

Approaches to quantify the effect of extracted plant material on PHC levels.

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Abstract

Often when “soil” samples containing a high amount of organic material are extracted, the organic material is co-extracted with the hydrocarbons. Especially problematic are samples that contain a large amount of peat, compost samples, or samples containing amendments, in addition to contaminating petroleum hydrocarbons.

The analysis may show high residual amounts (esp. for fraction 3); even after silica gel treatment was applied to remove the extracted organic material.

Chromatographic interpretation may infer the possible presence of plant material; it cannot however determine the amount of interfering material.

The tier 1 CCME method may therefore not be appropriate for these types of samples. One suggestion to deal with this issue is to obtain a proper control sample, that is, an uncontaminated sample and subtract its measured result from that of the contaminated sample.

When no proper control sample can be found, other approaches to determine how much plant material is co-extracted with the hydrocarbons may need to be applied. BTG Calgary has been using (1) the TOC model, where the plant extractables were subtracted from the total amount extracted, giving the “petroleum hydrocarbons”; (2) the before and after silica gel treatment approach, where sample results are compared before and after silica gel treatment; (3) the standard addition method, where the samples are “spiked” with hydrocarbon and the change in response observed. A variation of the TOC method, with the added analysis of a loss of ignition (LOI) on the extracted material, could also be considered as to arrive at a good approximation of the amount of “plant material.”

Gas chromatography hydrocarbon analysis

Chromatography is an analytical technique used for separating a mixture of chemical substances into its components so that these can be identified and/or analyzed.

In all types of chromatography, the analyte, which is a sample of the mixture being analyzed, is applied and allowed to adhere inside the column to a stationary material known as the stationary phase, or adsorbent. Another material, known as the mobile phase, carrier fluid, or eluent, is then made to flow through the adsorbent.

In gas chromatography, the mobile phase is generally a chemically inert gas, such as nitrogen, helium, argon, or carbon dioxide. The sample to be analyzed by gas chromatography is vaporized and then injected into the column. It is then transported through the column by the flow of the mobile phase.

Separation of the components in the mixture depends on the component's attraction to the stationary phase, or its mobility through it. For example, larger size compounds may have a stronger attraction to the stationary phase and will therefore have a longer elution time. Smaller size compounds will prefer the mobile phase instead and show a quicker elution from the column. When the components elute of the column, they pass through a detector that measures a change in signal.

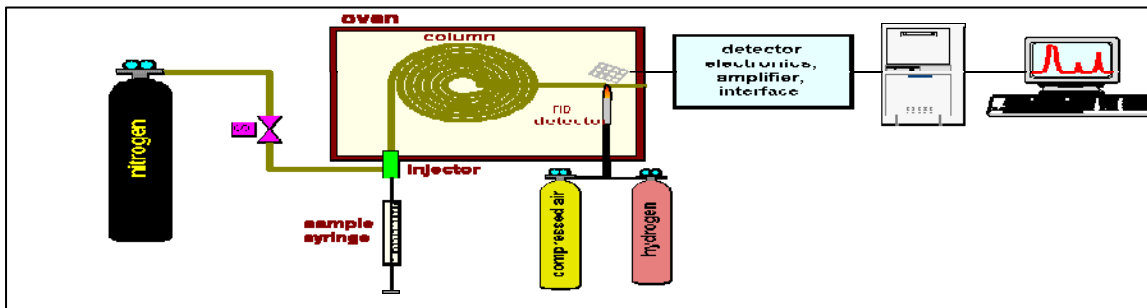


Figure 1. Gas chromatographic system

The output of a chromatographic analysis is referred to as a 'chromatogram.' It is a plot that consists of several different peaks representing the different components of the sample mixture.

