

Guide to understanding “TPH” tests using the The HWOL Acronym System

| Acronym | Description |
|--------------|--|
| HS | Headspace analysis |
| EH | Extractable hydrocarbons - i.e. everything extracted by the solvent(s) |
| CU | Clean-up - e.g. by florisil, silica gel |
| 1D | GC - Single coil gas chromatography |
| Total | Aliphatics & Aromatics |
| AL | Aliphatics only |
| AR | Aromatics only |
| 2D | GC-GC - Double coil gas chromatography |
| #1 | EH_2D_Total but with humics mathematically subtracted |
| #2 | EH_2D_Total but with fatty acids mathematically subtracted |
| + | Operator to indicate cumulative e.g. EH_CU+HS_1D_Total |
| MS | Mass Spectrometry |

Table 1. The HWOL Acronym System

This guide was compiled by HazWasteOnline™ (www.hazwasteonline.com) to help stakeholders better understand the various hydrocarbon tests offered by soil testing laboratories in the UK and Ireland in order to help improve hazardous waste classification practice and understanding.

Understanding a laboratory’s hydrocarbon test suites is critical for both waste classification and other users of “TPH” data. This understanding is made more difficult because;

- a) the laboratories use the same terminology (TPH, Total TPH, TPH1, EPH, DRO, mineral oil etc.) to mean different things, and
- b) workers see the “P” in “TPH” and just think petroleum hydrocarbons, ignoring other sources of (non-petroleum) hydrocarbons such as those from peat, coal, ash, humics present in soils and fatty acids found in cells and industrial processes.

Much of this complexity is not actually appreciated by workers as most only order one “TPH” test from their favourite laboratory at any given time. However, when you start ordering more than one type of “TPH” test from the same laboratory (examples in Table 3 & 4) or comparing reports from different labs, the inconsistencies appear and confusion increases.

For both hazardous waste classification and the inert WAC assessment (and no doubt contaminated land assessments), ordering the correct “TPH” test can make the difference between a hazardous or non-hazardous outcome and, if the non-hazardous waste is going to landfill, passing or failing the inert WAC.

This document acts as a guide to the HWOL Acronym System and also to the basic components of hydrocarbon characterisation using gas chromatography.

The HWOL Acronym System

The HWOL Acronym System (Table 1) is a set of two letter acronyms that when combined together in a text string, allows the users of laboratory reports to better understand what type of hydrocarbon testing was actually undertaken on their sample.

Some examples of their application are demonstrated in Table 2.

| Example terms (Various Labs) | HWOL Acronyms | Explanation |
|------------------------------------|-------------------|---|
| GRO >C5-C10 | HS_1D_Total | Analysis of the headspace volatiles, by GC-FID, Aliphatic and Aromatic fractions |
| EPH (C10-C40) | EH_1D_Total | Analysis of everything extracted, by GC-FID, Aliphatic and Aromatic fractions |
| TPH (C10-C40) | EH_1D_Total | Analysis of everything extracted, by GC-FID, Aliphatic and Aromatic fractions |
| EPH (C10-C40) with clean-up | EH_CU_1D_Total | Analysis of everything extracted, followed by a chemical clean-up step, by GC-FID, Aliphatic and Aromatic fractions |
| Mineral Oil | EH_1D_Total | Analysis of everything extracted, by GC-FID, Aliphatic and Aromatic fractions |
| Mineral Oil | EH_CU_1D_AL | Analysis of everything extracted, followed by a chemical clean-up step, by GC-FID, Aliphatic fraction only |
| TPH-CWG (C5-C35) | EH_CU+HS_1D_Total | Analysis of everything extracted, followed by a chemical clean-up, plus the HS results, by GC-FID, Aliphatic and Aromatic fractions |

| | | |
|---------------------|----------------|---|
| TPH-CWG (C5-C35) | EH_2D_Total | Analysis of everything extracted, GC-GC, Aliphatic and Aromatic fractions |
| TPH-CWG (C5-C40) | EH_2D_Total_#1 | Analysis of everything extracted, GC-GC, Aliphatic and Aromatic fractions with estimate of contribution from the humics mathematically subtracted |
| Aliphatics: >C8-C10 | EH_CU_1D_AL | Analysis of everything extracted, followed by a chemical clean-up step, by GC-FID, Aliphatic fraction only |
| Aromatics: >C5_C8 | HS_MS_1D_AR | Analysis of the headspace volatiles, by GC-FID, Aromatic fraction only |

Table 2. Examples of acronyms usage for a selection of typical laboratory names.

