

RegenOx™

Advanced Chemical Oxidation

Total Petroleum Hydrocarbon Analysis: Analytical Challenges and Recommendations

Introduction

The use of chemical oxidants to degrade total petroleum hydrocarbons (TPH) may produce confusing results, particularly when addressing dissolved-phase contaminants. Where the target contamination is petroleum and the goal is to reduce TPH in groundwater, the initial step of any chemical oxidation (including that performed by RegenOx™) will increase dissolved-phase mass by forming soluble species, thus driving up the relative concentration of the total dissolved-phase contaminant. This tendency may be amplified by the high pH generated by the alkaline chemistries immediately following chemical oxidant injection. Depending on the analytical technique used, these newly formed soluble species may exist within the TPH range. Therefore, groundwater treatment by chemical oxidation, if undertaken to degrade dissolved species, may appear to increase the contamination.

When examining this process, it is important to understand (1) the caveats associated with analytical methods typically used for TPH, (2) the chemical, physical, and biological mechanisms involved in the degradation of TPH and (3) that both the analytical methods and the degradation mechanisms have site-specific soil matrix effects that make it difficult to predict performance from similar sites.

Variations of TPH Analyses

Gross parameters describing hydrocarbon contamination in soils and sediments include oil and grease, mineral oil and grease, total extractable hydrocarbons, light hydrocarbons, total petroleum hydrocarbons, and total hydrocarbons. In the top half of Figure 1 (below), typical petroleum products are arranged by number of carbon atoms. In the bottom half of Figure 1, the ranges of analytical methods used to measure petroleum components are depicted. TPH is usually defined as the sum of purgeable and extractable hydrocarbons. Several “fractionated” TPH analyses were developed in the late 1990s. These include Massachusetts volatile petroleum hydrocarbons (MA VPH) / extractable petroleum hydrocarbons (MA EPH); Alaska 101AA/102AA; TPH Criteria Working Group Method; and the Canada-Wide Standard for Petroleum Hydrocarbons (CWS-PHC). A fractionated TPH analysis essentially divides the range of hydrocarbons analyzed for by molecular class (alkanes and aromatics), and by carbon chain length (via boiling-point ranges).

Analytical Challenges with TPH

The major problems with typical TPH analyses are that (1) non-dissolved petroleum is frequently entrained within a sample (via grab sampling in monitoring wells where an oil layer is present or entrained within the grab sample colloid particles having adsorbed hydrocarbons), and (2) polar non-hydrocarbons are present from natural sources within the subsurface matrix and from biological and chemical oxidations (Zemo and Foote, 2003). If a TPH analytical method must be employed, the best practice, from an analytical perspective, would be to use a fractionation method, and first filter the samples to remove any turbidity and then filter again with silica gel to remove polar non-petroleum hydrocarbons. Unfortunately, however, fractionation methods are often not employed, even though it is mandated by many standard methods.

