

## Ken Knows TPH (Total Petroleum Hydrocarbons)

TPH is a term used to define any mixture of hydrocarbons (chemical made up of carbon and hydrogen) that are found in or derived from crude oil. In Environmental testing it is often used as a catch all term for a broad range of analytical methods, instrumental techniques and data outputs.

TPH in some form is commonly used as contaminant of interest, indicator or identifier of various forms of environmental contamination, hazardous waste classification or risk assessment, and is prevalent on the significant majority of testing schedules received in the lab.

TPH is closely linked to PAH (Polycyclic Aromatic Hydrocarbons), indeed PAHs being one of the sub divisions of chemicals within the TPH heading, due to the known toxicological and carcinogenic impact of PAHs, with Benzo(a)pyrene used as the primary indicator compound within the established USEPA suite of PAHs.

TPH testing will fall into 2 main types with one often used in conjunction with the other to support decision making.

- Qualitative: identification and classification of hydrocarbon types and potential sources
- Quantitative: determination of physical concentrations of the required species in the sample

TPH covers a range of products and individual compounds and for the majority of our uses are within the C5 – C44 range meaning they contain between 5 and 44 carbon atoms in the molecules. Some compounds are easy to pin down in terms of their position in the range, straight chain Aliphatics (Hexane, Octane, Decane, etc.) follow the rule nicely (C6, C8, C10, etc.), but for Aromatic compounds (those containing a Benzene 'ring') we use an equivalent carbon number (EC) which is calculated for each compound based on its boiling point and relative retention time on a Gas Chromatogram. For example, Benzene (the simplest aromatic) has 6 carbons but an EC of 6.5. Benzo(a)pyrene has 20 carbon molecules but an EC of 31.34. The EC and therefore relative positioning of the peaks in the chromatogram/areas of concentration is important when looking at qualitative determination.

### Qualitative Analysis

Typically done using GC-MS (Mass Spectrometry) or GCxGC-FID (2 dimensional GC with flame ionization detector) as we need a detailed breakdown of the contamination make up. Matching reference chromatograms along with the identification and relative abundances of known marker compounds can enable differentiation between and identify different fuel types. This can be of use when trying to identify a source of contamination, spillages, forensic determination and in the process of waste classification to rule out the presence of certain fuels known to have specific carcinogenic effects (gasoline/diesel).

### Quantitative Analysis

There are several commonly used techniques available in labs, ranging from very simplistic to the highly complicated! Here's a quick summary:

Gravimetric/solvent extraction: used for simple coal tar quantification or Fats, Oils and Grease in discharge consents; an organic solvent (Dichloromethane, Petroleum Ether, etc.) is used to extract the hydrocarbon content from the sample (soil, water, etc.), the solvent is then removed leaving behind the contaminants to be assessed by weight. Cheap, simple, high detection limits and prone to interferences due to the broad nature of the extraction and lack of distinction in the extracted material.



Headspace (GS): a technique for assessing volatile compounds (those with low boiling points) whereby the chemicals are forced out of solution using heat/agitation/saturation into a contained air space (or headspace) and then the gas is analysed by either Mass Spectrometry (MS) or Flame Ionisation (FID). This covers the C5 – C10 range of compounds, including BTEX and MTBE often tested with the TPHCWG suite

Gas Chromatography: used for the extractable range of compounds (C10 – C44). Samples are extracted into a solvent (DCM, Hexane, Acetone, etc.) and then injected in low volumes ( $\mu\text{l}$ ) into a GC where they are volatilised at high temperature and then the compounds can be separated using a capillary column as the sample mixture is pushed through under pressure of an inert gas. The column contains what is known as a static phase, essentially a chemical with which the compounds interact to different degrees so then pass through to the detector at different times. The same basic principle can be applied to a couple of variations:

