

Detection of Natural Organic Matter in the Total Petroleum Hydrocarbon Method

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Abstract

Positive detections of Natural Organic Matter (NOM) – also known as biogenic hydrocarbons - in the Total Petroleum Hydrocarbon (TPH) analytical method in soil and water samples are not necessarily due to anthropogenic (human derived) petroleum hydrocarbon contamination, but instead may be compounds extracted from NOM such as plant based resins, oils and natural hydrocarbons. The TPH method involves a crude solvent extraction, which will extract both anthropogenic contaminants as well as NOM. The method of quantitation involves a relatively non-specific gas chromatographic method with Flame Ionisation Detection (FID). The FID detection method does not allow speciation of anthropogenic hydrocarbons from NOM. Examination of the chromatogram in combination with further analysis of the extract will allow an experienced Analyst to differentiate the source of the contamination, which will help to reduce the instances of productive soil being unnecessarily sent to landfill.

Introduction

The TPH method analytical method name is somewhat of a misnomer. The results are usually reported as carbon bands between C7 (n-pentane) to C36 (n-hexatriacontane). Therefore, it cannot be considered a true total because hydrocarbons lighter than C7 and heavier than C36 are excluded. In addition, NOM compounds such as plant based resins, oils and natural hydrocarbons pinene are often detected, meaning that the test is not restricted to anthropogenic sources of petroleum compounds. Finally, non-hydrocarbon synthetic organic compounds such as pesticides, phthalates, pentachlorophenol (PCP) and polychlorinated biphenyls (PCB) can also be detected if present at high enough level in the soil or water sample. While this may be seen as a weakness in terms of the poor specificity of the test, it can also be harnessed as a strength to screen for other unforeseen contaminants.

Analytical Procedure

The TPH method itself is fairly straightforward. In the case of soil, the sample is extracted in an organic solvent (e.g. 1:1 DCM:Acetone or 1:1 Acetone/Hexane) using various means (end-over-end shaking or sonication)), cleaned up to remove polar organic molecules using silica, and then the solvent extract analysed by Gas Chromatography (GC) with either Flame Ionisation Detection (FID) or in some cases Mass Spectrometry (MS).

The GC is typically run using a temperature programme from 40°C - 350°C, so compounds with a wide range of boiling points can be determined. However, very volatile compounds with a boiling point less than n-heptane (carbon number C7), and very heavy compounds with a boiling point greater than n-tetratetracontane (carbon number C44) are not included. Therefore, the term “Total” is somewhat of a misnomer. The FID is much cheaper but much less specific than the MS and hence the FID cannot be used to differentiate anthropogenic contaminants from biogenic

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sources. The output from the detector is plotted to form a chromatogram, and this visual plot is very helpful when it comes to finger-printing the type of contamination present (see Figures 1, 2 and 3 below).