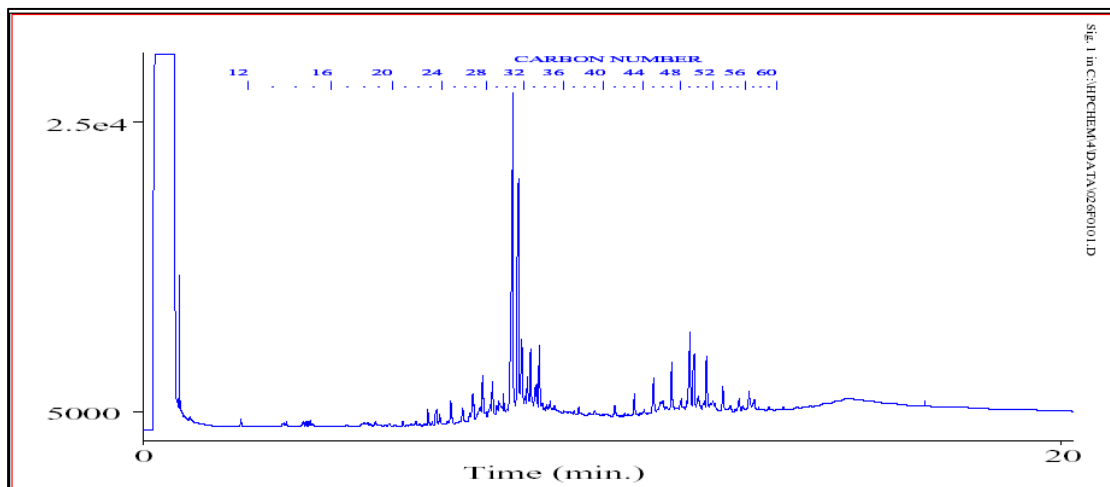


Figure 2. Gas chromatogram of peat

The X-axis of a chromatogram shows the elution time, the Y-axis the amount passing through the detector. In gas chromatography used for hydrocarbon analysis, more volatile compounds will elute first (reach the detector first), while the less volatile compounds (heavier molecular weight) will elute last. Analyzing a reference standard allows the generation of a carbon scale (as seen on top of the chromatogram). This scale depicts the elution time of a hydrocarbon with a certain number of carbon atoms to elute off the column.

As refined petroleum products have defined carbon ranges, a chromatogram can thus be used to identify hydrocarbon types by looking at the chromatographic pattern of the compound and its carbon range. For example, a diesel will have a chromatogram where the majority of the compounds eluting will fall between the C12 to C24 carbon range.

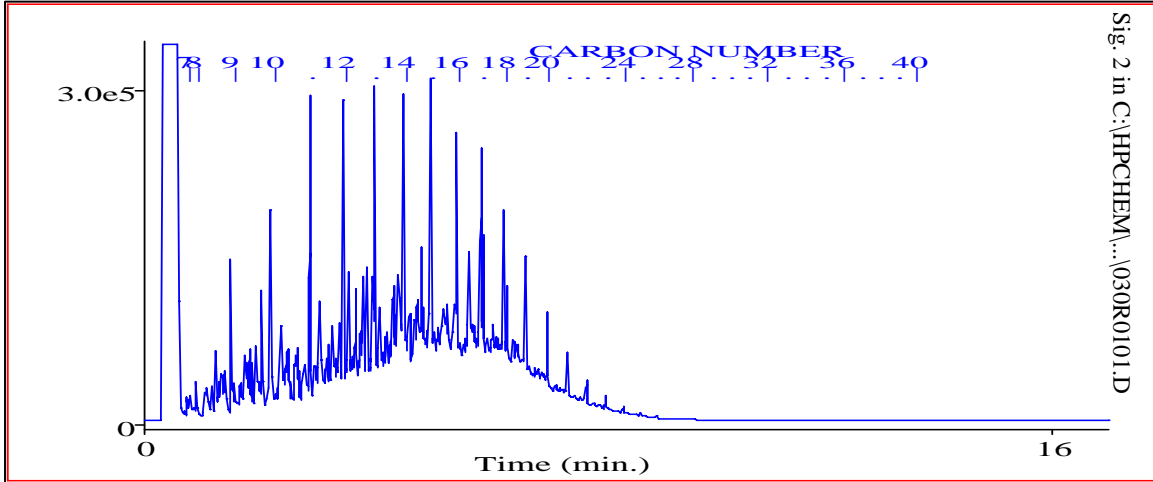


Figure 3. Gas chromatogram of diesel

Aging and weathering of the hydrocarbon product will produce a different chromatogram from that of the fresh product. Often the more volatile part of the product is evaporated and the individual hydrocarbons have a lower abundance.