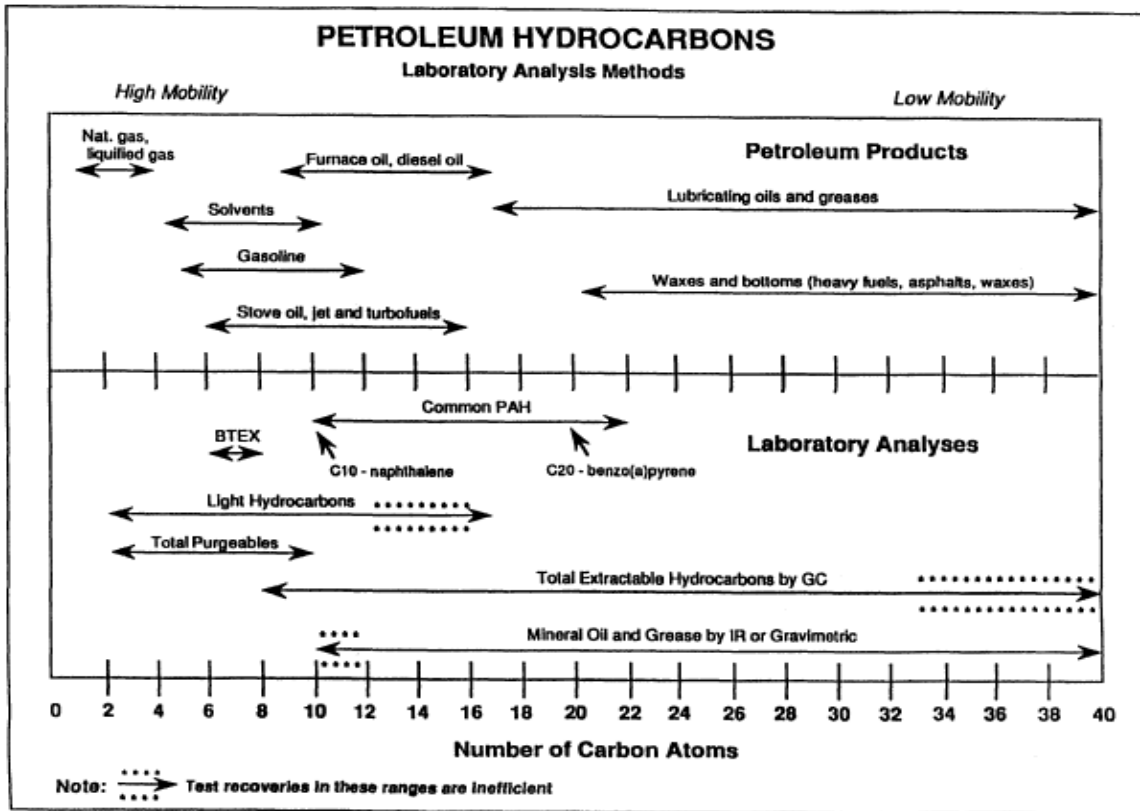
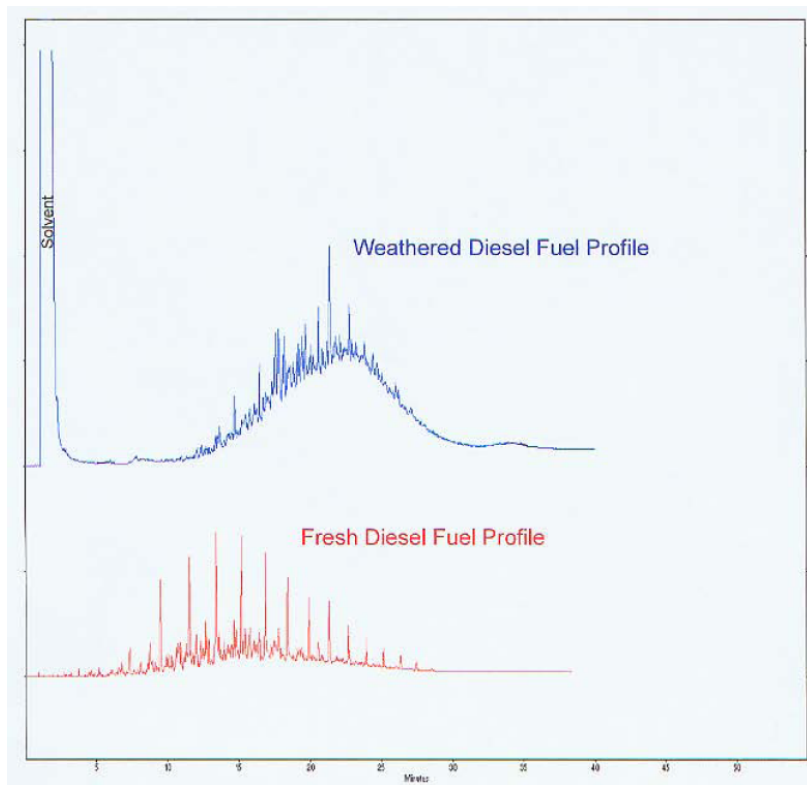


Figure 1: Petroleum Hydrocarbon Components and Typical Analytical Ranges.(Alberta Environment, 1993)



In the environment, volatilization, biodegradation, partitioning into water, and photodegradation alter the component profile of diesel fuel. The effect of this "weathering" process is that the component profile shifts to the higher boiling range and loses the regularly spaced n-alkane peaks. The exaggerated hump in the weathered diesel profile is a predominant feature.

