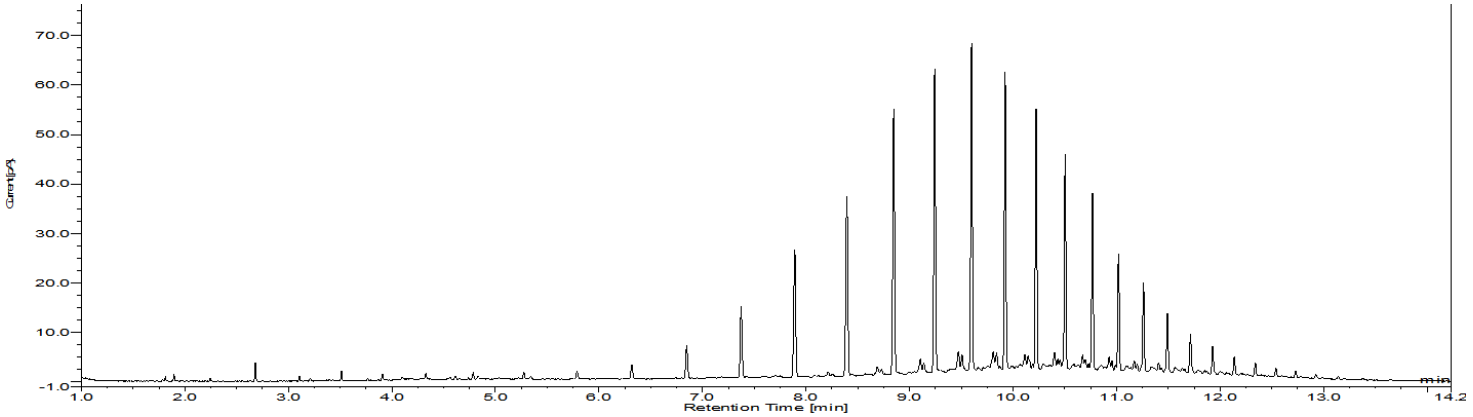
TPH-CWG

5,000 mg/kg

Aliphatics

EH_CU_1D_AL

(dominated by waxes)



Summary

- You need to understand;
  - the basics about both hydrocarbons and Gas Chromatography

and

  - what type of “TPH” test or tests the lab has actually completed.

- So, make sure you tell your lab that you want the HWOL acronyms on all your reports;
  - whether for phase II, WAC or waste classification assessments,
  - and ask for the chromatograms.

- Make sure you know when your lab is giving you GC-GC and if so whether there is / you need a clean-up step.

- Consider purchasing more than 1 test: “EPH”, cleaned-up “EPH” (or TPH-CWG) and TICS for more complicated/forensic problems.

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Is “TPH” always “TPH”

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