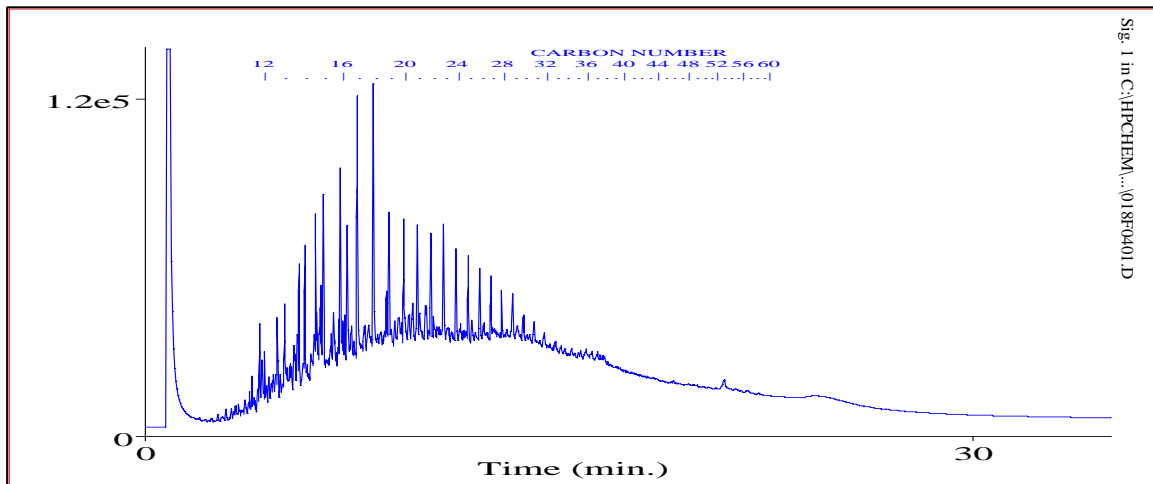


Figure 4. Partially weathered crude oil

Identification of the hydrocarbons in the sample is thus achieved by matching chromatograms of the sample with profiles of standard hydrocarbon types. Be aware that this assessment is made by a chromatographer comparing chromatograms and that this assessment often has a judgment based on experience, especially with aged, weathered or biodegraded products, and cannot be considered absolute.

Quantitative analysis

The capillary column gas chromatography/ flame ionization detection (GC/FID) method is applicable to qualitative and quantitative determination of petroleum hydrocarbons which are less volatile than gasoline in soil (i.e., extractable hydrocarbons).

The soil sample is extracted with a solvent; the organic fraction (solvent fraction) is decanted, dried, and concentrated. An amount is analyzed using GC/FID.

The concentration of the hydrocarbons in the sample is calculated in mg/kg (ppm), using an external petroleum hydrocarbon standard.

The sum of the peak areas of the sample are obtained from the chromatogram and compared to the corresponding value of the standard.

This is a non-specific method, and only groups or fractions of chemical hydrocarbons are determined. This GC/FID analysis is thus used for the analysis of PHCs, like in CCME, Alberta Tier 1, EUB D50 situations.

After oil spills, oil hydrocarbons often mix with other background “hydrocarbon” sources in the impacted area. One of the potential sources of hydrocarbons contributing to the background is biogenic hydrocarbons. The drawback therefore of using a generic GC/FID analysis is that it also detects non petroleum hydrocarbons like these biogenic “hydrocarbons”, and thus increases the risk of false positives.

Distinguishing biogenic hydrocarbons from petrogenic hydrocarbons

Biogenic hydrocarbons are generated by biological processes coming from plants, animals, and bacteria.

It has been recognized that the biogenic hydrocarbons have the following chemical composition characteristics: (see figure 2)

- (1) n-alkanes show a distribution pattern of odd carbon-numbered alkanes being more abundant than even carbon-numbered alkanes in the range of n-C21 to n-C33;
- (2) notable absence of the “unresolved complex mixture (UCM)” hump in the chromatograms;

Silica gel treatment

The CCME Tier 1 method minimizes the influence of the biogenic material by treating the sample extract with silica gel. The principle used here is that silica gel treatment removes polar organic material from the soil extract. One difficulty is that the amount of silica gel used may not effectively remove all the biogenic material when that is present in large amounts.