Figure 2: Comparison of GC-FID Chromatograms of Fresh and Weathered Diesel Fuel

Sample "Cleanup" with Silica Gel

All petroleum hydrocarbon mixtures undergo similar degradation in the environment, and all have a signature revealing their petroleum product precursor. However, extensive scientific investigation of the true nature of water-soluble petroleum hydrocarbons indicates that the analytical signature should be composed of discrete peaks and should not have an unresolved complex mixture or "hump" in the chromatogram (as in Figure 2). This hump can be resolved by silica gel filtration of the sample. The CWS-PHC and MA EPH methods recommend a silica gel cleanup, and specifically recommended the more stringent column cleanup method over the in-situ (slurry) cleanup method. One may wonder why silica gel cleanup is not a standard method. In fact, the original infrared spectrum method (Method 418.1) designed for TPH had a silica gel cleanup step. However, the current GC-FID method for TPH is a modification of EPA Method 8015, which was designed to measure discrete non-halogenated organics, including polar compounds such as alcohols, ketones, and aldehydes. Not using silica gel cleanup effectively made that TPH analysis a total organic measurement rather than a total petroleum hydrocarbon measurement.

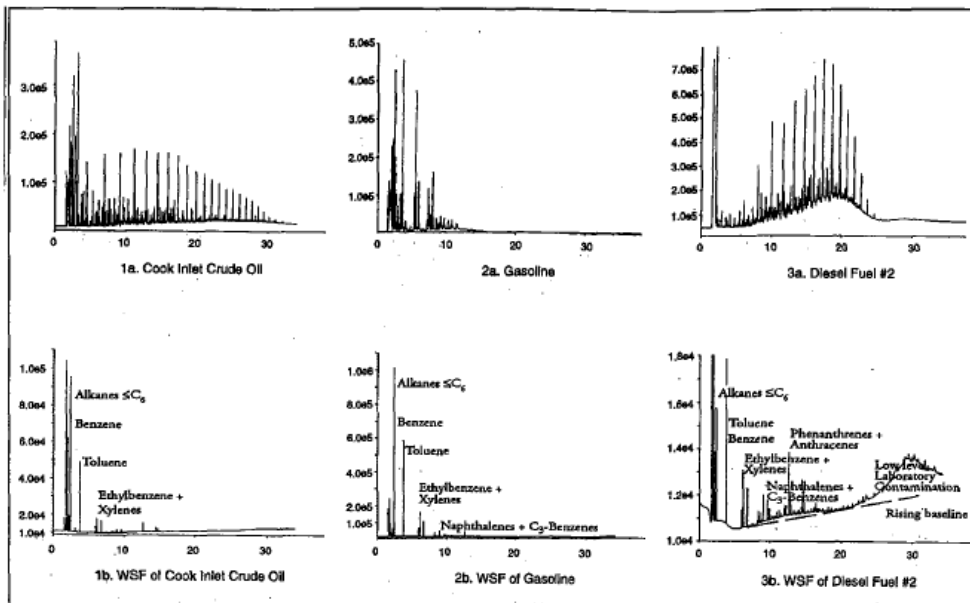


Figure 3. GC-FID chromatograms for various fresh petroleum products and their water-soluble fractions (Adapted from Bruya and Friedman, 1992).

Sample Preparation by Silica Gel Cleanup

When employing analytical techniques used to quantify the TPH in groundwater, silica gel cleanup during sample preparation should limit the amount of oxygenated species.

Summary

When used as a performance parameter for TPH degradation in groundwater, the results of TPH analyses are often misleading and can be misunderstood. For that reason, TPH analyses are not recommended for that purpose. However, if TPH analyses must be used, these guidelines should be followed:

1. Do not use acid-preserved samples or allow acidification during any step of the analysis. Adding acids will convert the organic acids produced by chemical oxidation back to the alkane.
2. Always employ silica column sample cleanup to remove polar organics.
3. Filter all turbid samples through glass-fiber filter media.
4. Use fractionated TPH analysis, such as the CWS-PHC Method (Anonymous, 2002).
5. Analyze an uncontaminated soil blank to determine possible background interferences.

References

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