Note that the HWOL acronyms do not define the carbons bands, extraction solvents or chemical clean-up methods. These details should be present in each laboratory’s PDF report and method statements.

Background

The challenge when assessing “TPH” results is to understand what the laboratory has actually reported. Whilst every laboratory will typically state the carbon bands that their test covers, they do not always make it clear whether the results are measurements of;

- a) all the hydrocarbons extracted from the sample,
- b) just the “cleaned-up” or “scrubbed” results i.e. a subset of a), and
- c) just the aliphatic fraction, just the aromatic fraction or the total of both the aromatics and aliphatics fractions, in a) or b).

The **HWOL Acronym System** was devised by One Touch Data to make a laboratory’s “TPH” results more transparent and easier to understand. All the laboratories certified to publish HazWasteOnline’s .hwol data files are also required to include the HWOL Acronym System, both in their .hwol data files and more critically in their formal PDF laboratory reports. This means that even if you receive a PDF report from a third party (i.e. you don’t have a contractual relationship to the laboratory so can’t ask questions about that data set), you will still be able to understand the type of hydrocarbon testing that was actually undertaken. With this information, you will be better able to assess whether the results are fit for purpose or more suitable testing needs to be done.

Table 3 demonstrates the use of the HWOL acronyms in a laboratory report.

| | | | |
|--|---------|--------|------|
| 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 |

Table 3. Example of a laboratory report that presents three different “TPH” tests and shows how the HWOL Acronym System allow the reader to differentiate between them.

| 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 |

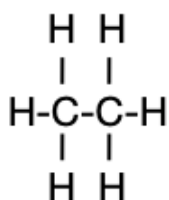
Table 4. For the same sample, the WAC results. These demonstrate that this laboratory’s mineral oil test actually measures everything extracted from the sample, i.e. EH_1D_Total and not just the petroleum hydrocarbons.

Explanation of Terminology

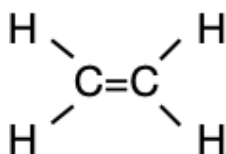
Hydrocarbons

In organic chemistry, hydrocarbons (compounds composed primarily of carbon and hydrogen) are divided into two classes: the aliphatic compounds and the aromatic compounds.

Aliphatics compounds comprise one or more carbon atoms arranged in chains, branched chains or in rings (cyclic). They can be saturated which means that every carbon has four other elements attached to it by a single bond (alkanes), or unsaturated, with one or more double bonds (alkenes) or triple bonds (alkynes). The least complex aliphatic compound is methane CH_4 .



Alkane

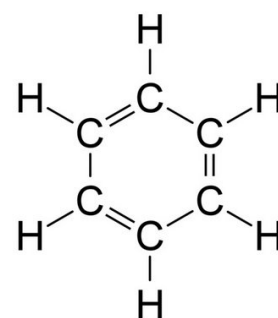


Alkene



Alkyne

Aromatics compounds are cyclic structures that contain a benzene ring as part of the structure; benzene (C_6H_6) being the simplest aromatic compound. The reason that this group differs from the aliphatics is that the bonds in the benzene ring are not true double bonds, like those in the alkenes; instead the electrons are shared across all the carbons in the ring, an arrangement called conjugation. Other examples of aromatic molecules include the rest of the BTEX (toluene, ethyl benzene, xylene), the phenols and all the poly aromatic hydrocarbons (PAHs) Besides hydrogen, other elements can also be bound to the carbon chain, the most common being oxygen, nitrogen, sulfur and chlorine.