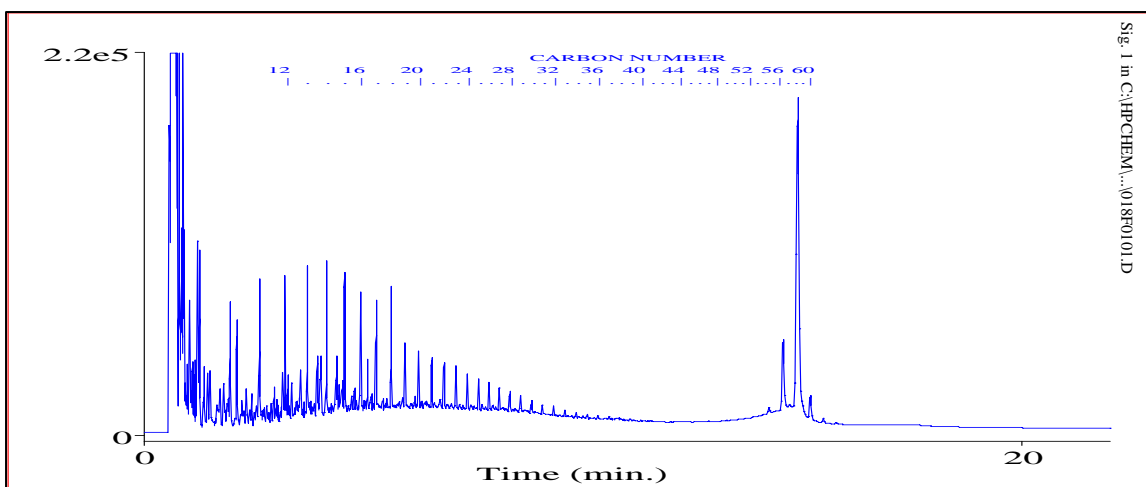


Figure 5. Fresh crude oil and canola oil.

Some jurisdictions, like BC and Alaska actually use the silica gel treatment to prove that there are biogenic materials. First, the interpretation of sample chromatogram must be done by an experienced analyst for qualitative match of the chromatographic pattern to known sources of fuel product and or biogenic interference.

Once biogenic interference has been determined, the sample extract (already analyzed without SG cleanup) is flushed through a SG column. New hydrocarbon results are generated, now after silica gel cleanup. This procedure also provides a means to calculating the amount of biogenic material: it is the difference of measurements taken before and after the silica gel treatment.

Approaches to quantify the biogenic interference

There may thus be some biogenic interference left after silica gel cleanup, that is, not all is removed. One may need to know just how much is left to thus adjust the hydrocarbon measurement. In bioremediated mixtures, for example one need to determine the amount of interference from organics (e.g., Canola meal and wood shavings) and this number obtained will be subtracted from the total extractable hydrocarbons to give the total “petroleum” hydrocarbons.

The amount of residual extractable hydrocarbons (total organic material) present in the amendments is measured from the total extractable hydrocarbon measurement of these amendments. This establishes the relationship between a total organic carbon (TOC) measurement and the total organic material (TOM). This relationship can then be used to extrapolate the TOM using the TOC from samples. The TOC to use would be the one determined from the sample before extraction.

Silica gel treatment

The principle used here is that silica gel treatment removes polar organic material from soil extracts. One difficulty is that the amount of silica gel may not effectively remove all the OM when it is there in large amounts. Still an estimation about the amount of organic

material present could be made from looking at the results before and after silica gel treatment.

Blanks

When uncontaminated blanks are available, the amount found in the extract could be used to subtract this value from contaminated samples and thus arrive at the true hydrocarbon number. The assumption made is that the blanks that are available have undergone the same weathering as the samples, so as to be representative of the organic material in the samples.

As an example, when a blank peat is available, then one would analyze the sample without silica gel treatment and subtract the blank value.

Chromatographic separation

Without a blank, an estimation may in very rare circumstances be possible from an integration of separate parts of the chromatogram. An ideal example would be the crude oil and canola seen in Figure 5.

Mass spectral detection

As mentioned already, the problem with the GC/FID analysis of hydrocarbons is that other extractables like organic material interfere with the analysis. The general FID detector cannot distinguish between them.

Theoretically, a GC/MS system should be able to differentiate between a petroleum hydrocarbon and organic material as they would have distinct mass spectra. Finding a few marker compounds belonging exclusively to organic material would help. The problem remains in finding the ratio of these marker compounds to the overall amount of organic material. The best way again would be with the use of blanks. But when no blanks are available, the ratio obtained will just remain a (albeit good) guess.

Standard additions

It should be possible to spike contaminated soil samples with certain amounts of hydrocarbons and measure the increase in response. When a few spikes are done (at increasing concentrations) a curve could be obtained so that when extrapolating to zero, the amount of organic material is arrived at. This approach could be used in a scenario of crude oil and peat, as shown in Figure 6.