- FID: a simple detector that identifies contaminants only based on the time taken to pass through the column (RT or Retention Time). Historically used as the main tool for TPH, allows quantification of whatever is extracted (including potential interferences) so for more detailed analysis the extract would need to be 'prepared' carefully to only contain the compounds of interest
- MS: a more complex detector which uses RT and also the fragmentation patterns of molecules when bombarded with electrons to identify contaminants. The predictable way in which molecules fragment allows a high degree of selection and accuracy. This technique has been used for TPH but is more commonly found in things like PAHs where specific chemical compounds need to be targeted
- GCxGC: also called 2D GC, this uses a 2-stage chromatographic separation where compounds of interest are initially split based on carbon chain length, then further split on a second column to distinguish the aliphatic and aromatic compounds. This generates a 2D chromatogram and allows the analyst to differentiate the various types of contamination (including potential contamination) without the need for additional preparation of the extract

## Clean up or not?

For a genuine TPH, we are specifically interested in **Petroleum** hydrocarbons, but the extraction methods employed will also pick up a range of other hydrocarbons (compounds containing Carbon and Hydrogen but not necessarily derived from crude oil) so we need to be able to discount them from our quantification as and when needed. Commonly this is done in 1 of 2 ways:

- Chemical fractionation: using a Solid Phase Extraction (SPE) the extract is loaded onto a sorbent material (Silica or Florisil) and then selectively eluted using variable solvents to remove only the aliphatic or aromatic portions. This generates 2 'samples' for analysis and is labour intensive. High levels of non-petroleum hydrocarbons can overload the clean-up column and allow excess material to pass through if multiple clean up stages are not performed
- Instrumental: using either GC-MS or GCxGC-FID as detailed above an analyst can interpret the data produced to identify which elements are interference and which are genuine compounds of interest



## Which TPH do I want?

- **TPH** can be the generic overall term when clarity is not available but generally refers to the full C5 – C44 range
- **EPH** (Extractable Petroleum Hydrocarbons) covers the C10 – C44 range, the Diesel range (DRO: C10 – C20 or C10 – C24) and Mineral Range (MRO: C20 – C44 or C24 – C44)
- **VPH** (Volatile Petroleum Hydrocarbons) covers the C5 – C10 range, also known as Gasoline Range or Petroleum Range (GRO/PRO)
- **Banded Hydrocarbons** (EPH and/or VPH) can cover the full range or a sub set, but breaks down the results into smaller increments e.g. TEXAS bandings (C6-C8, C8-C10, C10-C12, C12-C16, C16-C21, C21-C40) or the 3-band (C5-C10, C10-C20, C20-C40)
- **Mineral Oil** is based on the C10 – C40 Aliphatic compounds and was a traditional requirement of Waste Acceptance Testing (WAC)
- **Speciated Hydrocarbons** is a further subset of banded hydrocarbons where the smaller groups are then split into the Aliphatic and Aromatic portions, with the common example being TPHCWG (Criteria Working Group). This is a defined suite of Ali/Aro groups between C3 and C35 (later extended to C44) designed for groundwater impact assessment and human health risk assessment. Is also typically reported with BTEX compounds and MTBE from the Aromatic VPH range.

## FAQs

Is GCxGC better?

It is more flexible as it doesn't require manual clean ups and labour-intensive extractions to split Aliphatic and Aromatic compounds. First employed to help with qualitative determinations (particularly in coal tar) and investigatory works, it is now becoming the standard approach for TPH analysis, in particular when looking at TPHCWG.

Should we have a clean-up?

It depends what you want to know. For specifically assessing the petroleum hydrocarbon content then it would be required but for a screening assessment it may be suitable to go without. However, it must be clear to the data user as to how the result was generated.

What are all these weird letters after my result?

This is likely the acronym-based system invented by Ian Bishop at HazWasteOnline to give some clarity as to how a TPH result was generated. They include coded references as to which extraction technique was used, which instrument, whether a clean-up was employed and if it is based on Aliphatic, Aromatic or total TPH.

What should I get for WAC testing?

Traditionally this was C10 – C40 Aliphatic as this is the definition of Mineral oil. There are some standards that link this to a total C10 – C40 (Ali + Aro) with clean up but until a further industry wide standardisation can be obtained we'll be reporting based on the original definition.



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