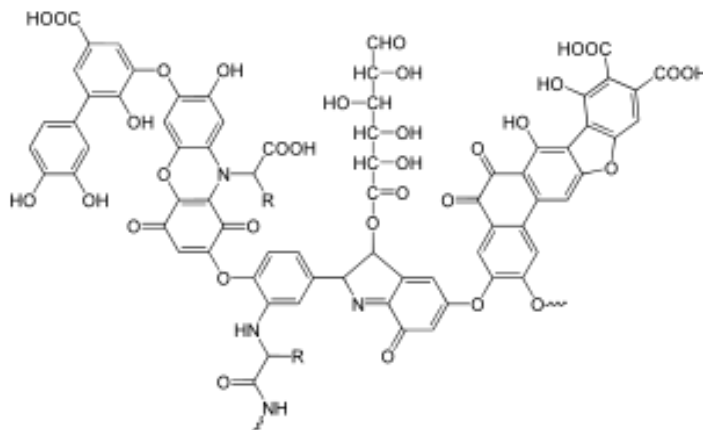
Petroleum Hydrocarbons

This term refers to the hydrocarbons that are found in crude oil and in particular those hydrocarbons produced from the refining of crude oil to make the fuels, lubricants and feedstocks used in machines and chemical processes. The term does not apply to hydrocarbons from other sources such as those originating from peat, rotting leaves, coals, coal tar, solvents, fatty acids present in surfactants or the naturally occurring humics found in soils.

For hazardous waste classification, the technical guidance WM3 provides a set of hazard statements for use when classifying an unknown oil (or a mixture of two or more oils), over the range C6 to C40. This is enacted in HazWasteOnline™ by the determinand: "TPH (C6-C40) petroleum group". Whilst this determinand can be used for other sources of hydrocarbons, it would be considered a worst case approach.

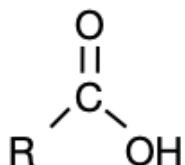
Humics

Humic substances (humic acids, fulvic acids and humin) are important components of the organic fraction of soils, sediments, peat and coal. Humic substances are produced by the biodegradation of tissues from dead plant and animal matter.



Fatty Acids

Fatty acids are long chained aliphatic molecules (R) that contain one or more carboxyl groups (-COOH). Fatty acids are important structural components in cells (triglycerides, phospholipids, cholesterol). Industrial uses include the production of soap and as precursors to surfactants, detergents and lubricants.



Laboratory Analysis using Gas Chromatography (GC)

Hydrocarbons can be analysed in a multitude of ways. This article outlines the analysis by a method called gas chromatography which is a laboratory technique for separating all the different hydrocarbon compounds present in a mixture into a series of peaks that can be displayed in a graph called a chromatogram. At its simplest, each peak represents a different compound, with the size of the peak indicating its concentration.

Solvent Extraction

When a laboratory receives a sample, the first step is to extract the hydrocarbons from the sample. To do this, a solvent is added and by various mechanical and thermal means, the hydrocarbons are extracted from the sample. Typical solvents include hexane, acetone, pentane, dichloromethane (DCM) or a combination thereof. At this point, this extract can then be volatilised and injected into a GC for analysis.

Chemical Clean-up

The solvent extract often contains non-petroleum hydrocarbons that were present in the original sample (see above). These are molecules containing elements other than hydrogen such as oxygen. A clean-up step can be used to remove these non-petroleum hydrocarbons from the extract. The main clean-up agents used by the soil laboratories are Florisil and silica gel. Following the clean-up step, the resulting fraction can also be volatilised and injected into a GC for analysis.

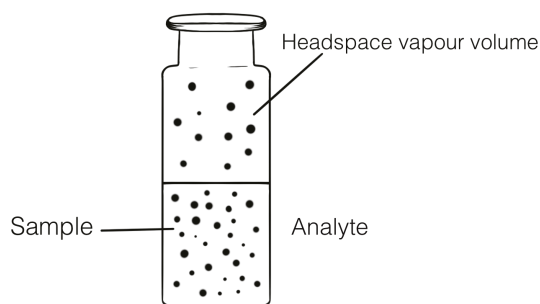
TPH-CWG Protocol

The TPH-CWG protocol (**EH_CU+HS_1D_Total**) is a particular instance of the clean-up step where the solvent extract is cleaned-up twice, once to estimate the aliphatics and a second time to estimate the aromatics. TPH-CWG is the standard test required for human health risk assessments and the hydrocarbons are presented in defined aliphatic and aromatic bands, typically between >C5 and C35.