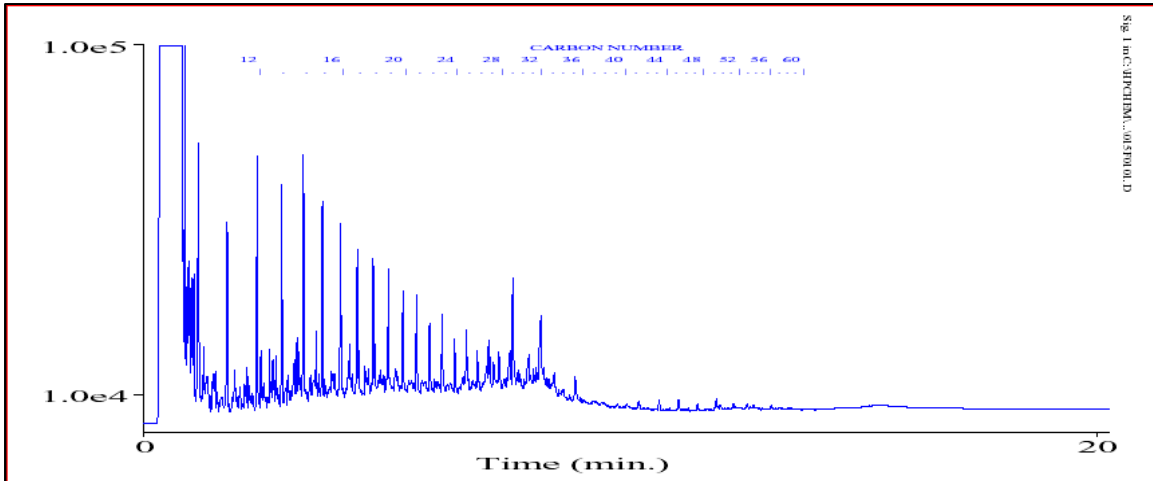


Figure 6. Crude oil and peat.

A standard addition experiment would involve the generation of a normal addition curve. Figure 7 offers some insight.

Just plant material in sample would show at (A); while plant material plus petroleum hydrocarbons would be at point (B)

A couple of spikes (PHC spikes) need to be done. Extrapolation back to the zero amount (back to A) and calculation the plant material (OM) as the offset from zero would follow.

The problem is to use “normalized” graphs, using TOC, moisture, and bulk density for normalization.

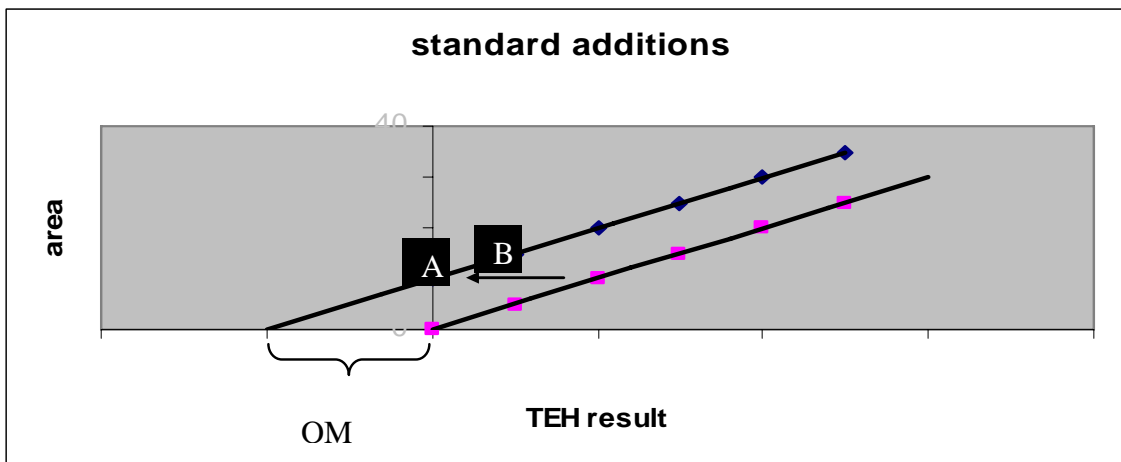


Figure 7. Standard addition curve

Combination approach

A combination approach has successfully been used a couple of times and continues from the standard addition experiments. When all the approaches lead to the same conclusion, the confidence in the estimate of the biogenic interference is increased.