Figure 1: Chromatogram of 91 Petrol

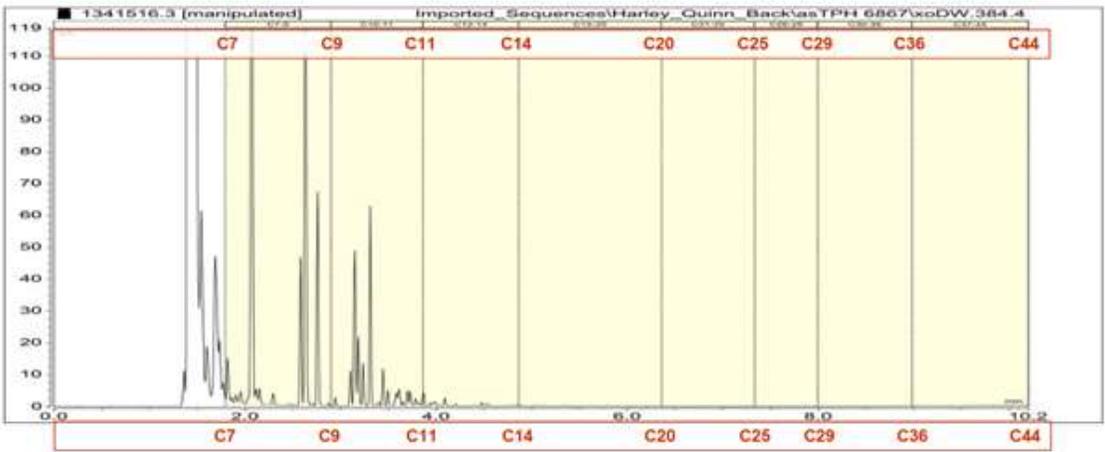


Figure 2: Chromatogram of Diesel

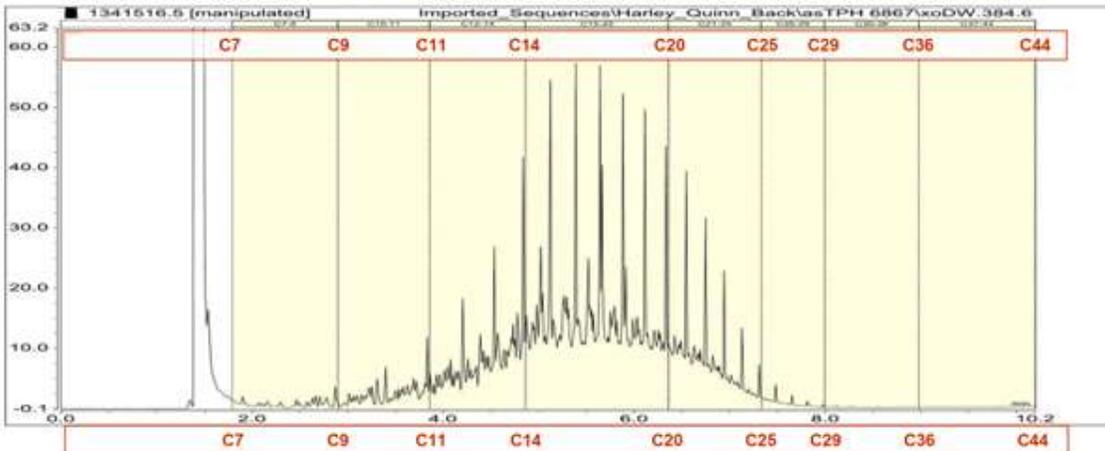
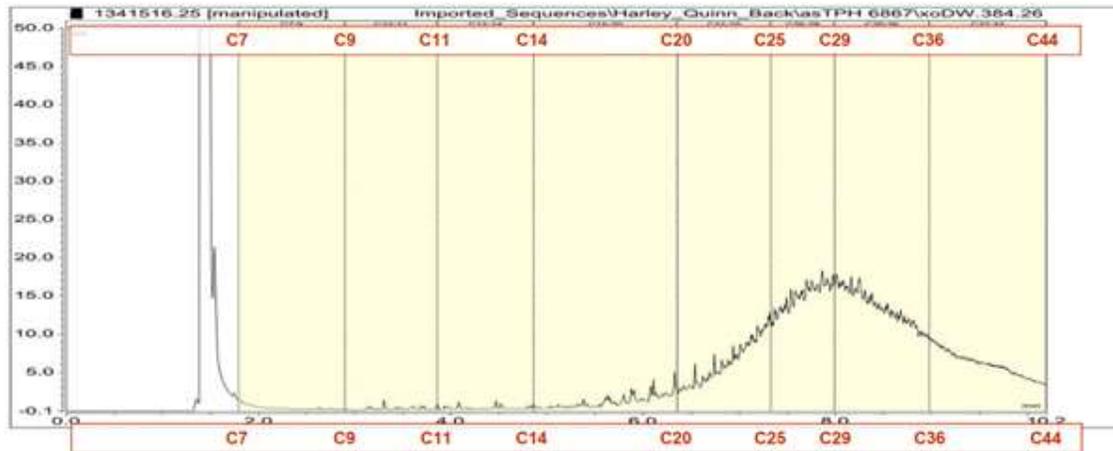


Figure 3: Chromatogram of Used Car Oil


The various chromatograms produced by analysing fresh petrol, fresh diesel and used lubricating oil are completely different as evidenced above, and it is quite easy to identify the product. This is one of the main advantages of using the TPH method.