Where the waste classifier uses TPH-CWG data, they will need to sum all the concentrations of both the aromatic and aliphatic bands between C6 and C40. In the cases where the results only run to C35, the classifier will need to obtain the missing results from C36 to C40.

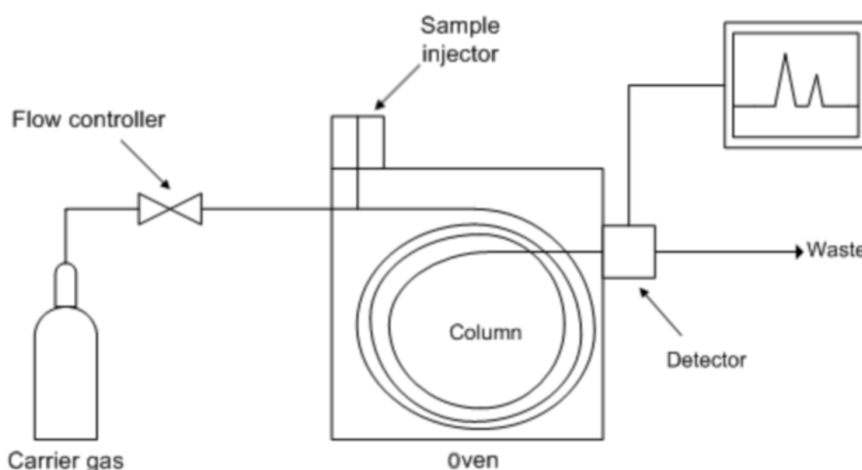
Headspace Analysis

Headspace analysis can be loosely defined as the analysis of volatile compounds associated with liquids or solids without direct sampling of the matrix. The actual headspace is the volume of vapour or gas above the sample. Once equilibrium has been reached, an aliquot of the headspace is withdrawn and injected into a GC for analysis. Headspace analysis generally covers the range >C5 to C10, which includes the BTEX, with the results often referred to as the gasoline range organics (GRO).



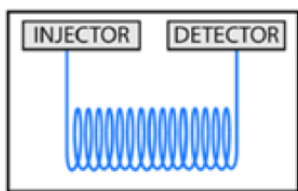
Gas Chromatography

Gas chromatography is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be vaporised without decomposition. Effectively it comprises an oven with a column inside through which flows a carrier gas. The volatiles are injected into the column and the smaller and more volatile compounds (i.e, lower carbon numbers) exit the column before the larger compounds. The detector is either a Flame Ionisation Detector (FID), which creates the classic chromatogram, or a Mass Spectrometer (MS), which effectively looks at identifying the compound that generates a given peak within the equivalent chromatogram.

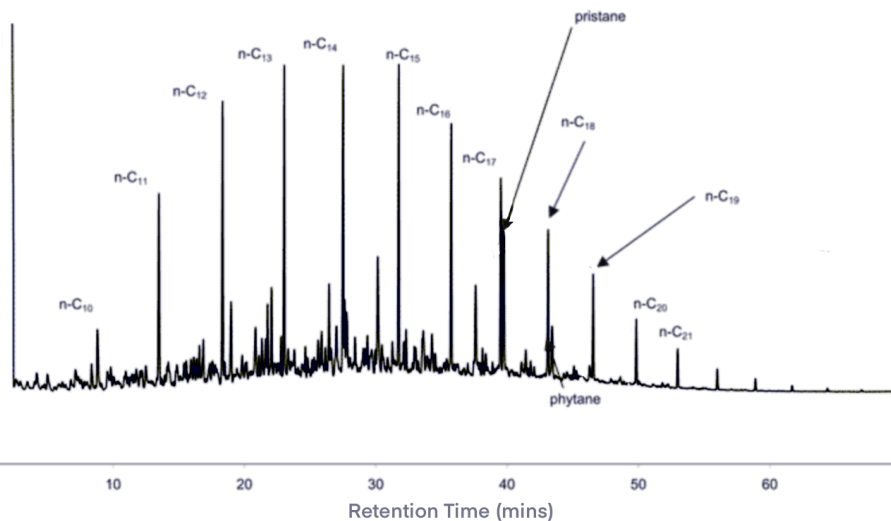


1D Gas Chromatography

Where a single column is used, this is referred to as 1D gas chromatography. A volatilised sample is injected into a single (non-polar) column. Generally, the smaller compounds travel through the column more quickly than the bigger compounds. The output or effluent from the column is passed into a detector, either a Flame Ionisation Detector (FID), to create a chromatogram, or a Mass Spectrometer (MS) to physically identify individual compounds.



Vapor Pressure

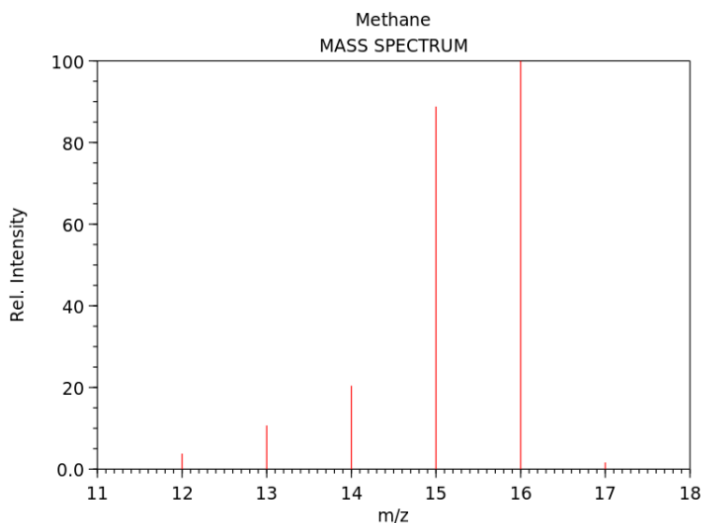


The X axis on the chromatogram is labeled retention time and reflects the number of minutes it took for a particular compound (or group of compounds) to travel through the GC.

Detectors

FID: The flame ionisation detector effectively burns the effluent from the column and measures the current produced by changes in ion concentrations. Each peak in the chromatogram represents the intensity of a particular compound (or compounds, if two or more compounds elute at the same time).

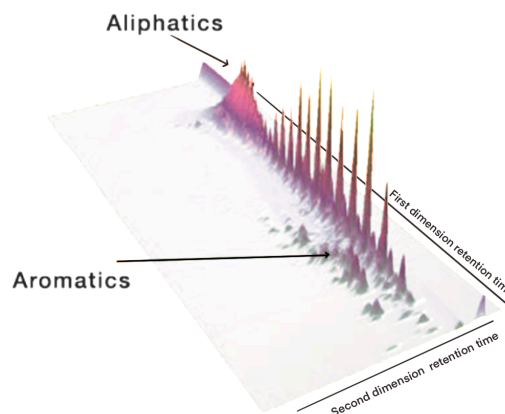
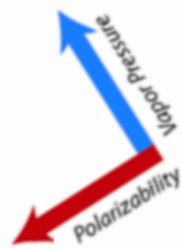
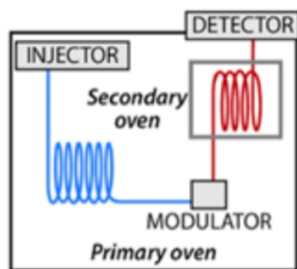
MS: A mass spectrometer is used to effectively analyse the compound that creates a particular peak in a chromatogram. The chosen compound is fed into an ionisation chamber, broken into its ions and these are accelerated through a magnetic field and focussed on a detector. The way a particular compound breaks up into its ions (right) can be compared with a library to identify the compound.