It should be noted that the large peak just before C7 in all the chromatograms is the solvent peak, which is so large that it is truncated on the signal scale (Y-axis), otherwise the detail of the remaining chromatogram would be lost. The discrete peaks that follow soon after in the petrol chromatogram (Figure 1) are individual compounds such as toluene and xylene. Similarly, the discrete peaks that sit on top of the broad hump in the diesel chromatogram (Figure 2) are also individual compounds such as n-pentadecane and n-hexadecane. The broad humps in the diesel and lubricating oil chromatograms are a complex mix of many petroleum hydrocarbons that can't be separated, so they appear as one broad peak rather than sharp discrete peaks.

Additional Compounds Detected by the TPH Analysis

Despite the treatment of the solvent extract with silica, some polar compounds still can make it through the clean-up and be detected by the FID (or MS). In reality then, the TPH test measures any compounds which extract into the solvent, are not lost during the extraction due to volatility, and can be analysed by GC (below C44). These compounds include a vast number of both NOM and synthetic chemicals such as PCB, as can be seen in Figures 4, 5 & 6 below:

Figure 4: Chromatogram showing sewage components

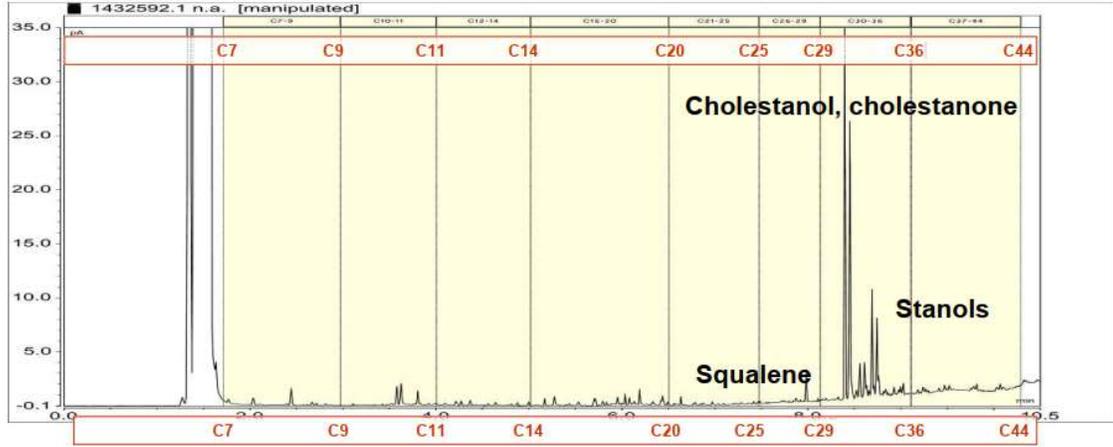


Figure 5: Chromatogram showing Gum Terpentine

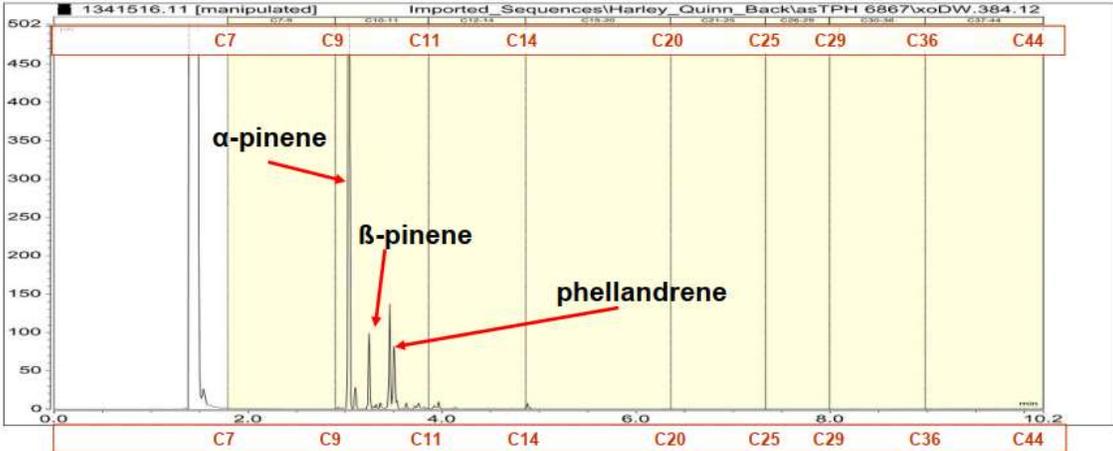
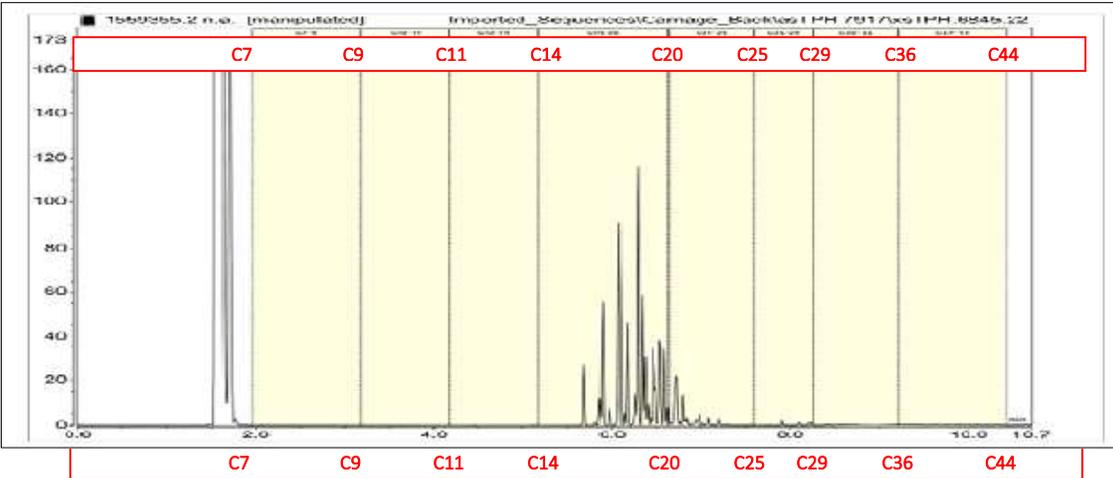