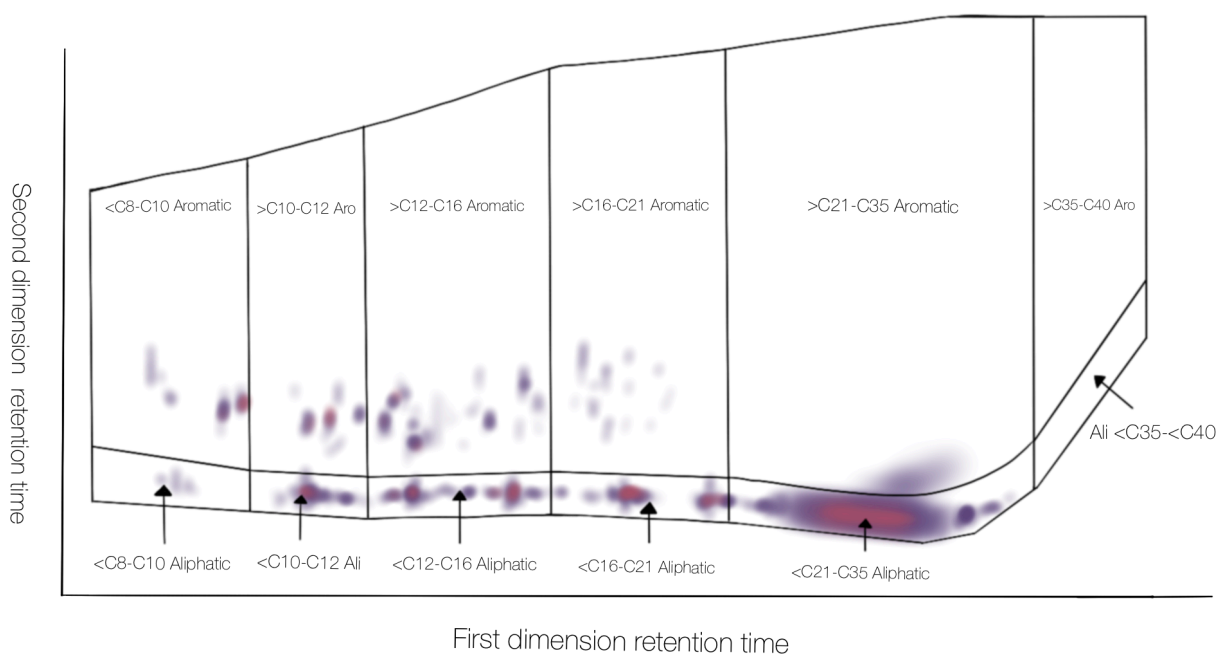
NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

2D Gas Chromatography

2D gas chromatography or GC-GC utilises two columns. Typically, the volatilised sample is first injected into the conventional non-polar column. At the end of the first column is a modulator, effectively a doorway that opens every few seconds to allow whatever compounds have reached the doorway to be captured and injected into the second column. This second column is polarised so compounds with a greater affinity for the stationary phase in the column (i.e. the column's coating) reach the FID at the end of the column more slowly than those compounds that have a greater affinity for the mobile phase (i.e. the carrier gas).



The 3D plots shown above can be also viewed in plan view (below). Calculation grids or positioning standards are used to mathematically calculate the concentrations of the carbon fractions in the various bands.

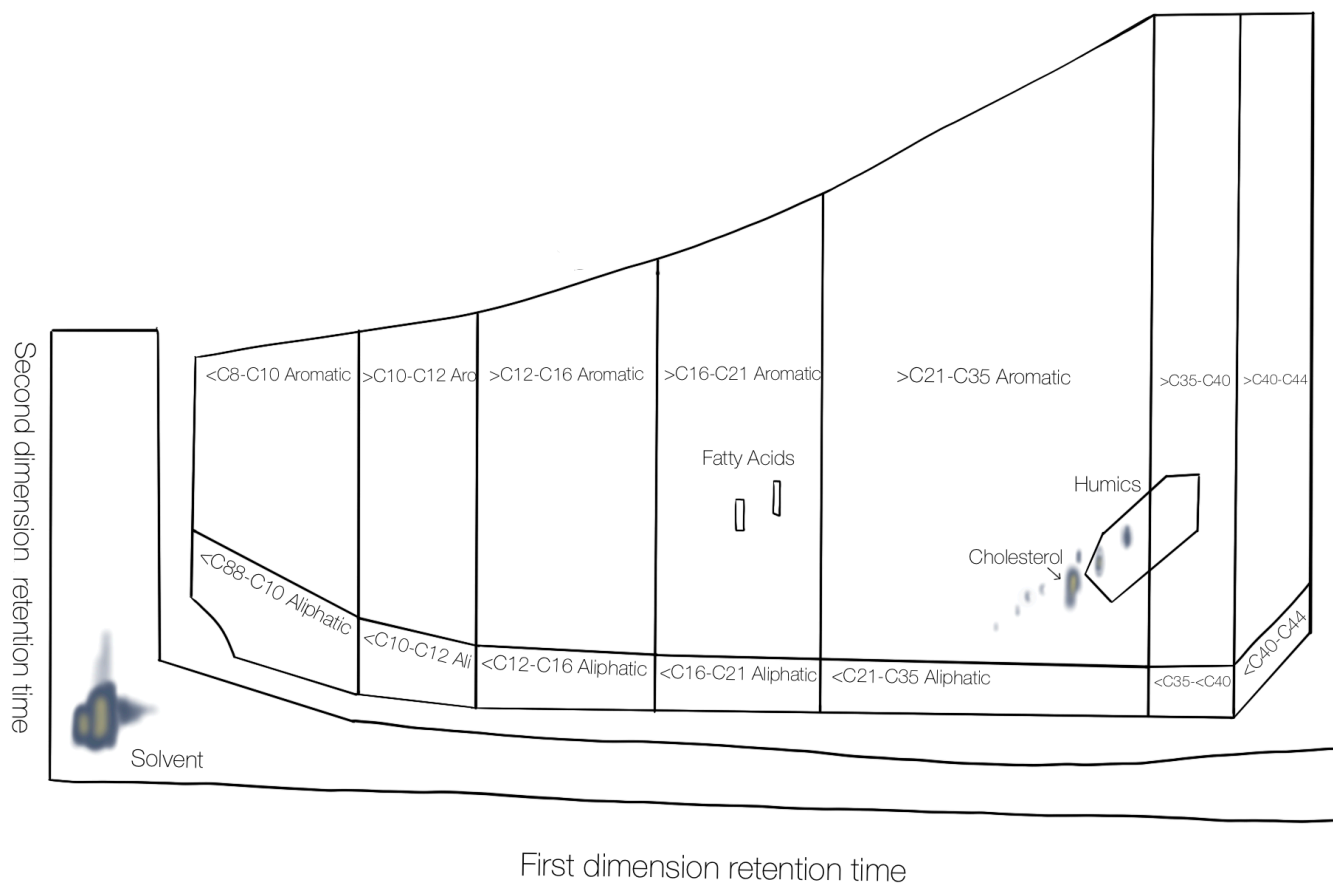


GC-GC 2D plot for a mixture of diesel and lubricating oil (www.agilent.com 2015)

Similar to 1D gas chromatography, individual peaks in a GC-GC 2D plot can be analysed using mass spectrometry to identify unknown compounds.

Note that unless a chemical clean-up step has been undertaken prior to injection into the GC-GC, the results measure everything extracted from the sample (i.e. EH_2D_Total) which therefore includes non-petroleum hydrocarbons like the humics.

To better meet the objectives of the TPH-CWG protocol (EH_CU+HS_1D_Total), one UK laboratory instigated a mathematical correction rather than a chemical clean-up step. ALS identified a polygonal area in their 2D GC-GC plots (see example overleaf) where they believe the humics are located. Any hydrocarbons within this polygon are mathematically subtracted from the total, with the result reported as EH_2D_Total_#1.



GC-GC 2D plot of hydrocarbons in a filter cake resulting from the hydrolysis of a hoof and horn meal. The figures show the area where ALS have identified humics.

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