Figure 6: Chromatogram of PCB

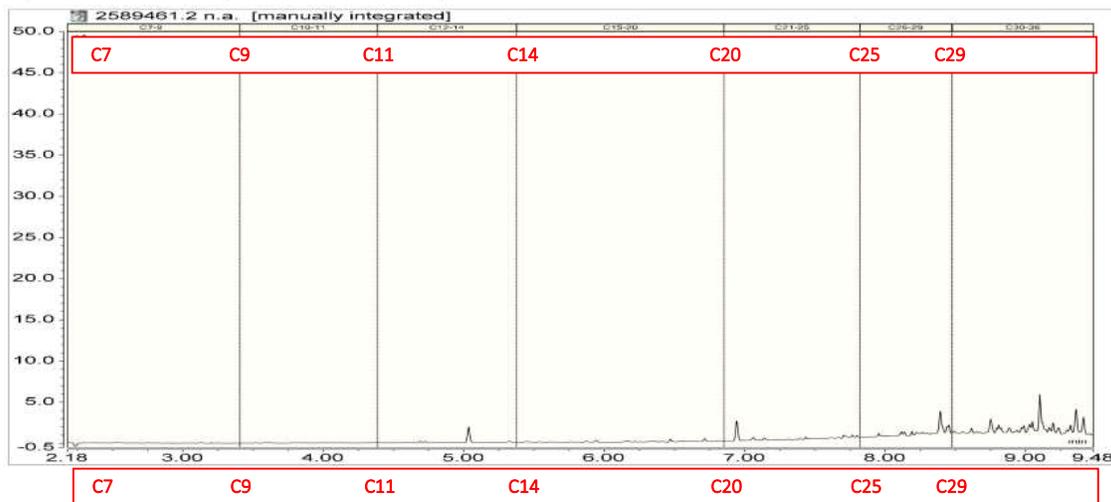


As mentioned earlier, despite the TPH method being analytically flawed, it can be used by those who understand the method as an effective screening tool and in some cases with classic fingerprints (PCBs, Phenols, bitumen vs coal tar etc).

Detection of Natural Organic Matter

The consequence of the above discussion is that the TPH method can detect organic compounds that have been extracted from NOM. This may result in the incorrect assignment of the TPH result as an anthropogenic contaminant when in fact it is NOM. An example is shown in Figure 7, and while the chromatogram doesn't immediately indicate that a significant concentration is present, the C15-C36 band returned a result of 340 mg/kg dry weight, which is sufficient to classify the sample as contaminated above background and requiring managed fill for disposal.

Figure 7: Chromatogram of Natural Organic Matter



Personal experience at both Hill Laboratories Ltd and Analytica Laboratories Ltd has demonstrated that in many cases the TPH method has resulted in hydrocarbon detections that are largely the result of a NOM source, typically in the 50-500 mg/kg range. This has been particularly noted in peat samples where there is often a significant amount of extractable organic matter that is not removed by silica clean up and results in a TPH detection. It has been noted in both laboratories that many top soils with moderate to elevated levels of organic matter can result also result in positive detections and are occurring at increasing frequency as new land is developed.

What steps can be taken to determine whether one is dealing with petroleum hydrocarbon contamination, or NOM? We would suggest two steps:

1. Examination of the Chromatogram

A close examination of the chromatogram is the first and easiest method of determining whether one is dealing with NOM. As evidenced above, the chromatogram is usually characterised by an indistinct group of peaks sitting on a low broad lump of complex apparent hydrocarbons in the range C20 – C36. This profile is not a classic hydrocarbon fingerprint.

2. Analysis of the solvent extract by GCMS

To confirm the identity of some of the discrete peaks in the chromatogram, a request can be made to the laboratory to analyse the extract by GCMS. The lab will add a Library Search Report (LSR) to the job report, which will include “Tentatively Identified Compounds” and a list of the best matches for these compounds. The LSR will include the Chemical Abstract Service (CAS) numbers, which can be used for web searching purposes to confirm whether or not the compounds are naturally occurring. Alternatively the laboratory may include a simple summary of the type of NOM compounds identified and a conclusion that the source is more likely NOM than anthropogenic.

Conclusion

It is clear that the current analytical protocol for TPH does provide a very good screening procedure for anthropogenic sources of petroleum hydrocarbons. However, care should be taken in interpreting the chromatograms and resulting data because a range of NOM compounds and other anthropogenic sources of organic contaminants (e.g. synthetic PCB etc) may also be included in the result. The relatively low specificity of the method can result in a false confidence that all results must be derived from a petroleum hydrocarbon source when in fact there may be an alternative natural source or potentially a much more serious anthropogenic source (e.g. PCBs, pesticides etc).

Where the chromatogram does not provide a classic fingerprint for a petroleum hydrocarbon source, it would be advisable to further investigate the solvent extract using more specific analytical tools such as GC-MS.

Personal experience at both Hill Laboratories Ltd and Analytica Laboratories Ltd has demonstrated that in many investigations involving soil that has moderate to elevated levels of organic matter, the TPH method has resulted in hydrocarbon detections that are largely the result of NOM sources. Disposal to landfill of such soil is a waste of productive soil, contributes to unnecessary emissions, and imposes unnecessary economic burden to developments.